THE EFFECT OF SOME METEOROLOGICAL FACTORS ON OZONE VARIATIONS IN THE NORTHERN HEMISPHERE

Thesis
Submitted to the Faculty of Graduate Studies and Research in the Partial Fulfillment of the Requirements for the Degree of Master of Science In the Division of Environmental Engineering University of Saskatchewan

By
Ashour Salah Sassi
Saskatoon, Saskatchewan
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Dedication

To my parents and family
ABSTRACT

Ozone measurements using Dobson ozone spectrophotometer have been made in Canada since the late 1950s. These instruments were installed between 1957 and 1964 at five Canadian sites and replaced by the more advanced Brewer instruments in the mid-1980s. Ozone measurements have also been made from satellites and in particular the daily global total ozone has been measured by the Total Ozone Mapping Spectrometer (TOMS) during the period October 1978 through May 1993. Since the 1970s the vertical profile of ozone concentration has also been measured with balloonsondes at several Canadian sites.

Recent studies of ozone trends over Canada have shown negative trends in total ozone (WMO, 1994). In this thesis ozone trends in the troposphere and the lower to mid-stratosphere are examined using the three types of data sets. The purpose has been to investigate the ozone variation pattern in the northern hemisphere and to determine the possible effects of some meteorological factors on this variation during the period from January 1979 to December 1992.

A statistical model for a trend analysis of the ozone time series has been used. The model included terms for seasonal variations in mean ozone and seasonal variations in ozone trends as well as the effect of some meteorological factors. An attempt to assess stratospheric temperature and ozone-temperature trends in the troposphere and lower and mid-stratosphere has also been made. It is concluded that while there is clear evidence for a negative trend in the total ozone column, the full coupling is masked by the seasonal variation.
ACKNOWLEDGMENTS

I would like to express my deep thanks to my supervisor Professor Llewellyn for his help during my graduate studies at the University of Saskatchewan. Also I wish to express my thanks to all members of my advisory committee for reading this thesis.

Last but not least, I want to thank my family and friends for their moral support and encouragement.
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<tbody>
<tr>
<td>UV</td>
<td>Ultraviolet radiation</td>
</tr>
<tr>
<td>(XY)</td>
<td>The ground electronic state of the molecule</td>
</tr>
<tr>
<td>(XY')</td>
<td>Electronically excited states of a molecule</td>
</tr>
<tr>
<td>(X,Y)</td>
<td>Atom or molecule</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>(X^1\Sigma_g^-)</td>
<td>The ground state of molecular oxygen</td>
</tr>
<tr>
<td>(a^1\Delta_g)</td>
<td>The first electronically excited state of molecular oxygen</td>
</tr>
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<td>(^3P)</td>
<td>The ground state of atomic oxygen</td>
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<td>(^1D)</td>
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<td>(^2D)</td>
<td>Excited state</td>
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<td>(J_2)</td>
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<td>Reaction rate constant</td>
</tr>
<tr>
<td>(hv)</td>
<td>Energy of photon</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Wavelength</td>
</tr>
<tr>
<td>(ppmv)</td>
<td>Part per million by volume</td>
</tr>
<tr>
<td>(e)</td>
<td>Electron</td>
</tr>
<tr>
<td>(\mu m)</td>
<td>Micrometer</td>
</tr>
<tr>
<td>PSC</td>
<td>Polar Stratospheric Cloud</td>
</tr>
<tr>
<td>NAT</td>
<td>Nitric Acid Trihydrate</td>
</tr>
<tr>
<td>mb</td>
<td>Millibars</td>
</tr>
<tr>
<td>(\mu mb)</td>
<td>Micro-millibars</td>
</tr>
<tr>
<td>Gt(C)</td>
<td>Giga tonne, (1 \text{ Gt(C)} = 10^{12} \text{ Kg(C)} = 10^{15} \text{ g(C)})</td>
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<tr>
<td>WMO</td>
<td>World Meteorological Organization</td>
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CHAPTER I

INTRODUCTION

1.1 Role of ozone in the atmosphere

Ozone ($O_3$) is a relatively unstable molecule composed of three oxygen atoms and is an important component of the Earth's atmosphere as it provides an important radiation shield. Atmospheric ozone is produced through the solar photolysis of oxygen in the upper atmosphere but is still only a minor species; indeed if all of the ozone contained in the atmosphere were collected at the Earth's surface, it would form a layer of gas only about 3mm thick.

Ozone is distributed throughout the atmosphere from the Earth surface up to the 100 km level and has its maximum molecular concentration in the stratosphere in a layer at an altitude near 30 km. In this layer, ozone absorbs and filters out most of the ultraviolet radiation (UV), specifically UV-B, which is emitted by the sun. This is important as radiation with a wavelength below 320 nm is particularly harmful to living organisms. Fortunately, the most dangerous form of ultraviolet radiation UV-C is absorbed completely by oxygen and ozone above the stratosphere. The other form of ultraviolet radiation, UV-A (longest wavelength) is the least damaging form of UV radiation and its photons are only partially blocked by the atmosphere.
A significant decrease in the amount of stratospheric ozone, and the accompanying increase in UV-B radiation reaching the Earth's surface, could have potentially harmful effects in the troposphere (the lowest region of the atmosphere). One obvious effect would be on humans as long term exposure to UV-B is associated with an increased risk of skin cancer, and eye damage. Ozone also plays an important role in regulating the Earth's temperature. Like carbon dioxide, ozone is a greenhouse gas so that an increase in its concentration would return more infrared radiation to the Earth's surface and so exacerbate global warming. In the stratosphere, where the ozone absorbs ultraviolet radiation, it is an important contributor to the atmospheric temperature profile. Thus a change in the ozone concentration can modify the temperature balance of the atmosphere and so affect the atmospheric heat engine and the climate (Miller et al., 1986).

1.2 The problem of ozone depletion

The 'ozone hole' (i.e stratospheric ozone depletion) has been observed since the mid-1970s. It was first discovered with ground-based instruments and balloon sondes from Halley Bay on the Antarctic coast by Farman and co-workers (Farman et al., 1985) and was later confirmed by satellite measurements (Dieminger et al., 1996).

Since 1970 ozone measurements have indicated an increasing in the Antarctic springtime ozone hole that has been attributed to anthropogenic influences. The ozone depletion process begins with the release of chemicals known as halocarbons, compounds that contain chlorine, fluorine, bromine, carbon and hydrogen. The most common ozone depleting substances are thought to be chlorofluorocarbons, or CFCs, a
family of commonly used industrial compounds. These compounds were invented in 1928 by Thomas Midgley, Jr. and become known as the “Miracle compound” as they were inert and believed to be totally safe.

CFCs are efficient refrigerants, making excellent coolants in home and car conditioners, propellants for dispensing aerosol sprays, filler in foam packaging and insulation. They have also been used as a cleaning agent in the manufacture of electronic components. Much of the modern lifestyle of the 20th century had been made possible by the “Miracle compound”.

CFCs are very stable substances that can persist in the lower atmosphere for many years before they diffuse up into the stratosphere. It is their stability that leads to their ozone depleting properties. While CFCs remain in the lower atmosphere, they are protected from ultraviolet radiation by the ozone layer. However, once CFCs reach the stratosphere they are rapidly dissociated by the solar ultraviolet radiation. This releases chlorine atoms that react strongly with ozone molecules in a destructive catalytic cycle. In the Antarctic, where the first ozone hole appeared, the temperature in the lower stratosphere can drop below -80° C and allow the formation of clouds composed of ice and nitric acid, called Polar stratospheric clouds (PSCs). These low temperatures are associated with the stable polar vortex and are essential factors for PSC formation. These polar stratospheric clouds (PSCs) provide a surface for heterogeneous reactions that in the extremely cold polar night of the southern hemisphere can divert chlorine into nonreactive reservoirs. However, with the return of the sunlight at the end of the polar night chemical reactions, that occur on the surface of ice particles within the clouds, convert the chlorine from the usual long-lived, inert reservoirs into more active
forms. This initiates the catalytic destruction of ozone and the formation of the ozone hole.

1.3 Differences between the Northern and Southern Hemispheres

Is ozone being depleted over the Arctic? This question has been asked since the discovery of the Antarctic ozone hole. Results of recent studies of the upper atmosphere over the Arctic show that there is no dramatic ozone hole that can compare with the one in the Antarctic. The reason appears to be the lack of stability in the Arctic vortex which precludes an extended region of cold temperature that allow PSC formation. In addition, there are differences in planetary wave activity in the two hemispheres that break down the polar vortex formation and allow the transport of ozone-rich air to polar latitudes.

It is the vertical transport associated with planetary waves, and the absence of a stable vortex, that tends to enhance Arctic ozone by injecting poleward moving ozone-rich tropospheric air from the equator into the lower stratosphere (Salby and Garcia, 1990). However, recent results have shown that the highest levels of chlorine monoxide (ClO), with smaller amounts of bromine monoxide (BrO), that were measured by the Second Airborne Arctic Stratospheric Expedition (AASEII) over Canada and northern New England in winter 1991-1992, are high enough to destroy ozone at a rate of one to two percent a day in mid-January. In addition, the low temperatures that allow PSCs to form could be expected to occur in the northern hemisphere a result of stratospheric cooling caused by an increase in CO$_2$ emission into the atmosphere. Some computer modeling results suggests that within fifty years cooling climatic conditions in the stratosphere,
brought about by an increase in $CO_2$ of anthropogenic origin, could cause the long-term formation of an ozone hole over the Arctic (Austin et al., 1992).

In summary, ozone concentration depends on meteorological conditions, specifically temperature and the duration and size of the polar vortex. Inside this vortex, the stratosphere cools and allows the formation of polar stratospheric clouds (PSCs) that are an essential component of the process by which chlorine is released from its stable reservoirs into active forms, thus priming the vortex for ozone destruction. The instability of the polar vortex in the northern hemisphere has not been studied. Rather the goal has been to examine the northern hemisphere data to see if these factors that control ozone in the southern hemisphere polar region are detectable in the northern hemisphere.

1.4 Previous studies

Following the predicted impact of human activity on the ozone layer in 1970 and since the discovery of Antarctic spring ozone depletion by Farman and his co-workers (1985), there have been extensive efforts to analyze ozone data from ground-based, radiosonde and satellite measurements for evidence of these depletions.

Johnson (1971), Angell and Korshover (1973, 1976), and many others have studied ozone patterns in the atmosphere. These analyses were based on statistical methods and estimated the deviations from the monthly mean and the overall mean. However, these studies could not provide a satisfactory explanation for the derived downward trends in total ozone. Angell and Korshover (1978) estimated global ozone trends from ground-
based data but the limited data set, and the poor distribution of the observation network, restricted their findings.

Other authors have considered time series analyses and applied their models to many ground stations throughout the world. Reinsel et al. (1981) using data from 36 ground stations in the northern hemisphere found little evidence of ozone depletion in the 1970s. The same result was found by Angell and Korshover (1983), Reinsel et al. (1987, 1988) and Hill et al. (1977, 1986). These trends results were all based on ground measurements with Dobson spectrometers. In all studies of total ozone trends before 1988, no significant trend in total ozone in the northern hemisphere was found. In the 1988 results of trends panel, as reported by the World Meteorological Organization (WMO), indicated that there are significant downward trends in the winter time northern hemisphere. These results, which were based on ground-based data and were confirmed by satellite measurements, showed a clear downward trend in the total ozone column over the northern hemisphere (e.g., Stolarski et al., 1992; Hood and McCormack, 1992; Gleason et al., 1993, Reinsel et al., 1994). In addition Stolarski et al., (1992) and Reinsel et al. (1994) found evidence for an increase in total ozone depletion over the high and the mid-latitude region of the northern hemisphere in the 1980 and 1990s. Harris et al., (1997) studied the long-term ozone trends at mid-latitudes in the northern hemisphere by using both ground-based and satellite measurements for the period 1979 to 1994. Their results showed significant negative trends in all seasons about 0.7% per year and larger trends in winter and spring than in summer and fall.

Previous studies of ozonesonde data obtained from the Brewer-Mast (BM) type (Logan, 1985) and from both BM and Electrochemical concentration cell (ECC) sondes (Wang
et al., 1993; London and Liu, 1992; Tiao et al., 1986), indicated a positive trend in such data up to the mid 1980s. A recent estimation of ECC ozonesonde trends (Oltmans, 1993) for four Canadian stations has shown significant negative trends at two of them, for data from 1980-1990. Using ECC sonde data from 1980-1991, Logan (1994) has reported significant negative trends at three Canadian stations. Kerr et al., (1995) examined the nonseasonal and seasonal trend behavior of the ozone profile data from both ozonesonde and Umkehr measurements for the period 1968 to 1991. Their results showed a significant negative trends in both lower and upper stratosphere about 0.6% per year.

Dobson and Harrison (1926) and Dobson et al., (1929) were the first to report a relationship between meteorological parameters and total ozone variation in the lower stratosphere. Reed (1950) presented the relationship between ozone and surface weather and suggested that short-term variations of total ozone may result from the effect of horizontal advection below the tropopause, or vertical motion in the lower stratosphere associated with trough/ridge patterns. Since total ozone amounts increase toward the poles, advection of air from the north into the trough would be expected to cause an increase of ozone, while advection from the south would result in a decrease in ozone amount for the northern hemisphere (Barsby and Diab, 1995).

Newman and Schoeberl (1986) and others have attempted to study the relationship between temperature and ozone. These studies indicate the relationship of the ozone-temperature decline and the effects of wave events on these changes. Thus total ozone reduction can be partially explained by temperature changes, but accurate circulation or mass transport calculations must be made before this scenario can be precisely verified.
Sekiguchi (1986) has found a very high correlation ($r = 0.96$) between monthly mean values of ozone and stratospheric temperature that supports the idea of a relationship between stratospheric circulation and ozone. The relationship between ozone and temperature trends in the lower stratosphere has also been detected by others (McCormick and Yue., 1994; Petzoldt et al., 1994).

1.5 Objectives, summary and outline

The present work reports an analysis of the data of ozone columns measured by ground-based and satellite techniques, ozone profiles and of temperature measured by radiosondes. There are two main objectives in this work. The first is to use these data to examine ozone and temperature trends in troposphere and lower to mid-stratosphere using time series models. The second objective is to highlight the relationship between the ozone column and temperature and the effect of other meteorological parameters. The study used six Canadian stations located at mid to high latitudes and a data period from January 1979 to December 1992. A brief summary of ozone photochemistry in the stratosphere is presented in Chapter 2 and describes the mechanisms of ozone production and loss, with particular emphasis on the effects of different gas species. Chapter 3 gives a background on stratospheric ozone perturbations, both natural effects and those due to anthropogenic effects. The various data sources are described in Chapter 4. This chapter also includes a discussion of the impact of missing and incorrect data. The data analysis and the statistical models for estimating the trends for all types of data are presented in Chapter 5. The conclusion from this analysis, and recommendations for future work are presented in Chapter 6.
CHAPTER II

MECHANISMS OF OZONE PRODUCTION AND LOSS

2.1 Introduction

The various atomic and molecular constituents of the terrestrial atmosphere undergo a carefully balanced cycle of destruction and renewal. Solar radiation, particularly at wavelengths below 300 nm, is the natural driver in this cycle that must necessarily exhibit daily, seasonal and solar cycle variations. However, some trace gases that are being introduced into the atmosphere, as a result of human activity, can affect these various cycles either through the absorption and emission of radiation, which can modify the atmospheric temperature profile, or by directly modifying the atmospheric chemistry.

2.2 Absorption in the terrestrial atmosphere

As shown in Figure 2.1 the penetration depth, or unit optical depth of the solar radiation is a function of wavelength that depends on the different absorbing species. Thus, the atmosphere controls both the amount of energy that reaches the Earth from the sun and the amount of radiation that is reflected, or scattered, back into the space. It is apparent from the details presented in Figure 2.1 that the most important absorbing gases are molecular nitrogen, molecular oxygen and ozone, although there is also important absorption by water and carbon dioxide in the infrared region. However, for the mesosphere and stratosphere the most important absorbers are molecular oxygen and ozone.
Figure 2.1: Depth of penetration of solar radiation as a function of height (after Brasseu and Solomon, 1984).
Although the energy absorbed in the atmosphere represents only a few per cent of the total solar flux reaching the Earth its effect is very important, as it is responsible for the temperature structure in the atmosphere. The absorption of the solar flux by the different atmospheric molecules is more than a simple change in the energy state of the molecule, rather it is a photodissociation process. In this process the molecules are dissociated into atoms, that may be excited, and so initiate an entire chemical scheme that is of great importance in the middle atmosphere. The primary step of in the photochemical process can be written as equations 2.1 and 2.2,

\[
XY + hv \rightarrow XY'
\]  
(2.1)

\[
XY' \rightarrow X + Y
\]  
(2.2)

The rate of photolysis is determined by the absorption cross-section of the molecule and the incident solar flux. The production rate for the different products depends on the quantum yield for the various product channels at the absorbing wavelengths. The quantum yield is defined as the ratio of the number of product molecules/atoms to the number of photons absorbed; for some photochemical reactions this value can be larger than unity.

The absorption of solar energy in the upper mesosphere and lower thermosphere is mainly through molecular oxygen while in the stratosphere and lower mesosphere it is due to ozone. It is interesting to note that at the wavelength of the solar Lyman $\alpha$ line, 121.6 nm, there is a window in the oxygen cross-section that allows the solar flux to penetrate into the mesosphere. In the other parts of the Schumann-Runge continuum
absorption occurs in the thermosphere, but within the Schumann-Runge bands (175-200 nm) the radiation can penetrate deep into the mesosphere and the upper stratosphere. The various regions of the atmosphere are shown in Figure 2.2.

2.2.1 Ozone formation and destruction in the atmosphere

In the early 1930s in a set of seminal papers Chapman (1930; 1931a; 1931b) proposed a photochemical scheme that could explain the distribution of atomic oxygen and ozone in the Earth's atmosphere. The reactions are initiated by the dissociation of molecular oxygen through the absorption of solar energy in the range 170 to 245 nm in the Schumann-Runge bands and the weak Herzberg continuum. In this dissociation the molecule is split into two oxygen atoms according to equation 2.3.

\[ O_2 + h\nu \rightarrow O + O \]  

(2.3)

where \( J_2 \) is the photolysis rate.

Oxygen atoms may then recombine in presence of a third body (usually \( O_2 \) or \( N_2 \) and denoted by \( M \)) according to equation 2.4,

\[ O + O + M \rightarrow O_2 + M \]  

(2.4)

or a single oxygen atom (\( O \)) may recombine with an oxygen molecule to form ozone according to equation 2.5,

\[ O_2 + O + M \rightarrow O_3 + M \]  

(2.5)
Figure 2.2: The average variation of temperature with altitude within the atmosphere (after Wallace and Hobbs, 1977).
where $K_{11}$ and $K_{12}$ are the appropriate reaction rates.

If only reactions 2.3, 2.4, and 2.5 occurred in the atmosphere then the entire oxygen content of the atmosphere would be converted to ozone. However, the free oxygen atom may react with ozone to form two oxygen molecules according to equation 2.6,

$$O_3 + O \xrightarrow{K_{12}} O_2 + O_2 \quad (2.6)$$

Ozone is also destroyed by the absorption of ultraviolet radiation (UV) in the wavelength range of 200 to 320 nm, within Hartley continuum and the Hartley-Huggins bands, and by longer wavelength radiation in the Chappuis band (see Figures 2.3 and 2.4) according to reactions 2.7 and 2.8,

$$O_3 + h\nu(\lambda < 320 \text{nm}) \xrightarrow{J_3} O(3D) + O_2(\text{a} \Delta_g) \quad (2.7)$$

$$O_3 + h\nu(\lambda > 320) \rightarrow O_2(\sum^+_{\Delta_g}) + O(3P) \quad (2.8)$$

where $J_3$ is the ozone photolysis rate. The effect of this photochemical scheme is to produce an ozone layer centered near 30 km. The photodissociation processes described by equations 2.3 and 2.8 are the primary source of atomic oxygen in the atmosphere. In the steady state the overall effect of these reactions is the conversion of solar energy to heat. This heating effect, due to the absorption of solar ultraviolet radiation, is balanced by cooling through the infrared emission from CO$_2$ (15 $\mu$m band), and to a lesser extent, from ozone (9.6 $\mu$m band) and water in a number of different bands (Brasseur and Solomon, 1984).
Figure 2.3: Huggins band of ozone (after Brasseur and Solomon, 1984).

Figure 2.4: Chappuis band of ozone (after Brasseur and Solomon, 1984).
If there were no other chemical reactions in the atmosphere and the effects of meteorological influences could be ignored this chemical scheme would balance and result in an equilibrium in which the average quantity and distribution of ozone in the atmosphere would change little over the years.

However, neither the climate nor the atmosphere is static and, therefore, the ozone layer is not constant. Indeed the amount of ozone in the stratosphere varies with latitude and altitude and at different times of the year, as well as from year to year, in an extremely complicated fashion. Latitude, altitude and seasonal effects are all expected as the solar flux incident on any altitude is a function of these quantities. However, there are also local and inter-annual changes associated with transient meteorological systems, as well as with large-scale fluctuations in the year to year patterns of the general circulation. These are particularly apparent in the lower stratosphere. Ozone concentrations can also be affected by solar variability, the concentrations of atmospheric trace gases and other geophysical variables.

In summary, ozone molecules in the stratosphere are constantly being created and destroyed in an unending cycle. The new ozone molecules are created through chemicals reactions initiated by the absorption of solar ultraviolet radiation (UV) and are destroyed by both sunlight and chemical reactions.

2.2.2 The photochemistry of some other species

The Chapman reaction scheme was generally accepted until the late 1950s and was thought to include the main reactions that controlled ozone formation and destruction in the atmosphere. However, as measurements of the reaction the rate constants improved
it become apparent that reaction 2.6 is considerably slower than Chapman had believed. This, together with good measurements of ozone amounts, indicated that the ozone content is approximately a factor 2 less than that predicted by the Chapman scheme (Seinfeld and Pandis, 1998). Thus, either the Chapman scheme is completely in error or it represents simplification. With the identification of the OH Meinel bands in the airglow (Meinel, 1950), it become apparent that ozone destruction could in fact occur in a catalytic cycle such as described by equation 2.9.

\[
\begin{align*}
X + O_3 & \rightarrow XO + O_2 \\
XO + O & \rightarrow X + O_2 \\
O_3 + O & \rightarrow O_2 + O_2 
\end{align*}
\] (2.9)

where X is a catalyst and can be H, OH, NO, Cl, or Br. The exact importance of each cycle depends on the concentration of the species X and the rate constants for the reactions in the cycle.

2.2.2.1 Odd-Hydrogen catalytic cycles

The effects of hydrogen compounds on the behavior of ozone have been examined by a number of authors including Crutzen (1970) and Nicolet (1971).

Odd hydrogen involves three groups of species:

1- \( H_2O, H_2 \) and \( CH_4 \) \hspace{1cm} \text{(Source species)}

2- \( OH \) and \( HO_2 \) \hspace{1cm} \text{(Reactive radical species)}

3- \( H_2O_2 \) \hspace{1cm} \text{(Reservoirs)}
\( \text{HO}_x \) is produced in reactions between water, or methane, and oxygen atoms in the \( O(^1D) \) state that are produced in the photolysis of ozone, reaction 2.7, according to the following chemical scheme,

\[
\begin{align*}
O_3 + hv (\lambda < 320 \text{nm}) & \rightarrow O(^1D) + O_2 \\
O(^1D) + H_2O & \rightarrow 2OH \\
O(^1D) + CH_4 & \rightarrow OH + CH_3
\end{align*}
\]

While water vapor is quite abundant in the troposphere (>10 ppmv) there is freezing at the tropopause by the low temperatures (i.e. a cold trap) which limits the direct transport of water into the stratosphere. Thus, a considerable fraction, approximately one half, of the water vapor in the stratosphere actually results from the oxidation of methane that has leaked into the stratosphere from the troposphere (Seinfeld and Pandis, 1998).

The first catalytic cycle for ozone destruction was proposed by Bates and Nicolet (1950) in order to explain the OH Meinel bands in the airglow. This cycle, equations 2.13 and 2.14, involved hydrogen atoms and the hydroxyl radical,

\[
\begin{align*}
H + O_3 & \rightarrow OH + O_2 \\
OH + O & \rightarrow H + O_2 \\
O_3 + O & \rightarrow 2O_2
\end{align*}
\]

The second hydrogen catalytic cycle is described by equations 2.15 and 2.16,
In the upper stratosphere, the combined effect of these two catalytic cycles is to recombine oxygen atoms according to reactions 2.17, 2.18 and 2.19,

\[
\begin{align*}
OH + O_3 & \rightarrow \ HO_2 + O_2 \\
\frac{HO_2 + O}{O_3 + O} & \rightarrow \ OH + O_2 \\
O + O + M & \rightarrow \ O_2 + M
\end{align*}
\]

In the lower stratosphere, there is another catalytic cycle that converts two ozone molecules into three oxygen molecules, reactions 2.20 and 2.21,

\[
\begin{align*}
OH + O & \rightarrow \ H + O_2 \\
H + O_2 + M & \rightarrow \ HO_2 + M \\
\frac{HO_2 + O}{O + O + M} & \rightarrow \ OH + O_2 \\
2O_3 & \rightarrow \ 3O_2
\end{align*}
\]

An \( HO \) reservoir species, other than \( H_2O \), is provided by hydrogen peroxide which affects the concentrations of both \( OH \) and \( HO_2 \). This is shown by reaction 2.22, 2.23, and 2.24,

\[
\begin{align*}
HO_2 + HO_2 & \rightarrow \ H_2O_2 + O_2 \\
H_2O_2 + hv & \rightarrow \ OH + OH \\
H_2O_2 + OH & \rightarrow \ H_2O + HO_2
\end{align*}
\]
2.2.2.2 Odd-Nitrogen catalytic cycle

While almost all of the atmospheric nitrogen content is in the form of molecular nitrogen it is possible for dissociation to provide a source of atmospheric odd nitrogen. Reactive nitrogen $NO_x$ is defined as the sum of the two oxides of nitrogen $NO_x$ and all species that are products of the atmospheric oxidation of $NO_x$ that contain one or more nitrogen atoms, examples of such species are $HNO_3$, $HONO$, $NO_3$, $N_2O_5$, and $HNO_4$.

Ion pairs that are produced during solar proton events (see section 3.1.2) can affect the composition of the lower atmosphere and increase the rate production of some atoms, such as nitrogen and hydrogen.

In the thermosphere the dissociative recombination of nitrogen ions that are formed through electron precipitation can lead to the formation of nitrogen atoms as indicated by equation 2.25,

$$N_2^+ + e \rightarrow N(^4S) + N(^2D) \quad (2.25)$$

The nitrogen atom, which is produced in the excited $^2D$ state, can react with molecular oxygen to form nitric oxide according to equation 2.26,

$$N(^2D) + O_2 \rightarrow NO + O \quad (2.26)$$

The ground state ($^4S$) nitrogen atoms can also react with molecular oxygen to form nitric oxide although this reaction, equation 2.27, is extremely slow.

$$N(^4D) + O_2 \rightarrow NO + O \quad (2.27)$$
The nitric oxide that is formed as a result of electron, or proton, precipitation can then diffuse downward into the upper stratosphere where it can react with ozone according to reactions 2.28 and 2.29,

\[
\begin{align*}
NO + O_3 & \rightarrow NO_2 + O_2 \quad (2.28) \\
NO_2 + O & \rightarrow NO + O_2 \\
O_3 + O & \rightarrow 2O_2 
\end{align*}
\]

It is apparent that these two reactions form a catalytic cycle that has the same effect as the hydrogen catalytic cycle (reactions 2.13 and 2.14).

However, the major natural source of \( NO_x \) in the stratosphere is nitrous oxide, \( N_2O \), that is released from the ground. The \( N_2O \) is converted to nitric oxide (\( NO\)) according to the chemical scheme outlined by reactions 2.30, 2.31 and 2.32.

\[
\begin{align*}
N_2O + hv & \rightarrow N_2 + O(\text{D}) \quad (2.30) \\
O(\text{D}) + N_2O & \rightarrow 2NO \quad (2.31) \\
O(\text{D}) + N_2O & \rightarrow N_2 + O_2 \quad (2.32)
\end{align*}
\]

In the lower stratosphere this \( NO_x \) can form a catalytic cycle that converts ozone molecules into molecular oxygen, reactions 2.33, 2.34 and 2.35

\[
\begin{align*}
NO + O_3 & \rightarrow NO_2 + O_2 \quad (2.33) \\
NO_2 + O_3 & \rightarrow NO_3 + O_2 \quad (2.34) \\
NO_3 + hv & \rightarrow NO + O_2 \\
2O_3 & \rightarrow 3O_2
\end{align*}
\]
At nighttime this process is self-limiting as the NO$_3$ that is formed in equation (2.34) cannot be photolyzed.

However, the NO$_3$ may react with NO$_2$ to produce N$_2$O$_5$ which acts as a low temperature reservoir. However, the NO$_3$ and NO$_2$ are easily reformed photolytically or through an increase in temperature, equation 2.36.

\[
NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M
\]  
(2.36)

During the daytime the NO$_3$ is easily photolyzed.

\[
NO_3 + hv \rightarrow NO_2 + O \]  
\[
\rightarrow NO + O_2
\]  
(2.37)  
(2.38)

and can participate in the null cycle that effectively increases the ozone photolysis rate.

\[
NO + O_3 \rightarrow NO_2 + O_2
\]  
(2.39)

\[
NO_2 + hv \rightarrow NO + O
\]

\[
O_3 + hv \rightarrow O_2 + O
\]

(2.40)

2.2.2.3 Odd-Chlorine catalytic cycle

The oceans are a natural source of chlorine as there is a significant amount of sodium chloride in seawater. However, sodium chloride that enters the atmosphere is rapidly removed by precipitation and so has little chance of reaching the stratosphere where it could be dissociated. There is, of course, some chlorine injected into the atmosphere through volcanic eruptions. One natural source of chlorine in the stratosphere is methyl chloride (CH$_3$Cl) which is produced by biological processes in the oceans and from the
burning of biomass. The $CH_3Cl$ is removed by reaction with OH radical in the stratosphere and also photolyzed in the upper stratosphere as shown in equations 2.41 and 2.42.

$$CH_3Cl + OH \rightarrow CH_2Cl + H_2O \quad (2.41)$$

$$CH_3Cl + hv \rightarrow CH_3 + Cl \quad (2.42)$$

However, it is quite unlikely that there is an important natural chlorine cycle in the atmosphere so that anthropogenic source of free chlorine could be quite important.

The term odd-chlorine species $Cl_x$ includes $Cl, ClO, HCl, ClONO_2$, and $HOCl$ with the main source of stratospheric chlorine coming from chlorofluorocarbons, or CFC's. The photolysis reactions of CFCs release chlorine (Cl) atoms into the stratosphere, over the wavelength range 185-210 nm (Molina and Rowland, 1974). This source is described by reactions 2.43 and 2.44,

$$CFCl_3 + hv \rightarrow CFCl_2 + Cl \quad (2.43)$$

$$CF_2Cl_2 + hv \rightarrow CF_2Cl + Cl \quad (2.44)$$

The released chlorine atoms react rapidly with ozone and produce chlorine monoxide which in turns combine with atomic oxygen to release the chlorine atom according to equations 2.44 and 2.45,
Thus these reactions also form a catalytic cycle for the destruction of ozone. The chlorine monoxide may also react with NO to release atomic chlorine according to reaction 2.47,

\[
ClO + NO \rightarrow Cl + NO_2
\]  

(2.47)

and so nitric oxide can replace atomic oxygen in the second part of the chlorine cycle.

In the absence of NO, the concentration of ClO will increase and form the reservoir compound Cl₂O₂ which is easily photolyzed in the polar spring. This is important as ozone depletion over the Antarctic, by the reaction 2.46, is not possible with the low oxygen atom concentration available during September and October when the solar zenith angle is high. Thus another catalytic cycle must be responsible for the ozone loss at that time (Molina and Molina, 1987).

As noted the simple gas-phase chemistry that is associated with the ClOₓ and NO cycles can not explain the polar ozone hole phenomenon that is observed each year in the Antarctic spring. Rather, heterogeneous reactions that occur on polar stratospheric cloud particles play the pivotal role in polar ozone depletion (McElroy et al., 1986; Solomon et al., 1986; Molina, 1991). Polar stratospheric clouds (PSCs) are classified into two broad types, the so-called Type-I and Type-II. Type-I PSCs have been further subdivided into a Type-Ia and a Type-Ib. Type-Ia PSCs are composed of condensed
nitric acid trihydrate, $HNO_3\cdot3H_2O$ or NAT, which forms at temperatures below -80°C. The second form of Type-I PSCs, Type-Ib, consists of supercooled ternary solutions of $HNO_3 - H_2SO_4 - H_2O$, that also form at about the same temperature threshold (Seinfeld and Pandis, 1998). Type-II PSCs consist of $H_2O$ (water ice) that form at a temperature below the ice frost point.

The formation of a liquid droplet from a supersaturated vapor, or on a solid particle in vapor or the formation of a frozen grain in a supercooled liquid, is defined as nucleation. The nucleation mechanism in type-I PSCs begins both naturally, and anthropogenically, with sulfur dioxide that is injected into the stratosphere, from volcanic eruptions or other sources, being converted to sulfuric acid and condensed to form a sulfuric acid droplet. If homogeneous nucleation occurs, the formation of new particles through $H_2SO_4 - HNO_3 - H_2O$ ternary reactions may be the most favorable mechanism for the formation of stratospheric aerosols (Hamill and Toon, 1991). If the temperature cools to 195°K nitric acid trihydrate particles will form, and if the temperature drops to 188°K, water ice type-II PSCs can grow on the nitric acid trihydrate. If there is sufficient growth these aerosols will fall out of the stratosphere due to gravitational sedimentation.

The actual heterogeneous chemical scheme for ozone depletion is quite complicated but begins with the release of chlorine ($Cl$) atoms through the photodissociation of chlorofluorocarbons. The released chlorine may react with methane $CH_4$ to form hydrochloric acid ($HCl$) shown in reaction 2.48,
\[ Cl + CH_4 \rightarrow CH_3 + HCl \quad (2.48) \]

Of course the atomic chlorine may react with ozone to form \( ClO \) according to reaction 2.49,

\[ Cl + O_3 \rightarrow ClO + O_2 \quad (2.49) \]

The \( ClO \) can then react with \( NO_2 \) to form \( ClONO_2 \) according to equation 2.50.

\[ ClO + NO_2 \rightarrow ClONO_2 \quad (2.50) \]

and in the process potentially remove both \( Cl \) and \( NO_x \) from the atmosphere, thus limiting the ozone destruction. However, the \( HCl \) that is produced in reaction 2.48 can dissolve in the PSCs particles which can in turn react with the gas phase chlorine nitrate \([ ClONO_2 ]\) that is produced in reaction 2.50.

This initiates a set of reactions, 2.51 through 2.54.

\[ HCl(s) + ClONO_2(g) \rightarrow Cl_2(g) + HNO_3(s) \quad (2.51) \]

\[ Cl_2 + hv \rightarrow Cl + O_3 \quad (2.52) \]

\[ 2[Cl + O_3] \rightarrow ClO + O_2 \quad (2.53) \]

\[ \frac{ClO + NO_2 + M}{HCl(s) + NO_2 + 2O_3} \rightarrow \frac{ClONO_2 + M}{ClO + HNO_3(s) + 2O} \quad (2.54) \]

that convert the reservoir species \( HCl \) and \( ClONO_2 \) into \( ClO \) and nitric acid. The symbols \((g)\) and \((s)\) in these equations refer to gas and solid respectively. Atomic chlorine is produced through the photolysis of \( ClO \) which is released in reaction 2.51,
while $HNO_3$ remains in the ice and so stops the termination of the catalytic chain. Two factors are important for these reactions to occur, cold temperatures and sunlight. The cold temperatures are essential for PSCs to form and sunlight is required to photolyze the various active forms of chlorine, $Cl_2$, $HOCl$ and $ClNO_2$.

Overall the cold temperatures of the polar region are important as they allow the formation of polar stratospheric clouds. If these particles are able to grow large enough they will fall out of the stratosphere (sedimentation) and so remove the odd nitrogen that would allow the active chlorine to be bound in $ClONO_2$. It is this sequence that allows ozone depletion in the Antarctic region as the sun rises each springtime. This is illustrated in the reaction scheme described by equations 2.55 through 2.58,

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \quad (2.55)$$

$$Cl_2O_2 + hv \rightarrow Cl + ClO_2 \quad (2.56)$$

$$ClO_2 + M \rightarrow Cl + O_2 + M \quad (2.57)$$

$$\frac{(Cl + O_3)}{20_3 + hv} \rightarrow \frac{ClO + O_2}{3O_2} \times 2 \quad (2.58)$$

In addition, the abundance of $ClO$ can increase the rate of ozone loss because of the coupling between the chlorine and bromine chemistry as shown in reactions 2.59 through 2.61 (McElroy et al., 1986).

$$ClO + BrO \rightarrow Br + ClO_2 \quad (2.59)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (2.60)$$

$$\frac{Br + O_3}{2O_3} \rightarrow \frac{BrO + O_3}{3O_2} \quad (2.61)$$
Although bromine species are only present in small amounts in the stratosphere, relative to chlorine compounds, they are extremely important as bromine is a very efficient catalyst for ozone destruction. The reason is that both $HBr$ and $BrONO_2$ are very rapidly photolyzed; the photolysis lifetime of $BrONO_2$ in the lower stratosphere is only 10 minutes compared to $ClONO_2$ which is 6 hours.

2.2.3 Photochemistry-temperature coupling

There are two main factors that control the thermal structure of the atmosphere. The first is the external energy inputs from heating sources, such as solar radiation, and the other is the internal sources of energy such as heating or cooling, that are associated with the chemical reactions. It is the dissociation of ozone by the absorption of solar energy within the Huggins and Hartley bands, that is the conversion of the solar energy into a heat source in the stratosphere and mesosphere. In the lower thermosphere the important energy input is from the absorption of solar energy by molecular oxygen in the ultraviolet Schumann-Runge continuum.

Overall, the distribution of temperature in the middle atmosphere is a balance between the sum of the solar heating and infrared heating and cooling. The distribution of this radiative heating has a strong seasonal dependence, with maximum heating at the summer pole and maximum cooling at the winter pole. At equinoxes, there is cooling at both poles and maximum heating at the equator.

As many of the important reactions that affect ozone chemistry are temperature dependent any change in temperature will necessarily affect the reaction rates, and so
modify the ozone concentration. If the atmospheric temperature changes as a result of some external perturbation then ozone concentration will change in response. In general a decrease of temperature will slow the chemical reactions that deplete the ozone and so cause its concentration to increase.

A cooling of the lower stratosphere is expected as a result of the increase in the concentration of carbon dioxide. This gas is an important atmospheric radiator as it has a strong infrared emission at 15 \( \mu m \). Such cooling could increase the frequency and extent of polar stratospheric clouds (PSCs) that are an essential component of ozone destruction. Thus, the possible increase in greenhouse gases could exacerbate the ozone depletion problem. However, when the atmosphere cools, as a result of decreased heating or increased cooling, there is an adjustment in the hydrostatic equilibrium that will alter the local rates of formation of ozone through the three-body association of \( O \) with \( O_2 \). The net result (Chandra et al., 1979) is that the effect of temperature feedback is reduced at altitudes above 30 km and complicates the determination of those factors that control ozone perturbation.
CHAPTER III

STRATOSPHERIC OZONE PERTURBATION

3.1 Introduction

There are many geophysical factors that can cause ozone variations in the atmosphere. As ozone variations are related to temperature dependent photochemical processes and to the local concentration of other species, both the natural solar flux variations (e.g. seasonal) and atmospheric dynamics can have a large effect on the global ozone concentration and its distribution.

3.2 Natural ozone variations

In the following subsections some of these natural ozone variations are described in more detail.

3.2.1 Solar variations

The investigation of the behavior of atmospheric ozone and its relationship to variations in solar ultraviolet irradiance has been the topic of extensive research for many years. Numerous investigators studying long-term ozone data have considered the possibility that stratospheric ozone might be correlated with the 11 year solar cycle (Angell and Korshover, 1976; Keating et al., 1987; Keating, 1978; Blackshear and Tolson, 1978; London and Reber, 1979). Some of the studies have suggested that there is a relationship between ozone amount and the solar cycle, but this is not always the case. London and Reber (1979) have found that there is a high correlation between total
stratospheric ozone and solar activity if a small segment of declining phase of the solar cycle is matched with regular seasonal variation of ozone but not otherwise. Callis and Nealy (1978) and Pener and Chang (1978) have estimated the theoretical maximum variation of ozone and of several trace gas concentrations due to the 11-year solar cycle. The results of these calculations are shown in Figure 3.1 for a UV intensity variation of \( \pm 15\% \), below 260 nm, and suggest that solar cycle and ozone variations should be easily detected.

The response of the middle atmosphere to the short-term 27-day solar ultraviolet variability has been detected by Keating et al., (1987). The importance of this short-term solar variation is that it may be obtained within one year while a similar number of 11-year cycles requires nearly 150 years of observations. The measurements of the short-term solar UV variations at 205nm (205nm radiation is responsible for ozone production by \( O_2 \) photodissociation) exhibited a 27 day periodicity that was also present in the ozone measurements (Keating, et al., 1985; Hood, 1986). As the amplitudes of both the short-term and long-term variations seem to be comparable it is possible to use the short term variation to make improved estimates of the atmospheric response to the 11-year solar cycle variation (Keating et al., 1978).

### 3.2.2 Cosmic ray and precipitation particles

Ruderman (1974) has suggested that cosmic ray particles and \( \gamma \) rays could cause a substantial destruction to the ozone layer. He proposed that the mechanism for ozone destruction is due to the formation of large quantities of nitrogen oxides in the atmosphere through the ionizing effects of the incident radiation (Chapter 2). Crutzen
Figure 3.1: A theoretical estimate of the maximum variation in ozone and several other trace species, between solar maximum and solar minimum due to changes in UV fluxes (after Whitten and Prasad, 1985).
(1978) has also suggested that the high levels of ionizing radiation in the Earth's stratosphere that are associated with solar proton events could lead to increased concentrations of nitrogen oxides and so decreased ozone concentrations.

Other cosmic events such as collisions with large meteors, or comets, can cause significant atmospheric perturbations. The dissipation of the kinetic energy of the impacting body heats the air along the flight path and generates NO\textsubscript{x} that can in turn lead to a decrease of the amount of ozone in the stratosphere.

Auroral electrons, as with other sources of ionization such as X-rays ($\lambda < 10$ nm) and EUV radiation ($10$ nm $< \lambda \leq 120$ nm), produce large numbers of ion pairs and hence NO and OH molecules in the lower thermosphere. However, the probability that NO and OH reach the lower stratosphere is small because the NO molecules are rapidly photo-dissociated in the upper atmosphere (Frederick and Hudson, 1979) and the lifetime of OH is so short that vertical transport for distances in excess of 1-2 km is not significant (Bauer, 1979). Thus although the precipitating auroral electrons do not reach the stratosphere their interactions in the lower thermosphere do give rise to X-rays that can cause ionization in the stratosphere and so start the catalytic cycle.

3.2.3 Volcanic eruptions

The biggest explosive volcanic eruptions of the 20th century that have injected material into the stratosphere were El Chichon in Mexico, in March of 1982, and Mt. Pinatubo in the Philippines during June of 1991. The effect of these volcanic eruptions on the stratosphere are considered to be bigger than previous volcanic eruptions as they
injected large amounts of sulfur dioxide into the stratosphere that could cause an increase in the amount of stratospheric aerosols (Seinfeld and Pandis, 1998).

Although such large volcanic eruptions do not occur frequently, volcanic activity continues to provide a perturbation to the chemical, optical, and thermal structure of the atmosphere, and probably has significant global climatic and local meteorological effects (Solomon et al., 1984). The impact of volcanic eruptions can also include heating at stratospheric altitudes and cooling at the ground level, most probably as a result of an increase in the attenuation of solar radiation by scattering and an increase in the absorption of terrestrial and solar radiation. Thus volcanic eruptions affect the overall radiation balance of the Earth.

The mechanism for the conversion of $\text{SO}_2$ into $\text{H}_2\text{SO}_4$ aerosol in the stratosphere involves a two step reaction with OH radicals (Stockwell and Calvert, 1983).

$$\text{SO}_2 + \text{OH} + M \rightarrow \text{HSO}_3 + M \quad (3.1)$$

followed by

$$\text{HSO}_3 + \text{OH} \rightarrow \text{H}_2\text{SO}_4 \quad (3.2)$$

Volcanic eruptions can also inject hydrochloric acid ($\text{HCl}$) into the atmosphere where it could participate in the catalytic destruction of ozone. However, two factors may mitigate the effect of the injected $\text{HCl}$. Most eruptions are not powerful enough for the gases to reach the stratosphere and $\text{HCl}$ is very soluble in water, thus most HCl will remain well below the stratosphere until it is washed out by rain. Hence, most aerosol emissions associated with volcanic eruption are eliminated from the atmosphere quite
quickly and returned back to the surface of the Earth. The time for these aerosols to fall depends on the size of particles. Although \textit{HCl} from eruptions may not reach the stratosphere aerosols from volcanic eruptions can have profound effects on \textit{ClO} and the \textit{ClO}_x induced ozone depletion chemistry. Because \textit{N}_2\textit{O}_5 and water on the surface of aerosols both remove \textit{NO}_2 from the active reaction system, there is less \textit{NO}_2 available to react with \textit{ClO} to form the reservoir species \textit{ClONO}_2. Thus, any increase in stratospheric aerosol will enhance the effect of \textit{ClO} in the \textit{ClO}_x cycle.

\textbf{3.2.4 Sudden stratospheric warmings}

Other geophysical events can occur during mid-winter, and one such event is a dynamic effect in the stratosphere circulation. This event is a stratospheric warming and characterized by a rapid increase in the polar stratospheric temperature, over a period of ten days or less, that is accompanied by a reversal of the westerly mean winds to an easterly direction. There are two types of sudden stratospheric warming. A major warming when at 10 mb or below, the temperature increases poleward from 60° latitude and the mean winds reverse. If the temperature gradient reverses but the wind does not then it is called a minor warming. These warmings vary significantly from year to year and are much stronger in the northern hemisphere than in the southern hemisphere (Webb, 1966).

In the winter time northern hemisphere (where the lowest temperature occurs in the lower stratosphere) when a major stratospheric warming occurs the planetary-scale disturbances can be so strong that the polar vortex westerly flow is completely broken down and replaced by easterlies. As the vortex breaks down ozone rich air spreads from
low latitudes over the polar cap (WMO, 1989). Hence the effects of such warmings are to modify the winter polar vortex which is an essential factor in ozone depletion. Thus these warming events may be used to model ozone behavior, but the differences in the behavior of the events in different years, and between the northern and the southern hemispheres, may limit the value of the models.

3.3 Anthropogenic influences on ozone variations

With the increase in human activity over recent years there has been a clear increase in the abundance of some trace gases (e.g. CFCs, methane, nitrous oxide). These gases can, in some cases, have a large effect on the atmosphere, such as ozone and its variation, and may also lead to other potentially harmful effects.

3.3.1 Aircraft and rockets

During the last several years there has been much concern voiced about the potential climatological impact of a fleet of operational supersonic transports. Careful studies led to the conclusion that large fleets of commercial aircraft, both subsonic and supersonic, both of which use high temperature combustion engine, release large amounts of NOx directly into the stratosphere and so modify the atmospheric ozone content (Grobecker et al., 1974).

If the NOx is released near 20 km altitude there is ozone depletion through an enhancement of the NOx cycle. In contrast, if the release of NOx is at a lower altitude (10 to 12 km) there is a slight increase in ozone concentration (Crutzen, 1970). One reason for this is the associated large increase of water vapor in the troposphere,
compared to that in the relatively dry stratosphere, and another is that the presence of hydrocarbons in the upper troposphere that can react with NO$_x$ to form ozone. This last process is essentially the same as that in an urban polluted atmosphere. The heterogeneous conversion of NO$_x$ to N$_2$O$_5$ proceeds through NO$_3$ (Evans et al., 1985) and leads to a heterogeneous reaction on the surface of the aerosol that generates ozone, the conversion also acts to nullify the effect of the NO$_x$ cycle (Chapter 2).

As aircraft emissions are primarily limited to air traffic routes that are near the upper troposphere and the lower stratosphere the distribution of aircraft flight patterns causes the emissions to occur over relatively small areas of the Earth. Thus, for these reasons even relatively low emissions rates from aircraft may have a large effect on the ozone concentration.

Generally speaking, while emissions of carbon dioxide, nitrogen oxide, water vapor, and sulfate particles from aircraft can change the atmospheric composition directly they can also have an indirect effect through chemical chain reactions. These changes can affect both the climate, through the greenhouse effect, and the amount of ozone in the stratosphere.

3.3.2 Nuclear Explosions

The high temperatures that are produced in nuclear explosions can also lead to production of NO$_x$. Roughly 50 million tonnes of NO$_x$ could be generated by these explosions and deposited at high altitudes (Whitten and Prasad, 1985), with a subsequent decrease in the ozone content. Indeed the possible destruction of the Earth’s ozone shield by nitric oxide generated in nuclear explosions in the atmosphere has been
suggested by many authors. Foley and Ruderman (1973) first recognized that the large NO\textsubscript{X} injection associated with the Soviet atmospheric nuclear test series of 1961 and 1962 should produce a small reduction in the stratospheric ozone content. They evaluated the upper and lower limits of the nitric oxide injection into the stratosphere and compared the value to the upper limit of the production of NO\textsubscript{X} by supersonic aircraft. They also examined ozone data for the world for the period 1960-1965 but were unable to detect a significant reduction of ozone that correlated with the possible formation of NO\textsubscript{X} from nuclear explosions.

Several other authors have also attempted to estimate the magnitude of ozone change as a result of nuclear explosions. Goldsmith \textit{et al.} (1973) have estimated the production of nitrogen oxides in the shock waves of explosions associated with the atmospheric testing of nuclear weapons in the atmosphere. Their analysis of ozone records reveal that the data appear to limit the maximum possible ozone decrease to about less than 2\%, although the models suggest a decrease of about 2-3\%. However, the uncertainties in the data and the models are so large that firm conclusions could not be reasonably drawn (Whitten and Prasad 1985).

3.3.3 Halocarbons

'Halocarbons' is the general term that refers to halogen-containing organic compounds that have a wide variety of anthropogenic and natural sources. These compounds are produced in biological processes in the oceans, from biomass burning and from industrial activity. The lifetime of the halocarbons in the atmosphere depends on their production and removal, and ranges from a few days to several centuries.
As mentioned there are a variety of anthropogenic and natural halocarbons present in the atmosphere but the major anthropogenic impact on stratospheric ozone is due to a family of chemical compounds known as chlorofluorocarbons, CFCs (Molina and Rowland, 1974). The CFCs also play an important role in the atmospheric greenhouse effect because they persist for a long period of time and absorb radiation in the infrared region. There is an executive industrial use of Chlorofluorocarbons for refrigerants (CFC-12, HCFC-22), cleaning agents (CFC-13) and blowing agents (CFC-11, HCFC-22). The CFCs include methyl chloroform (CH$_3$CCl$_3$), ethylene dichloride (CH$_2$Cl$_2$), and tetrachlorethylene (C$_2$Cl$_4$) that are used as degreasers and for dry cleaning. The industrial solvent methyl bromide widely used in agriculture although methyl chloride (CH$_3$Cl) and methyl bromide (CH$_3$Br) are both products of biomass burning. The dissociation of the CFCs produces chlorine atoms that can react with ozone molecules in a catalytic cycle and destroy them (Chapter 2).

3.3.4 Water vapor and methane

The water vapor budget of the stratosphere comes from many sources. It comes partly by transport from the troposphere (Brewer, 1949; Dobson, 1956) and partly from the oxidation of methane (transported from the ground) in the stratosphere. Water vapor is also exchanged between the troposphere and stratosphere at mid-latitude breaks in the troposphere. However, as there is an increase in the atmospheric methane abundance due to anthropogenic activity it is important to consider its effects.

The vertical distribution of water vapor in the atmosphere is shown in Figure 3.2 and it is clearly apparent that the minimum concentration of water vapor is at a low altitude,
Figure 3.2: The vertical distribution of water vapor (H$_2$O) in the atmosphere H$_2$O volume mixing ratio (ppmv) (after Dieminger et al., 1996).
approximately 20 km. This region is sometimes called the hygropause. There is a second minimum in the upper mesosphere-lower thermosphere region (Tsou et al., 1988; Peter et al., 1988). The maximum concentration is above the stratopause in the region, 50 to 70 km (Bevilacqua et al., 1983) and it is in this region that the oxidation of methane and the general \( HO_x \) chemistry takes place (Thomas et al., 1989).

Adding water vapor to the stratosphere causes a decrease in ozone, no matter how little is added. The major reaction involving water vapor in the stratosphere is its photodissociation by solar ultraviolet radiation

\[
H_2O + hv \rightarrow H + OH \quad (3.3)
\]

or

\[
\rightarrow H_2 + O \quad (3.4)
\]

Water vapor is also dissociated by the reaction with \( O(\text{'D}) \) to produce OH.

\[
H_2O + O(\text{'D}) \rightarrow 2OH \quad (3.5)
\]

In both cases the OH released, or formed, joins the \( HO_x \) family and plays an important role in the ozone chemistry.

### 3.3.5 Carbon dioxide

Currently 85% of the primary energy source is from fossil fuels (coal, oil, and gas) which are essential sources of carbon dioxide (\( CO_2 \)) emission into the atmosphere. The principal anthropogenic sources of \( CO_2 \) are the burning of fossil fuels and the production of cement (Seinfeld and Pandis, 1998). The total \( CO_2 \) emissions can be
estimated based on statistical analysis of those sources. The idea of increased atmospheric carbon dioxide due to fossil fuel burning was first suggested by Callendar (1938).

Bolin (1977) has reviewed the situation and examined the effect of deforestation and more recently, continuous surface CO₂ records from different sites at various of latitudes have provided information on the seasonal and latitudinal variations of CO₂. These all show a clear increase of CO₂ levels in recent decades. The trend and the seasonal cycle of the CO₂ mixing ratio as measured at Mauna Loa (Hawaii) since 1958 is shown in Figure 3.3.

Deforestation can also lead to a significant exchange of CO₂ between the biosphere and the atmosphere. The recent global budget for CO₂ reported by Intergovernmental Panel on Climate Change (IPCC, 1995) indicated that the exchange fluxes of CO₂ between the ocean and atmosphere, of about 90 Gt(C) per year, and between the terrestrial biosphere and the atmosphere, of about 60 Gt(C) per year. These numbers are an order of magnitude larger than the CO₂ emissions from fossil fuel burning of 5.5 Gt(C) per year, and from deforestation of 1.1 Gt(C) per year. The total anthropogenic flux is 7.1 Gt(C) per year with an atmospheric accumulation of 3.3 Gt(C) per year. The remaining 3.9 Gt(C) per year must be taken up by the oceans and the terrestrial biosphere.

Unlike the other gases considered, CO₂ does not act chemically to perturb ozone but can modify the atmospheric temperature structure. In the upper stratosphere CO₂ emits more infrared radiation into space than it absorbs. Thus an increase of CO₂ and its mixing
Figure 3.3: Trends and seasonal cycle of carbon dioxide mixing ratio measured at Mauna Loa, Hawaii, since 1958 (after Seinfeld and Pandis, 1998).
ratio will cool the upper stratosphere, and so affect the chemical reactions for ozone depletion that are all highly temperature dependent.

Wang (1989) have studied the effect of stratospheric change, due to a CO$_2$ doubling, on the tropospheric climate. Their study, based on a 2-D seasonal tropospheric climate model with a stratospheric level, indicated that interactions in the stratosphere, involving both the change in the dynamical heat fluxes and the change in ozone caused by the CO$_2$ increase, can influence both the warming in the troposphere and cooling in the stratosphere. This effect is particularly large at the northern high latitudes during wintertime. Thus study of the CO$_2$ problem and its impact on ozone requires an understanding of both emission sources, and also the transfer of CO$_2$ between the atmosphere, ocean and biosphere (Brasseur and Solomon, 1984).
CHAPTER IV

DATA CHARACTERISTICS

4.1 Introduction

The various factors that can affect the atmospheric ozone content have been described in Chapter 2 and Chapter 3. It is readily apparent that any study of these effects must have a suitable database available.

4.2 Available data

Ozone concentrations have been measured for many years using ground based spectrometers. Initially these were of the Dobson type but more recently the Brewer ozone spectrometer has become the world standard. Ozone profiles have been measured with balloon-sondes, up to 30 km, and with the occasional rocket experiment.

These data are all necessarily limited in their geographic extent and it is only with the advent of satellites that true global measurements have been possible. However, as with all standard systems the measurements must be validated so that these are an on-going need for ground-based and balloon-borne systems.

4.3 Types of data

4.3.1 Total Ozone Mapping Spectrometer (TOMS)

The Total Ozone Mapping Spectrometer (TOMS) experiment on board the Nimbus-7 satellite provided daily global measurements of the Earth's total ozone throughout the
period from October 1978 to May 1993. This instrument measures the backscattered Earth radiance in six wavelength regions from 312.5 to 380 nm. A single monochromator and scanning mirror are used to sample the backscattered solar ultraviolet radiation at 35 steps, 3 degrees apart, in an eight second period; this includes the one second for the mirror to return quickly (fly-back) to the first position without making measurements (McPeters et al., 1996).

TOMS has provided daily ozone measurements for the entire globe, at least over that part of the Earth that is illuminated by the sun. The total ozone is retrieved by calculating the radiance as a function of total ozone and the measurement conditions, such as surface pressure, surface reflectivity, and latitude. The measured radiance is then compared with the calculated radiance and the most recent pressure measurement (Dave, 1964). Unless noted otherwise, all equations that follow have been taken from McPeters et al., 1996).

\[ I_m(\lambda, \theta, \phi, \omega, P, R) = I_a(\lambda, \theta, \phi, \omega, P) + I_s(\lambda, \theta, \phi, \omega, P, R) \]  \hspace{1cm} (4.1)

where

- \( I_m \) = the backscattered radiance emerging from the top of the atmosphere as seen by a TOMS instrument
- \( I_a \) = atmospheric backscatter
- \( I_s \) = reflection of the incident radiation from the reflecting surface
- \( \lambda \) = wavelength
\( \omega \) = column ozone amount

\( \theta \) = satellite zenith angle

\( \theta_0 \) = solar zenith angle

\( \phi \) = azimuth angle

\( P \) = surface pressure

\( R \) = reflective coefficient at the reflecting surface

The surface reflection term is

\[
I_s(\lambda, \theta, \theta_0, \omega, P, R) = \frac{RT(\lambda, \theta, \theta_0, \omega, P)}{1 - RS_b(\lambda, \omega, P)} \tag{4.2}
\]

\[
T(\lambda, \theta, \theta_0, \omega, P) = I_d(\lambda, \theta, \theta_0, \omega, P) f(\lambda, \theta, \omega, P) \tag{4.3}
\]

where

\( S_b \) = fraction of radiation reflected from the surface that the atmosphere reflects back to surface

\( I_d \) = total amount of direct and diffuse radiation reaching surface at \( P \)

\( f \) = fraction of radiation reflected toward the satellite, in direction \( \theta \), that reaches satellite

In general the intensity of radiation received is given by
where

\[ \tau \] is the optical depth, and depends on the number of absorbers \( n \) and the absorption efficiency of the absorbers (\( \alpha \)).

Thus expression 4.4 may be written as

\[ I \alpha \exp(-n\alpha) \] (4.5)

As noted the ozone column is derived through a comparison of the measured and calculated brightness. The ratio of radiance to irradiance in the form of the \( N \) value which provides a unit for backscattered radiance that has scaling comparable to the column ozone, the multiplicative factor 100 is used to produce a convenient numerical range (McPeters et al., 1996).

\[ N = -100\log_{10}(\frac{I}{F}) \] (4.6)

The ozone calculation is actually a two step process. First, an initial ozone column is determined from the difference between the \( N \) values at two wavelengths, one wavelength is strongly absorbed by ozone and the other is insensitive to the ozone content. The estimated ozone is then used to calculate the optical extinction and the difference between the measured and estimated \( N \) values at other wavelengths used to improve the ozone estimate.
As TOMS has a 50 kilometer square field of view at the sub-satellite point the total ozone column is averaged over this area. Since TOMS makes 35 measurements every 8 seconds it provides approximately 200,000 ozone measurements each day. These measurements are reported in Dobson units (DU), 1 DU is 1 milli-atmo-cm. Thus a 300 DU column means that if the entire ozone amount were compressed to standard temperature and pressure it would be 3 mm thick.

During the first 7.5 months of operation, TOMS followed a regular ON/OFF schedule for spacecraft power management and operated for only 10 out of 12 days. At times, the instrument was operated on scheduled off days, this resulted in an actual duty cycle greater than 83 percent. There were some initial spacecraft malfunctions that prevented measurements from being made but, starting June 22, 1979, TOMS operated full time until May 6, 1993 when the instrument failed (McPeters et al., 1996).

The TOMS data set has also been used to determine cloud location and height. This information is useful in determining the altitude above which ozone is being measured (Grant, 1989). However, the matter is not simple as the presence of Polar Stratospheric Clouds (PSCs) in the upper stratosphere could have uncertain effect on the TOMS ozone readings. Type I PSCs may have produced an underestimate of up to 2% at solar zenith angles greater than 80 degrees and an underestimation of 5% may have occurred in the presence of Type II PSCs (McPeters et al., 1996).

Unfortunately the basic TOMS algorithm does not accurately retrieve the total ozone when volcanic clouds were present because the SO$_2$ absorption also occurs in the 290-320nm range and produces a false enhancement in the ozone measurements. However,
this effect only occurred for a short specific time as the $\text{SO}_2$ is rapidly converted into sulfuric acid aerosols.

The precision and accuracy of TOMS measurements has been checked by comparisons with other current instruments. Its precision is given as 2%, or better, and there is a small drift in the data of about 0.4% per year (Bhartia et al., 1984; Fleig et al., 1988). However, some of the work presented in this thesis suggests that this may not always be the case.

4.3.2 Dobson spectrophotometer

Although a number of ground-based and satellite techniques are used for measurements of atmospheric total ozone, the Dobson ozone spectrophotometer (Dobson and Normand, 1957) serves as the reference standard instrument in the global ozone observation system. The ground-based Dobson spectrophotometer measures the solar radiation in the Huggins bands (300-350 nm). The measurements are made at pairs of wavelengths. One wavelength is significantly absorbed by ozone while the other is only weakly absorbed and is attenuated in the instrument with a calibrated optical wedge to match the observed radiance at the two wavelengths. A null setting then allows the relative radiance, and thus the total ozone amount, to be determined. The total ozone amount ($X$) is given by the following formula (Unless noted otherwise, all equations that follow have been taken from Whitten and Prasad, 1985).

$$X = \frac{[\log\left(\frac{L_{\infty}}{L_{2\infty}}\right) - \log\left(\frac{L_i}{L_2}\right) - (\beta - \beta_2)m(P/P_0) - (\delta_1 - \delta_2)\sec\xi]}{(\alpha_1 - \alpha_2)\mu}$$  (4.7)
where

\[ X = \text{the total amount of ozone} \]

\[ L_1 \text{ & } L_2 = \text{the measured radiance at the top of atmosphere in relatively strong and weak ozone absorbing wavelength respectively} \]

\[ L_1 \text{ & } L_2 = \text{the measured radiance at the ground of atmosphere in relatively strong and weak ozone absorbing wavelength respectively} \]

\[ \beta_1 \text{ & } \beta_2 = \text{molecular scattering for air (atmosphere}^{-1}\text{) at wavelength of relative strong and weak ozone absorption respectively} \]

\[ \delta_1 \text{ & } \delta_2 = \text{the relative coefficients of scattering aerosol at wavelength of relative strong and weak ozone absorption respectively} \]

\[ \alpha_1 \text{ & } \alpha_2 = \text{ozone absorption (cm}^{-1}\text{) at wavelength of relative strong and weak ozone absorption respectively} \]

\[ P \text{ & } P_0 = \text{station pressure and mean sea level pressure respectively} \]

\[ m = \text{the optical path length allowing for refraction through the molecular scattering spherical atmosphere} \]

\[ m' = \text{the relative slant path through the aerosol atmosphere} \]

\[ \mu = \text{relative path length of the solar beam through the ozone layer for a spherical atmosphere} \]
\( \xi \) = the solar zenith angle

m, m' and \( \mu \) are only different from each other for \( \xi \geq 75 \), this implies that a flat Earth approximation is not valid for large solar zenith angles.

For a single pair of wavelengths, a differential measurement that includes the differential absorption of sunlight by ozone also includes the effects of differential scattering by atmospheric molecules and aerosols. Thus, the measurements are made for two separate pairs of wavelengths to cancel the errors due to aerosols in the atmosphere (Dobson and Normand, 1957). If the measurements for two close wavelengths pairs are combined the scattering effects are essentially cancelled because they are similar for the close wavelength pairs (Grant, 1989).

The most reliable measurements of the total ozone column are made using direct or scattered sunlight. Useful routine measurements can also be made on clear and cloudy zenith skylight spectra, or sometimes moonlight, by combining the different wavelength pairs to get the appropriate observing condition. The long-term annual mean ozone measurement precision is estimated to be 1% (at 2\( \sigma \) level), based on the standard deviation \( \sigma \) derived from an analysis of mean data from individual stations (WMO, 1980, 1981, 1982).

The Dobson spectrophotometer was replaced by the Brewer spectrophotometer in some Canadian stations in late 1981. Although the method of measurement of total ozone with the Brewer is similar to that for the Dobson instrument, there are differences in the sampling and reporting of daily data. These differences arise primarily because the
Brewer instrument is fully automatic and so is capable of sampling continuously throughout the day. Measurements are screened and only those that are believed to be of good quality are used to determine the reported daily mean total ozone value.

Results of the inter-comparison between the Brewer and Dobson instruments at Edmonton have been presented and compared with the results of the same inter-comparison for instruments at Toronto. The inter-comparison was made in a four step process. The Brewer ozone data were compared with the Dobson data as follows: (1) as measured; (2) corrected for $SO_2$; (3) corrected for $SO_2$ and an observed airmass dependence; and (4) corrected for $SO_2$, airmass dependence, and an observed annual variation (Evans, 1989). The overall result indicated an accuracy agreement between these instruments of better than 1% and the drift between them was found to be statistically insignificant.

As many factors can influence the accuracy of Dobson spectrophotometer measurements, these instruments undergo a frequent calibration by direct comparison with instrument No. 83 (WMO designated world primary standard Dobson spectrophotometer), or indirectly through intercalibrations with secondary standard Dobson spectrophotometers that were calibrated in Boulder in 1977. The world standard instrument is itself calibrated each summer (since 1962) at the Mauna Loa observatory in Hawaii. The filter ozone-meter (No. 83), which measures the ozone column by looking directly at the sun at 299 nm, was developed in 1963 and improvements were made in 1972 by adopting specific filter bandwidths and including a third filter to correct for aerosol effects.
Dobson spectrophotometers are believed to have a measurement accuracy of approximately 5% in comparison with the satellite Total Ozone Monitoring Spectrometer (TOMS) measurements, and 2-4% in the absence of aerosols (Bojkov et al., 1988).

4.3.3 Balloon ozonesondes

Two general types of ozonesondes are in use today, the Brewer Mast (BM) (Brewer and Milford, 1960), which uses one platinum and one silver electrode, and the electrochemical concentration cell (ECC) (Komhyr, 1969), which uses a platinum electrode only.

Balloon ozonesondes are balloon-borne instruments that are flown with standard meteorological radiosondes for the measurement of ozone, temperature, and pressure up to altitudes as high as 35 km. These instruments consist of an electrolytic cell that contains a solution of potassium iodide (KI), and are based on the reaction of this solution with ozone. When air containing ozone is passed through these cells (by a small pump) an electric current is generated that is proportional to the amount of ozone passing through the cell (Tiao et al., 1986). Thus measurements of the cell output current, and the airflow rate, allow the number of ozone molecules entering the cell per unit time to be determined.

Sondes are tested before launch and are rejected if there is excessive background current. The pump must also be conditioned with ozone prior to flight in order to minimize the ozone destruction by the pump. The pumps in the Brewer ozonesondes are lubricated with a thin film of oil that can destroy ozone. The BM sonde sensors are not
specific to ozone and can be affected by other species. For example, nitrogen dioxide will cause ozone readings to be too high, while sulfur dioxide will give the opposite effect (Tiao et al., 1986). This is important as SO$_2$ absorbs in bands throughout the 290 nm to 320 nm range, the same as those used for ozone. The effect of this absorption is to produce a false enhancement in the ozone measurements. BM sondes apparently give lower readings of tropospheric ozone than the ECC sondes, but ECC sondes also give high readings in the region between 50 and 20 mb. This has been attributed to outgassing from a glue used in the pump fabrication (Komhyr, 1969) and to anomalous background current in the cell (Barnes et al., 1985).

Most sondes, but especially the Brewer-Mast sondes, only rarely give the same total ozone amount as that measured simultaneously with an ozone spectrophotometer. The sonde profile is necessarily integrated and must include the ozone amount that is assumed to be above the balloon burst level, 30-35 km. To achieve an improvement in data quality, and to obtain the agreement between the integrated sonde profile and the corresponding measured total ozone, most ozonesondes measurements at all altitudes are multiplied a normalization, or correction factor (CF). However, the use of a constant multiplication factor for normalization may not be justified for soundings that exhibit large ozone losses within the instrument (Hilsenrath et al., 1981). It should be noted that there are differences in the correction factors (CF) between the Brewer-Mast (BM) and the electrochemical concentration cell (ECC) sondes. The acceptable value of the normalization factor for BM data ranges from (1.1-1.3), and for the ECC data the average is close to 1.0 (Tiao et al., 1986).
The foregoing discussion of available ozone data suggests that the quality of the database may not be as consistent as is frequently assumed.

4.4 Available data for study

The ozone data used in this study were kindly provided by Dr. C.T. McElroy, AES, who supplied a CD ROM of the data held at the World Ozone Data Center (WODC) in Toronto, Canada. The TOMS satellite data are also available from the NASA/Goddard Space Flight Center.

In the present work particular attention was paid to Canadian stations that could provide a direct comparison with the TOMS data. These stations are listed in Table 4.1, this table also indicates the amount of TOMS data that is available for each station; column 5 indicates the percentage of available data for each station. There is no missing data in the TOMS measurements for the period January 1979 to December 1992 for these stations, except for the stations at Alert and Resolute as no measurements are possible during the polar night each winter.

Routine measurements of total ozone using Dobson spectrometers were started at various Canadian stations in 1957 but the present study covers only the period from January 1979 to December 1992 for which there is concurrent satellite data. The available measurements of ground-based from the Dobson spectrometers, for the concurrent satellite period, are listed in Table 4.2.
Table 4.1: Canadian stations used in this study and the available TOMS data.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude (°N)</th>
<th>Total Monthly Record Available</th>
<th>Total Monthly Record Missing</th>
<th>Percent Record (%) Available</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alert</td>
<td>82.50</td>
<td>98</td>
<td>70</td>
<td>58.3</td>
</tr>
<tr>
<td>Resolute</td>
<td>74.72</td>
<td>112</td>
<td>56</td>
<td>66.7</td>
</tr>
<tr>
<td>Churchill</td>
<td>58.75</td>
<td>168</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Edmonton</td>
<td>53.55</td>
<td>168</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Goose Bay</td>
<td>53.32</td>
<td>168</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Toronto</td>
<td>43.78</td>
<td>168</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4.2: Canadian stations used in this study and the available total ozone data measured with ground-based spectrometers.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude (°N)</th>
<th>Total Monthly Record Available</th>
<th>Total Monthly Record Missing</th>
<th>Percent Record (%) Available</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alert</td>
<td>82.50</td>
<td>72</td>
<td>96</td>
<td>42.9</td>
</tr>
<tr>
<td>Resolute</td>
<td>74.72</td>
<td>85</td>
<td>83</td>
<td>50.6</td>
</tr>
<tr>
<td>Churchill</td>
<td>58.75</td>
<td>148</td>
<td>20</td>
<td>88.1</td>
</tr>
<tr>
<td>Edmonton</td>
<td>53.55</td>
<td>165</td>
<td>3</td>
<td>98.2</td>
</tr>
<tr>
<td>Goose Bay</td>
<td>53.32</td>
<td>163</td>
<td>5</td>
<td>97.0</td>
</tr>
<tr>
<td>Toronto</td>
<td>43.78</td>
<td>168</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

As mentioned previously (section 4.3.3) total ozone columns can also be determined from ozonesonde measurements. The available ozonesonde measurements, and the type of sonde used, are listed in Table 4.3.
Table 4.3: Available ozonesonde data

<table>
<thead>
<tr>
<th>Station</th>
<th>Available Data</th>
<th>Ozoneonde Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sep. 1979 - Dec. 1992</td>
<td>ECC</td>
</tr>
<tr>
<td></td>
<td>Sep. 1979 - Dec. 1995</td>
<td>ECC</td>
</tr>
<tr>
<td></td>
<td>Sep. 1979 - Dec. 1995</td>
<td>ECC</td>
</tr>
<tr>
<td>Goose Bay</td>
<td>June 1969 - Aug 1980</td>
<td>BM</td>
</tr>
<tr>
<td>Toronto</td>
<td>Nov. 1976 - Apr. 1978</td>
<td>BM</td>
</tr>
<tr>
<td></td>
<td>Apr. 1980 - June 1994</td>
<td>ECC</td>
</tr>
</tbody>
</table>

The ozone profile is usually presented as a mixing ratio at various pressure levels, typically 9 levels, rather than as a concentration at an altitude. However, the different pressure levels and their mean altitudes in the atmosphere are listed in Table 4.4.

The first part of this study involved a comparison between the TOMS and ground based data for at each station to verify the consistency of both and to identify obvious errors in the ground based data. This not a simple matter as the TOMS observations are always made near local noon while ground based measurement are made at other times, although it is usually possible to identify data collections that are separated by less than two hours. In addition, the TOMS spectrometer has a field of view that varies between 50 and 250 km depending on the angle from the nadir (Klenk et al., 1982). Thus the center of the TOMS field of view did not always coincide with the ground station although data collected within 0.5°, latitude and longitude, could always be identified.
Table 4.4: The atmospheric pressure layers (mb) and their mean heights (km) (Tiao et al., 1986)

<table>
<thead>
<tr>
<th>Pressure level</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mb)</td>
<td>700</td>
<td>500</td>
<td>300</td>
<td>200</td>
<td>100</td>
<td>70</td>
<td>50</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Altitude (km)</td>
<td>3</td>
<td>5.4</td>
<td>9</td>
<td>11.7</td>
<td>16.3</td>
<td>18.6</td>
<td>21</td>
<td>25</td>
<td>32</td>
</tr>
</tbody>
</table>

A summary plot of the total ozone measurements, both Dobson and TOMS, used in this study is given in Figure 4.1. It is clearly apparent that data was not recorded by TOMS over Alert and Resolute during the polar night. It also appears that the total ozone values from the two systems exhibit a systematic difference each year. This plot also indicates that the total ozone column has a strong seasonal pattern as well as a latitudinal dependence. This latter is quite clear from a comparison of the amplitude of the ozone variation at Alert and Resolute, high latitude stations, to that at Toronto, a mid-latitude station. For each matched pair of TOMS and ground-station measurements a difference was calculated according to equation 4.8,

\[
\text{Difference (\%)} = \left( \frac{\text{station amount} - \text{TOMS amount}}{\text{station amount}} \right) \times 100 \quad (4.8)
\]

The monthly differences for each of the six Canadian stations are shown in the plots given in Figure 4.2. The three stations Goose Bay, Toronto and Edmonton show good agreement between the satellite and ground based data, the monthly differences for those stations are only 3 or 4% throughout the period, except for the spring of 1989 when the data from Goose Bay is low by about 13%. The Churchill Dobson ozone record is in good agreement with TOMS for most of the year, the differences are about 3 to 5%, except for each winter (December to January), when the ground-based data is
Figure 4.1: Comparison of total ozone measurements from TOMS and Dobson spectrometers
Figure 4.2: Monthly differences of ozone for the six Canadian stations.
low by about 10 to 15%, for the period 1979 to 1986 and reaches 20% in the 1991 and 1992 winters. It has been suggested that this is due to the absence of direct sun observations during those months, because of the virtually constant cloudy conditions, and because the zenith-sky transfer charts in use are not made specifically for Churchill (Bojkov et al., 1988). However, it is also possible that the albedo factor used in the TOMS algorithm is in error for that period each year. The missing data for Resolute and Alert, make it difficult to recognize a systematic difference between the two techniques, although there are significant differences for these two stations.

4.5 Missing data

Missing data is a particular problem for this type of study. Some researchers prefer to exclude any cases, or variables, that contain missing values while other researchers prefer to fill data gaps through various statistical methods. The first approach is probably quite good if only a few cases have missing values, or if the missing values are concentrated in a few variables that have no effect in the data analysis. Generally, however, the missing values are scattered throughout the variables and cases and so make it difficult to simply exclude the data set from the analysis. Thus it is necessary to fill the data gaps. There are many procedures that can be used to fill the data gaps. Some procedures are based on prior knowledge using climatology while others simply insert mean values. These means are calculated using all available data.

Although there are missing data at most stations used in this study, especially for those using simple Dobson equipment, it is easier, and probably better and convenient, to
exclude any cases or variables that contain missing data. The obvious variability in high
latitude ozone columns supports this approach.

4.6 **Errors in the available data**

There are some errors in the total ozone values derived from the TOMS measurements
and these may be traced to several sources. The measurement of the radiance, the
adopted cross-sections, the parameterization of atmospheric properties used as input for
the radiative transfer calculations, and limitations in the way that the radiative transfer
models represent the physical processes in the atmosphere. Each of these error sources
can be manifest in one, or more, of four different ways: random error, an absolute error
that is independent of time, a time-dependent drift, or an error that will appear only
under certain conditions (McPeters *et al.*, 1996). Although there has been extensive
work on these error sources it is apparent from the work in this thesis that there is still
significant uncertainty.

The data from the Dobson station network used in this study must also be evaluated in
the same way as TOMS data. Some factors that need to be taken into account when
using data from the Dobson station network are:

1- Geographic variations based on changes of the pressure pattern and its variation from
one region to another.

2- Instrumental error and other local sources. The reduction of this effect is based on
calibration of the instrument; Dobson instruments are subject to long term
calibration, and this may affect the estimation of the measured ozone trend.
3- Statistical error in estimating the trend. This is dependent on the estimation of the trend; the selection of the appropriate model for ozone data can reduce the effect of this factor.

Similarly the BM and ECC ozonesondes, that are used to measure the vertical profile of ozone concentration, have significant errors (section 4.3.3) and particular care must be exercised with these data. In this work only data from ECC sondes have been used to eliminate any effects of the change of measurement method, from BM to ECC.

It is readily apparent that for the present study it is extremely important that the data quality be high. The use of the monthly average data reduces the effect of daily and short-term variations. The simple inclusion of data without a quality assessment can result in some residuals that lead to significant differences in the derived trends, even for stations that are located in the same geographic region.
CHAPTER V

DATA ANALYSIS AND RESULTS

5.1 Introduction

The ozone and temperature data from six Canadian stations (Chapter 4) have been analyzed using regression time series models. The included data were measured by ground-based, satellite and ozonesondes techniques during the period from January 1979 to December 1992. Any incomplete data were removed from the measurement data sets in order to eliminate, or reduce, the effects of any systematic errors or changes. The possible relationship between ozone and temperature is investigated for these stations and other meteorological effects that might affect ozone are also discussed.

5.2 Ozone variations in the Northern Hemisphere

Various geophysical factors can affect the natural ozone levels. Variations in the ozone concentration depend on the rates of the relevant photochemical processes and on atmospheric transport that is associated with meteorological effects. These variations can be quite different from one region to another, although natural processes do regulate the balance of ozone in the stratosphere. Ozone levels also change periodically as part of the regular natural cycles such as seasons, periods of solar activity, and changes in wind direction. The ozone concentrations are also affected by isolated events, such as volcanic eruptions that can inject material into the stratosphere. In general, the ozone content of the Earth's upper atmosphere controlled
by a complex dynamical system that is held in place by complicated and involved chemical reactions schemes, thermodynamics and density wave processes.

One prominent feature of the total ozone column is its strong seasonal variation and the associated latitudinal variation. The time-latitude cross-section of the averaged total ozone measured by TOMS, for the period January 1979 through December 1992, is shown in Figure 5.1. The contours are for 20 Dobson Unit intervals, data poleward of 60°N and 60°S must be treated with caution as TOMS data are not available during the polar night.

The total ozone reaches a minimum of less than 260 DU at equatorial latitudes and increases poleward in both hemispheres with maximum values above 400 DU. As the equator receives the most ultraviolet radiation most of the ozone is produced at, or near, the equator. However, atmospheric winds quickly move ozone away from the equator and distribute it around the globe, the decreased solar ultraviolet flux at high latitude moves the equilibrium at these latitudes to higher ozone column amounts.

It is clear that the latitudinal increase in the ozone column is a maximum during late spring in each hemisphere. The annual ozone maximum values seem to occur at approximately the same time over the northern hemisphere. This may be linked to the sudden stratospheric warmings which occur during winter and can transport ozone rich air. In the northern hemisphere total ozone reaches the annual maximum in late spring and the minimum is in October. Most spring ozone maximums appear clearly in the middle to high latitudes, reaching maximum values that are typically greater than 400 DU in March and April between 60°N and 75°N. In the southern hemisphere, ozone
Figure 5.1: Time latitude cross section of TOMS total ozone (DU)
reaches its maximum value of more than 380 DU in September and October at about 60°S, but the time of the maximum is delayed by one to two months at higher latitudes. The low ozone feature that appears around the south pole for approximately two months prior to the summer maximum occurs every year. The presence of this feature is consistent with the idea that the southern hemisphere polar vortex is more stable than the northern hemisphere vortex, and thus blocks poleward transport (Hilsenrath et al., 1981).

The total ozone column variation and the ozone variation in the lower and middle stratosphere are highly correlated since the Quasi Biennial Oscillation (QBO) plays a major role in the control of the ozone concentration. In this oscillation ozone is transported from the upper stratosphere to the lower stratosphere in the polar region. The correlation between the QBO and global ozone amounts was first noted by Bojkov (1986), and Solomon et al., (1986) and Schoeberl et al. (1986) have studied this relationship for the Antarctic. These authors all found that relatively low (high) total ozone values were linked with the westerly (easterly) phase of the QBO. Lait et al. (1994) have found that the correlation is improved if tropical winds at 30mb instead of 50mb are used, although they did not give the explanation of why this should be so. However, Lait and his coworkers did conclude that an increase of planetary wave activity in the middle and upper stratosphere would increase the polar temperatures, and so reduce the volume and frequency of polar stratospheric clouds. This, in turn, would allow more NOx to enter the vortex from mid-latitudes, and thus reduce the amount of active chlorine through the formation of ClONO₂ (WMO, 1989). The average period of the ozone QBO is about 27 months in the tropics while
the period of the zonal wind QBO is closer to 2 years in the same region. At the
equator the amplitude of the ozone QBO is minimum and its period is approximately
24 months. Zerefos (1983) has shown that at the equator the QBO in ozone is
apparently positively correlated with the QBO in temperature at 50 mb, thus maximum
ozone occurs with the maximum temperature. However, it should be noted that the
chemical production rate is reduced and the loss rate is increased as the temperature is
raised.

The seasonal and latitudinal variation of the region of maximum ozone is very clearly
tied to seasonal and hemispheric differences in the stratospheric circulation at levels of
25-40 km. These circulation differences result from variations in the equator to pole
temperature gradient and the different topographic features of the two hemispheres
(Mahlman et al., 1981).

The mean annual variations of the total ozone column, measured with TOMS for two
different stations located in the northern and southern hemispheres, for the period
January 1979 to December 1992 are shown in Figure 5.2. The curves show an annual
ozone variation that is similar in both hemispheres, but with the opposite phase and a
larger amplitude in the northern hemisphere. This latter is due to the stronger poleward
ozone transport in the northern hemisphere. It is clearly evident that maximum ozone
occurs in springtime in the northern hemisphere (March-April) and also in the
southern hemisphere in springtime (September-October).
Figure 5.2: Monthly variation of mean total ozone in different hemispheres.
5.2.1 Trend analysis for satellite ozone data

In order to investigate the seasonal behavior of ozone trends, a statistical time series model has been fitted to the monthly averages of TOMS ozone measurements at each of the six Canadian stations. Because the effects of season are dominant in the analysis of total ozone data, 6 and 12 months periodicities have been used in the model. The model does not include the other geophysical factors that might influence ozone variations, such as solar cycle and QBO. The multiple regression model that has been used is given by equation 5.1

\[ Y(t) = \beta_0 + \beta_1(t) + S(t) + \epsilon \]  \hspace{1cm} (5.1)

where

\[ \beta_0 = \text{The intercept (overall mean level)}. \]

\[ \beta_1(t) = \text{Ozone trend over time}. \]

\[ S(t) = \text{Annual and semiannual variation over time and is defined as} \]

\[ S(t) = \beta_2 \sin\left(\frac{2\pi t}{12}\right) + \beta_3 \cos\left(\frac{2\pi t}{12}\right) + \beta_4 \sin\left(\frac{2\pi t}{6}\right) + \beta_5 \cos\left(\frac{2\pi t}{6}\right) \]  \hspace{1cm} (5.2)

The term \( \beta_1(t) \) describes the linear trend in the total ozone where \( t \) is the time in months since 1979.

\[ i.e. \quad t = 0 \quad \text{for} \quad t_{yr} < 1979 \]
The model for the ozone variation, equation 5.1, was used in its simple regression form, after removing the seasonal variation terms, to estimate the trend of the TOMS ozone measurements at each of the individual stations for the 1979-1992 period, and to determine possible monthly trend variations. The data were grouped into twelve sets, one set for each month from January to December. Thus each set contains the measurements for the month for each of the fourteen years from 1979 to 1992.

The trend estimates for the six Canadian stations are listed in Table 5.1. The estimates of the seasonal trends of total ozone from the TOMS measurements over each individual station are shown in Figure 5.3. The trend values are given as cumulative percent changes per year by dividing the trend estimates with the overall mean and multiplying by 100 as in equation 5.3.

$$\frac{\beta_1}{\beta_0} \times 100$$  \hspace{1cm} (5.3)

The trend values were estimated for all months, January to December, for all stations, except Alert and Resolute as TOMS cannot make measurements in the polar night. The months January, February, October, November and December were missing from Alert, and the months January, February, November and December were missing from Resolute. The model fits, equation 5.1 shows that there is a negative trend most of the time for all of the Canadian stations studies. This is in agreement with the results of Stolarski et al. (1992) and Reinsel et al. (1994) who also indicate that the trends have become more negative with time at higher northern latitudes.
Table 5.1: Monthly trends estimated (percent/year) from TOMS data.

<table>
<thead>
<tr>
<th>Months</th>
<th>Alert</th>
<th>Churchill</th>
<th>Goose Bay</th>
<th>Resolute</th>
<th>Toronto</th>
<th>Edmonton</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>0.307</td>
<td>0.342</td>
<td></td>
<td>-0.536</td>
<td>-0.123</td>
<td></td>
</tr>
<tr>
<td>February</td>
<td>-0.183</td>
<td>-0.111</td>
<td></td>
<td>-0.765</td>
<td>-0.767</td>
<td></td>
</tr>
<tr>
<td>March</td>
<td>-0.061</td>
<td>-0.473</td>
<td>-0.008</td>
<td>-0.471</td>
<td>-0.661</td>
<td>-0.557</td>
</tr>
<tr>
<td>April</td>
<td>-0.863</td>
<td>-0.347</td>
<td>-0.150</td>
<td>-0.952</td>
<td>-0.463</td>
<td>-0.637</td>
</tr>
<tr>
<td>May</td>
<td>-0.268</td>
<td>-0.217</td>
<td>-0.019</td>
<td>-0.010</td>
<td>-0.403</td>
<td>-0.520</td>
</tr>
<tr>
<td>June</td>
<td>-0.337</td>
<td>-0.761</td>
<td>-0.308</td>
<td>-0.361</td>
<td>-0.389</td>
<td>-0.651</td>
</tr>
<tr>
<td>July</td>
<td>-0.382</td>
<td>-0.242</td>
<td>-0.039</td>
<td>-0.328</td>
<td>-0.270</td>
<td>-0.198</td>
</tr>
<tr>
<td>August</td>
<td>-0.044</td>
<td>-0.373</td>
<td>-0.402</td>
<td>-0.506</td>
<td>-0.078</td>
<td>-0.300</td>
</tr>
<tr>
<td>September</td>
<td>0.196</td>
<td>-0.360</td>
<td>-0.237</td>
<td>-0.053</td>
<td>-0.207</td>
<td>-0.171</td>
</tr>
<tr>
<td>October</td>
<td>-0.149</td>
<td>-0.094</td>
<td>-0.050</td>
<td>-0.060</td>
<td>-0.067</td>
<td></td>
</tr>
<tr>
<td>November</td>
<td>-0.622</td>
<td>-0.455</td>
<td>-0.275</td>
<td>-0.418</td>
<td></td>
<td></td>
</tr>
<tr>
<td>December</td>
<td>-0.194</td>
<td>-0.232</td>
<td>-0.435</td>
<td>-0.126</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.2.2 Trend analysis for the Dobson ozone data

The total ozone data from the Dobson network for the period from January 1979 to December 1992 was also analyzed according to equation 5.1. An annual trend estimate (year-round) was obtained by using the monthly average data for each individual station and fitting the complete regression model, including the seasonal variation terms. The trend values from the Dobson and TOMS data are listed in Table 5.2, the values have been scaled to percent per year with equation 5.3. These results suggest that the trend is a decrease in total ozone of between -0.1 and -1.6% per year over the 14 year period.
Figure 5.3: Seasonal trends of total ozone measured by TOMS.
The trend results from the two data sets appear to be in good agreement, although there are some small differences for Churchill and Goose Bay. Toronto, perhaps surprisingly which is in a region of high urban pollution, showed a very good agreement between the ground-based data and TOMS trends. The large standard errors for Dobson trends at Churchill and Alert probably represent the difficulty in making the Dobson measurements at these stations due to adverse weather conditions.

Table 5.2: Comparison of the trend estimates (percent/year) from TOMS and Dobson data sets

<table>
<thead>
<tr>
<th>Stations</th>
<th>TOMS Trend</th>
<th>Standard Error</th>
<th>Dobson Trend</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alert</td>
<td>-0.405</td>
<td>0.467</td>
<td>-1.608</td>
<td>2.550</td>
</tr>
<tr>
<td>Churchill</td>
<td>-0.280</td>
<td>0.338</td>
<td>-0.584</td>
<td>1.078</td>
</tr>
<tr>
<td>Goose Bay</td>
<td>-0.128</td>
<td>0.280</td>
<td>-0.480</td>
<td>0.390</td>
</tr>
<tr>
<td>Resolute</td>
<td>-0.340</td>
<td>0.358</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Toronto</td>
<td>-0.397</td>
<td>0.271</td>
<td>-0.432</td>
<td>0.260</td>
</tr>
<tr>
<td>Edmonton</td>
<td>-0.387</td>
<td>0.311</td>
<td>-0.588</td>
<td>0.400</td>
</tr>
</tbody>
</table>

These features are very clear from Figure 5.4, which is a comparison of the trend values estimated from the Dobson and TOMS data for each of the stations. In most cases the two trend curves are close to each other, although there is a large difference for Alert. This is probably due to missing data at this station as there is no TOMS data...
Figure 5.4: Annual trend estimates for all Canadian Stations

- Alert
- Churchill
- Goose
- Resolute
- Toronto
- Edmonton

Trend (Percent/Year)

Station

0.0

-0.5

-1.0

-1.5

-2.0

TOMS Trend
Dobson Trend
available during the polar night, and there were no Dobson measurements available until September 1988.

Monthly trends were also fitted with the simple form of equation 5.1 (i.e. without the seasonal variation terms) for all stations except Alert. This station was omitted from the analysis as there was not enough data available.

5.2.3 Further comparison of Dobson and TOMS trends

The results listed in Tables 5.1 and 5.3 are the total ozone trends estimates for the individual station, the estimates are given by percent per year for TOMS and Dobson data respectively. A plot of the month by month comparison of the trend results for TOMS and Dobson data sets is shown in Figure 5.5. The agreements between the two trends appear clearly in this figure, especially for Toronto and Edmonton which have nearly the same features. The Churchill and Goose Bay trends are also close to each other, except that the Dobson January result for Churchill is not consistent with TOMS result for the same month. Small differences are also obvious for the months of April and May at both of these stations and is probably due to the missing Dobson data.

The missing measurements in the TOMS data are clearly evident from the Resolute station from November to February and there is a small difference between the Dobson and TOMS trends for September and October at this station. In the TOMS curve, the highest decrease appears in summer and fall at Churchill and Goose Bay. The situation is different at Resolute, Toronto and Edmonton where the most negative trend occurs in winter and springtime. However, the wide variations in the monthly trends at Resolute and Churchill indicate that the dynamic nature of the polar vortex,
and adverse weather conditions, can make the identification of ozone behavior quite
different (see also Table 5.4).

Table 5.3: Monthly trends estimated (percent/year) from the Dobson data set.

<table>
<thead>
<tr>
<th>Months</th>
<th>Churchill</th>
<th>Goose Bay</th>
<th>Resolute</th>
<th>Toronto</th>
<th>Edmonton</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>2.430</td>
<td>0.830</td>
<td>0.740</td>
<td>-0.390</td>
<td>-0.190</td>
</tr>
<tr>
<td>February</td>
<td>-0.260</td>
<td>-0.110</td>
<td>1.090</td>
<td>-0.870</td>
<td>-0.950</td>
</tr>
<tr>
<td>March</td>
<td>-0.790</td>
<td>-0.230</td>
<td>-0.450</td>
<td>-0.770</td>
<td>-0.620</td>
</tr>
<tr>
<td>April</td>
<td>-0.720</td>
<td>-0.640</td>
<td>-0.800</td>
<td>-0.660</td>
<td>-0.560</td>
</tr>
<tr>
<td>May</td>
<td>-1.370</td>
<td>-0.500</td>
<td>-0.060</td>
<td>-0.630</td>
<td>-0.590</td>
</tr>
<tr>
<td>June</td>
<td>-1.100</td>
<td>-0.580</td>
<td>-0.340</td>
<td>-0.600</td>
<td>-0.780</td>
</tr>
<tr>
<td>July</td>
<td>-0.660</td>
<td>-0.200</td>
<td>-0.330</td>
<td>-0.340</td>
<td>-0.280</td>
</tr>
<tr>
<td>August</td>
<td>-0.325</td>
<td>-0.400</td>
<td>-0.350</td>
<td>-0.410</td>
<td>-0.380</td>
</tr>
<tr>
<td>September</td>
<td>-0.620</td>
<td>-0.420</td>
<td>0.630</td>
<td>-0.370</td>
<td>-0.210</td>
</tr>
<tr>
<td>October</td>
<td>-0.020</td>
<td>-0.260</td>
<td>1.170</td>
<td>-0.120</td>
<td>0.130</td>
</tr>
<tr>
<td>November</td>
<td>-1.050</td>
<td>-0.220</td>
<td>0.290</td>
<td>-0.350</td>
<td>-0.30</td>
</tr>
<tr>
<td>December</td>
<td>-0.920</td>
<td>0.080</td>
<td>0.770</td>
<td>-0.230</td>
<td>-0.270</td>
</tr>
</tbody>
</table>

The same complete model equation 5.1 has been used for the individual stations to
estimate the seasonal trend at the stations. The data were grouped into four seasons;
winter, spring, summer, and fall. December, January, and February (DJF) were
defined as the winter season, March, April, and May (MAM) were considered the
spring season, June, July, and August (JJA) the summer season, and September,
Figure 5.5: Comparison of monthly trends between TOMS and Dobson data
October, and November (SON) the fall season. The trend results, scaled to percent per year, for both TOMS and Dobson data sets are presented in Table 5.4.

Table 5.4: Seasonal trend results (percent/year) for TOMS and Dobson data.

<table>
<thead>
<tr>
<th>Stations</th>
<th>TOMS</th>
<th>Dobson</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DJF</td>
<td>MAM</td>
</tr>
<tr>
<td>Alert</td>
<td>-0.408</td>
<td>-0.258</td>
</tr>
<tr>
<td>Churchill</td>
<td>-0.022</td>
<td>-0.379</td>
</tr>
<tr>
<td>Goose B.</td>
<td>0.003</td>
<td>-0.041</td>
</tr>
<tr>
<td>Resolute</td>
<td>-0.503</td>
<td>-0.395</td>
</tr>
<tr>
<td>Toronto</td>
<td>-0.591</td>
<td>-0.512</td>
</tr>
<tr>
<td>Edmonton</td>
<td>-0.362</td>
<td>-0.572</td>
</tr>
</tbody>
</table>

As shown in Figures 5.6 and 5.7 the calculated ozone trends exhibit a seasonal dependence for both the TOMS and Dobson data sets. These figures also confirm, see Figure 5.5, that the largest decrease, according to TOMS occurred in spring (MAM) for Alert, Resolute, Toronto and Edmonton. For the Churchill and Goose Bay stations the largest decrease occurred in summer according to the TOMS data sets; the seasonal trend estimates from the Dobson data sets were not consistent.

However, it is clear from this analysis that the trend in total ozone for the Canadian stations in this study is negative, although these trends are quite variable from month to month and from season to season. The trends in the winter and spring season are much more negative than in summer and fall at Edmonton. At Churchill the maximum trend is in spring and summer, and at Goose Bay the largest trend is for the fall. These
Figure 5.6: Seasonal trends of the TOMS data
Figure 5.7: Seasonal trends of the Dobson
conclusions are drawn from the TOMS data set and it is noted that this is not in total agreement with Dobson data. However, this analysis omitted one important ozone feature in that it did not consider the latitudinal behavior of ozone. Although Alert and Resolute are located at high latitudes, they do not show the large negative trends in TOMS, or Dobson, data that have been reported for high latitude southern hemisphere stations. The trend values at those stations are generally more than -1.0 percent/year. This important difference may due to missing data from TOMS and the more dynamic nature of the northern hemisphere polar region.

5.2.4 Trend analysis for the vertical distribution of ozone.

A statistical analysis of the monthly average ozonesonde readings in the troposphere and lower to mid-stratosphere has also been used to assess ozone trends. The complete model equation 5.1, including the seasonal factors, has been used with data from five of the six stations. Toronto was eliminated as the available data set was too short. A list of the five stations used in this study and their periods of record are given in Table 4.4. The troposphere, lower and mid-stratosphere were divided into nine layers (700, 500, 300, 200, 100, 70, 50, 30, 10 mb). Only the data period 1979-1992 was considered because it exactly corresponds to the period of the available ground-based and satellite data. The type of sondes used at each station was also considered in an attempt to eliminate the effects of any systematic change in the measurement method caused by the Brewer Mast (BM) and Electrochemical concentration cell (ECC). The model equation 5.1 was also used to estimate the seasonal trends by dividing the year into four seasons (DJF, MAM, JJA and SON) as with the TOMS and Dobson trends analysis.
The results of this analysis are presented in Figure 5.8 where it is clear that there is no increase in tropospheric ozone for the Canadian stations, except perhaps at Edmonton which shows a small increase of about 0.2 % per year below 500 mb. This finding agrees with that of Oltmans (1993). The seasonal trends for the stations are presented in Figures 5.9 and 5.10. The increase in tropospheric ozone over Edmonton is clearly apparent in the seasonal trend values, Figure 5.9. The maximum tropospheric increase occurs in summer at 700 mb and in spring at 500 mb. The increase of tropospheric ozone below 500 mb for Edmonton is probably due to the change in the time of the measurements from early morning to late afternoon for the period 1985-1989. Ozone values for sondes released at 1600 (Local Time) are generally 20% larger than those from sondes released at 0400 (Local Time). This means that there is a strong diurnal variation in surface ozone near Edmonton in agreement with the findings of Angle and Sandhu (1986). However, this result could also happen if there are high levels of SO2 present, as these directly affect ozononde measurements, or if there is an increase of NOx levels in the troposphere.

It is quite clear from Figure 5.8 that in the stratosphere ozone is decreasing at all of the stations, the largest decrease being at Alert. The most significant trends were found in 700, 100, 70, 50 and 10 mb levels. On the other hand, there is no significant trend in the seasonal variation, except perhaps a decrease in summer over Churchill at 70 and 50 mb. No seasonal trend results are presented for the Alert station as the data were not available for more than 50% of the period.

In summary, there appears to be no long-term tropospheric change in ozone over these Canadian stations, except perhaps a small increase that has occurred over Edmonton
Figure 5.8: Trends in the vertical distribution of ozone at each station
Figure 5.9: Trends in the vertical distribution of ozone by season for Resolute and Edmonton
Figure 5.10: Trends in the vertical distribution of ozone by season for Churchill and Goose Bay
that could be due to a change in the measurement time. In the stratosphere an ozone
decrease occurred between 30 mb to 300 mb. The largest decrease was in winter at
Alert, Edmonton and Resolute and in summer at Churchill and Goose Bay.

At 10 mb the ozone measurements show an apparent trend increase. However, care
must be taken in assuming that this is real as the high altitude pumping efficiency
characteristics of ECC ozonesondes can introduce problems in ozone measurements at
high altitude. Ozone measurement accuracy for ECC ozonesondes is estimated to be
±10% in the troposphere, ±5% in the stratosphere to 10 mb, and ±5% to -20%
between 10 and 3 mb (Hilsenrath et al., 1981).

5.3 The possible effect of temperature and other parameters on ozone

Changes in the chemical composition of the atmosphere as a result of the increase of
gases released in anthropogenic activity, such as CFCs and CO₂, and from natural
isolated events, such as volcanic eruptions, may cause trends in temperature and other
variables. A knowledge of the relationship between total ozone and temperature, and
other meteorological parameters in the atmosphere, is important in the study of the
observed distribution and variability of atmospheric ozone.

The study of the relationship between ozone and meteorological parameters was
initiated by Dobson et al. (1929) who found that total ozone increased and decreased
with the passage of a cold and warm front respectively. In a later study Meetham
(1937) found a significant correlation between total ozone and temperature in the
middle atmosphere. In particular, he found that there is a positive correlation between
ozone and temperature in the lower stratosphere; this result is supported by Ohring and
Muench (1960) who also found a correlation between temperature and ozone. More recent studies by Schubert and Munteoun (1988) have determined that the correlation coefficient between ozone and temperature at 100 mb, from TOMS and weather data, is greater than 0.6. Thus there is clear evidence to suggest a correlation between the total ozone column and various meteorological factors.

5.3.1 Temperature trends

The morphology of temperature trends and its variation in the Northern hemisphere, and the relationship of ozone partial pressure and temperature have been studied to see if the observed total ozone decrease might be a result of, or contribute to, the decrease in stratospheric temperature. A mechanism external to the stratosphere, such as a climate shift in the troposphere or volcanic aerosol injection, could be acting to systematically reduce the temperature in the lower stratosphere and so cause the observed decrease in total ozone (Newman and Schoeberl, 1986).

The vertical profile of the average air temperature and monthly average ozone profile are shown in Figures 5.11 and 5.12 (respectively) for each of the five Canadian stations. It is clear that the temperature variation in the troposphere has the standard lapse rate of about 6°C/km. Above the upper boundary of the troposphere, the tropopause, the temperature is constant with altitude, ranging from -40°C to -50°C at all stations. However, on occasions the temperature drops to -70°C and or -80°C, although these low values do not always appear in the monthly mean. These low temperatures indicate that polar stratospheric clouds, that are essential factors in ozone depletion, might be present over the stations. This kind of cooling is seen at Alert and
Figure 5.11: Temperature (°C) profile over the five Canadian stations
Churchill quite frequently during the period 1979 to 1992. The cooling in the low stratosphere occurs mostly in the winter and spring season and is probably associated with the decrease in total ozone during springtime at those stations.

Above about 20 km the temperature rises with increasing altitude until the top of the stratosphere. A warming in the lower stratosphere is often detected and appeared in the winters of 1982 and 1986 over Churchill, and in the winter of 1983 at 70 and 50 mb, and in the winter of 1987 at 70 mb over Goose Bay. The strong warming in 1982 might be related to the eruption of the Mexican volcano El Chichon, in March and April 1982, that injected a large quantity of material high into the stratosphere. In earlier studies Newell (1970) and McInturff et al. (1971) have concluded that it is difficult to isolate the volcanic effect from other influences, or trends. It is quite probable that this warming was a combined effect of the eruption and the tropical stratospheric quasi-biennial oscillation, the latter is an important factor in ozone variation in the tropical region. From their study Parker and Brownscombe (1983) concluded that the equatorially-symmetric nature of the observed warming pattern was a result of the interaction between the equatorial waves that maintain the quasi-biennial oscillation and the equatorially-symmetric forcing of the wind fields by the thermal effect of the volcanic material.

The distribution of ozone over the five Canadian stations as a function of time is shown in Figure 5.12. In the troposphere there is no obvious increase in the ozone amount over each stations. However, the ozone concentration increases with increasing altitude with the largest content in the lower and mid-stratosphere. This is expected as the downward diffusion of ozone from the source region to the natural
sink at the ground would cause a positive gradient such as that measured. It is was
worth noting that all stations recorded a decrease in the ozone concentration between
70 and 50 mb in 1983, the same situation occurred over Goose Bay and Edmonton in
1985.

The seasonal variations of ozone and temperature at the 100, 70, 50, 30, and 10 mb
levels for the period from January 1979 to December 1992 are shown in Figure 5.13.
There appears to be a cooling at the 10 mb level in some years. The drop in
temperature below -80 °C at Alert could indicate the presence of polar stratospheric
clouds (PSCs). Unfortunately, the limited temperature data for this station does not
allow a clear picture of the temperature distribution in this layer. It is also noted that
the parallel changes in temperature and ozone indicate that the decrease in ozone
amount is associated with a decrease of temperature at 10 mb in agreement with the
work of Meethan (1937).

In the same way as the previous ozone trend analyses the temperature trend has also
been estimated from equation 5.1. The data were taken from radiosondes and the
atmosphere was divided into nine layers, as mentioned before, to estimate the trends at
the different levels through the period 1979-1992. It was believed that such a trend
might explain the derived trend in total ozone The temperature trends analysis reveals
that there are no significant negative trends, except perhaps at Edmonton and
Churchill at the 10 mb level. The results of this analysis are plotted in Figure 5.14 and
show a positive trend in the troposphere for most stations except for Goose Bay with
small negative trends in the lower and mid-stratosphere, except at Alert and Resolute.
Figure 5.12: Ozone partial pressure profile (μmb) over the five Canadian stations
Figure 5.13: Ozone partial pressure (μmb) and temperature (°C) at different layers
Thus, although the very low temperatures associated with PSCs have been recorded at Resolute and Alert this is not evident in the trend analysis shown in Figures 5.13 and 5.14. This should not be taken to mean that there is no cooling trend at these stations. Rather it is probably due to limited amount of 10 mb data at these stations.

5.3.2 The relationship between the observed ozone and temperature trend

The total ozone and temperature data were plotted together in Figure 5.13 and, as mentioned previously, it is easy to recognize the parallel change of ozone and temperature in almost any year, particularly at 50 and 30 mb. This clear relationship between stratospheric temperature and ozone indicates the importance of the effect of stratospheric circulation on both ozone and temperature behavior.

Sekiguchi (1986) has studied the relationship between stratospheric circulation, and temperature and ozone amount. He concluded that both the monthly mean temperature and ozone amount in the lower stratosphere may reflect the predominant atmospheric circulation (i.e., the monthly mean temperature in the lower stratosphere must be higher and the total ozone amount must be large when downward motion is predominant in that period).

Thus it could be concluded from the results presented in Figure 5.13 that the changes of ozone and temperature are parallel due to the effect of atmospheric circulation in which downward motions were predominant. Petzoldt et al. (1994) support this idea with their study of the correlation between ozone partial pressure, temperature and total ozone. They found a high correlation coefficient between temperature and ozone and suggested that this correlation might be due to the vertical motions that produced
changes in temperature as well as in ozone. As the ozone concentration increases with height, up to approximately 25 km, upward/downward motion will transport lower/higher contents of ozone to higher/lower levels, and simultaneously the temperature will be changed adiabatically. The dynamically-forced vertical motions could result in the detected positive correlation between ozone partial pressure and temperature.

In order to investigate this idea the ozone partial pressure and the temperature data from radiosondes were fitted using the standard time series model (equation 5.1) with the addition of a temperature term. Thus the equation becomes:

\[ Y(t) = \beta_0 + \beta_1(t) + \beta_6(t) + S(t) + \epsilon \]  

(5.4)

where

\[ S(t) = \beta_2 \sin\left(\frac{2\pi t}{12}\right) + \beta_3 \cos\left(\frac{2\pi t}{12}\right) + \beta_4 \sin\left(\frac{2\pi t}{6}\right) + \beta_5 \cos\left(\frac{2\pi t}{6}\right) \]  

(5.5)

\[ \beta_6(t) \] = Temperature effect factor over time.

The other terms are similar to those appearing in equation 5.1.

This model, equation 5.4, was fitted to the data for each individual level to determine the effect of temperature on ozone, and its behavior in each layer. The results of this fit are presented in Figure 5.15 and it is apparent that the pattern of ozone trends (model without temperature) is consistent with the pattern of ozone trends (model with temperature), except perhaps for the slight difference in the 500 mb layer above
Churchill and Resolute. This result is in agreement with that of Reinsel et al. (1981) who found no substantial differences in the global trend in ozone from a fit of the same models as used in this study with data from a global network of 36 ground-based Dobson stations over the period 1958 to 1979. These results may indicate that the seasonal variations in the temperature and ozone profile are masking the linear trend and so limiting the findings of the present study.
Figure 5.14: Temperature trends for the five stations
Figure 5.15: Differences in trend estimates for trends in the model with and without temperature
CHAPTER VI

SUMMARY AND CONCLUSIONS

6.1 Evaluation of the analysis

The objectives of this study were to estimate the trends for total ozone column values for data measured in the three ways that is ground-based, satellite and ozonesondes, and to evaluate the possible relationship between ozone and temperature in the lower to mid-stratosphere. A seasonal trend analysis had been performed with those data from six Canadian stations for the period from January 1979 to December 1992.

For the TOMS satellite data significant negative trends were found for all stations except Goose Bay which shows an insignificant negative trend. This finding is supported with the Dobson data from ground-based instruments that were analyzed for the same period. The results of fitting the regression time series model showed significant negative trends for all stations. The detected ozone trend of -0.1 to -1.6% per year is in agreement with other reported studies (Harris et al., 1997) for Canada. However, a closer comparison of the results of trends obtained from the analysis of TOMS and Dobson data showed that the absence of data could be important. For example, Alert shows quite a large difference between the two results. Toronto showed an interesting result where it was in a good agreement between the ground-based and TOMS trend although it is in a region of high urban pollution.

Generally, it is noted that TOMS and Dobson are not in total agreement although some consistencies occurred with some stations such as Toronto and Edmonton. In addition,
Although Alert and Resolute are located at high latitude they do not show the expected negative trends compared with the high latitude southern hemisphere stations. This may be due to the lack of data sets for those stations and due to the difference in the meteorological conditions in both hemispheres.

A seasonal trends analysis also gave a clear indication of negative trends at most stations for both the TOMS and Dobson data. Although these results are quite variable from month to month and from season to season, they confirmed the trend results of total ozone by TOMS and Dobson which showed that the most negative trends occurred in winter and spring for Alert, Resolute, Toronto and Edmonton. The opposite occurred at Churchill and Goose Bay, where the largest decreases were in summer and fall. Churchill showed a large difference in the trend for January between the TOMS and Dobson data. This might be due to the lack of data for this month, although it could well be due to an error in the albedo that is assumed in the TOMS algorithm.

A trends analysis of the vertical distribution of ozone also showed the downward trends in the lower and mid-stratosphere. The one positive result was in the trend in the troposphere, below 500 mb, at Edmonton. This is probably a result of the change in the time of the measurements from early morning to late afternoon. Although it is clear that there is slight cooling at 10 mb for most stations, probably associated with the PSCs, the trend results for the vertical distribution data showed positive trends in this layer. However, care must be taken in assuming that is probably due to an error in the ozonesonde reading since the ozone measurements accuracy for ECC ozonesondes is estimated $\pm 5\%$ to $20\%$ between 10 and 3 mb (Hilsenrath et al., 1981).
The temperature trends that were analyzed using data obtained from ozonesonde measurements showed both negative and positive trends at all stations, although the deviation from zero was small. Thus little new clear knowledge was gained on the matter of temperature trends at the stations and it is suggested that the dynamical nature of the northern hemisphere polar vortex may mask the effect.

However, the general relationship between temperature and ozone was found to be good, especially in spring at most stations. While this study tested the existence of a cooling in the lower and mid-stratosphere that could be related to ozone change through the formation of polar stratospheric clouds (PSCs), the conclusion is unclear. Certainly low temperatures associated with PSCs were found, but the ozone response was not detected. This could be due to the dynamical nature of the northern hemisphere pole which does not allow the same chemical processing as the southern hemisphere pole.

The increase and decrease of temperature has an effect on ozone changes, but the direct connection that is observed in the southern hemisphere is probably masked by other effects.

6.2 Recommendations for future work

Evidence of a negative ozone trend has been observed in the analysis of data for all selected Canadian stations. Although TOMS data provide an almost complete data set there are some differences between the trends in Dobson and TOMS data sets and this must be investigated further. This will require continued monitoring, a re-evaluation of the previous ozone databases, and long term calibrations of the instruments. In addition,
the knowledge of the chemistry of atmospheric trace gases and their measurement must be improved if the various effects are to be separated.

However, probably the most important recommendation is for an improvement in the quality of the measurements and long term data sets. At the present time the existing data are simply too marginal for this type of study that is indicated to identify those factors which cause ozone depletion in the northern hemisphere.
REFERENCES


middle atmosphere program, Sechrist, Jr. ed., SCOSTEP Secretariat, University of Illinois, Urbana, 14, 1981.


