Total Column Ozone Variability Over Toronto, Ontario, Canada

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Ozone data was examined for Toronto, Ontario, Canada using statistical analysis. It was found that total column ozone thickness has been decreasing at an average rate of 0.64 percent per year over the last 38 years. However, there is considerable variability on several time scales. A spectral analysis was performed on a 13 month running mean of the ozone data. Aside from the expected seasonal cycle, ozone varied at time scales consistent with the quasi-biennial oscillation (QBO) of the stratospheric circulation, and the sun spot cycle.

Keywords: total column ozone, quasi-biennial oscillation, sun spot cycle, Toronto

Ozone is capable of absorbing wavelengths (ultraviolet radiation) of biologically damaging ultraviolet light. This radiation has been linked to health and environmental concerns. Most of this ozone (90 percent) is found in the stratosphere, the layer of the atmosphere lying between the altitudes of 10 and 50 kilometers (Kowalok 1993). Heat generated from this absorption causes the temperature to increase with altitude in the stratosphere. The resulting temperature profile is largely responsible for the dynamic stability of the stratosphere (Shen et al. 1995). Hence, the presence of the stratospheric ozone layer is vital both to human health and to the dynamic stability of the stratosphere.

Most research on ozone depletion focuses on the dramatic changes in the Antarctic Ozone Hole. The purpose of this paper is to examine the temporal variability in the thickness of the ozone layer over the Great Lakes area, as typified by data collected at Toronto, Ontario, Canada (Hosseinian 2000). We wish to address the following two questions: has there been a decrease in total column ozone in this region? And what is the source of interannual and interdecadal variability in the total column ozone?

In this study, statistical analysis is used to examine the trend in the total column ozone concentration for the past four decades (1960 to 1998). Non-anthropogenic variations in the total ozone concentration are examined and some causal mechanisms for these variations are presented. The use of quantitative statistical analysis of the ozone data can readily enhance the search for unusual or abnormal changes in the ozone (Hill 1982). These analyses can be used to separate physical and chemical mechanisms from random variations.

Background
Ozone Circulation
Stratospheric circulation plays an essential role in determining the spatial and temporal distribution of ozone. Ozone circulation can be illustrated through the Brewer-Dobson circulation model (Figure 1).

It consists of a meridional circulation in each hemisphere, with air rising into the stratosphere in the tropics (where there is little seasonal variation in ozone), moving poleward, with descent and entrainment into the troposphere at high latitudes. This mass circulation transfers ozone from the tropical production regions and allows accumulation near the poles, accounting for the spring polar maximum (James 1994).

Ozone Chemistry
Human activity has caused a marked increase in the concentration of certain important trace gases in the
atmosphere, including OH, NO, ClO, and BrO (Brasseur and Hitchman 1988). These ozone destructive radicals can have a significant impact on ozone concentration, either directly through photochemistry or indirectly by changing the radiative budget and hence the temperature and chemistry. As the temperature structure changes, transport of chemicals by mean circulation and waves can also change.

Equations (1) and (5) describe photodissociation in the presence of solar radiation. Equation (1) occurs for wavelengths less than 246 nm and Equation (5) occurs for wavelengths less than 1140 nm but most strongly below 310 nm. Reactions (2) and (3) are three body collisions, the third body M being required to satisfy energy and momentum conservation simultaneously. In reactions (3) and (5), the odd oxygen particles (i.e., O and O₃) are converted into each other, and are much faster than reactions (1) and (4) in which odd oxygen particles are created and destroyed (Houghton, 1986).

However, the more recent theories of ozone chemistry not only take into account the classical theory, but they also account for other catalytic cycles that result in the net reaction 2O₃→3O₂ and which do not require the presence of an O atom. These catalytic cycles involve ozone destructive radicals. For example, a catalytic cycle based on the coupling of the OH and ClO families involve:

\[
\begin{align*}
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{HO}_2 & \rightarrow \text{HOC}_2 + \text{O}_2 \\
\text{HOCl} + \text{hv} & \rightarrow \text{OH} + \text{Cl} \\
\hline
\text{Net:} & \quad 2\text{O}_3 + \text{hv} \rightarrow 3\text{O}_2
\end{align*}
\]

Also, another catalytic cycle based on the coupling of BrO and ClO families involve:

\[
\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{Br} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2 \\
\text{ClO} + \text{BrO} & \rightarrow \text{Cl} + \text{Br} + \text{O}_2 \\
\hline
\text{Net:} & \quad 2\text{O}_3 \rightarrow 3\text{O}_2
\end{align*}
\]

(Oshen et al. 1995).

Ozone destructive radicals such as chlorine and bromine are greatly enhanced in the current atmosphere. They are transported to the stratosphere by means of other anthropogenically released chemicals, such as chlorofluoro carbons (CFCs). Once they are in the stratosphere, these chemicals break down through the process of photodissociation releasing the fixed Cl and Br radicals. CFCs are particularly effective at reducing ozone because of their long half-life of approximately 100 years and consequently CFCs have been strongly linked to the observed global ozone reduction in the latter part of the industrial era.

**Ozone Change Processes**

Changes in stratospheric ozone in the mid-latitudes can result from two broad categories of mechanisms;
chemical and dynamical. Ozone creation and destruction both cause variation in ozone concentration. Ozone destruction, as outlined in the previous section, is dependent on the introduction of ozone destroying radicals, such as derivatives of CFCs. Ozone creation is dependent on the supply of solar UV radiation. Any variations of this supply could result in variations in ozone. The solar sun spot cycle of approximately 11 years (Figure 2) provides the most temporally relevant variation, other than the seasonal cycle. The 11-year cycle is not constant, however, it varies between nine and 13 years with variations in recent decades at the low end of the range (Lean 1991). There is approximately a 0.1 percent decline in total solar irradiance from the maximum to the minimum of a solar sunspot cycle (Waple 1999). Dynamically, as outlined in Figure 1, ozone is transported poleward from the equatorial source region via the stratospheric circulation.

The most prevalent variation in the stratospheric circulation is the quasi-biennial oscillation (QBO) (James 1994). The QBO is observed in the middle and lower stratosphere as a variation in the equatorial zonal winds, which oscillate between westerlies and easterlies approximately every two to three years (Figure 3) (James 1994). When observed variations in the tropics are filtered for annual and semiannual periodicities and long-term trends, the residual variation shows a strong relationship between total ozone and the zonal tropical winds of the QBO (London 1985; Hamilton 1998). What is less well known, but increasingly becoming apparent operationally, is that the QBO signal also exists in the extratropical stratosphere. There is as yet no generally accepted explanation of how the equatorial QBO signal is transmitted to polar latitudes (Tung and Yang 1994; Kinnersley and Tung 1999).

Figure 2: Time series of solar sun spot number for 1960 - 1999.
Methods

Source of Data

The data used in this study was retrieved from the World Ozone and Ultraviolet Radiation Data Center (WUDC). WUDC is one of seven recognized World Data Centers which are part of the World Meteorological Organization, Global Atmosphere Watch program. The WUDC is operated by the Experimental Studies Division of the atmospheric Environment Service, Environment Canada, located in Toronto, Ontario, Canada (WUDC 1998).

For this study, the World Ozone Data Center (WODC) data set was used. There are over 300 stations represented in the archive, some of which contain over 35 years of continuous data. The data for this work was retrieved from station 065 located in Toronto (Elevation: 198 m, Latitude: 43.78° N, and Longitude: 79.47° W) and maintained by the Atmospheric Environment Service of Environment Canada. The data used from this archive are the daily Total Column Ozone which represents the total thickness of the ozone layer in Dobson Units (DU), defined as 0.01 mm thickness at standard temperature and pressure i.e., 0°Celsius and one atmosphere pressure, and it spans a period of nearly 38 years from January 1, 1960 to July 30, 1998.

To assess the influence of the solar sunspot cycle, data from the Solar and Terrestrial Physics Division of National Geographic Data Center were obtained. Tropical stratospheric wind data, measured over Singapore, were obtained from the Institute of Meteorology at the Free University of Berlin.

Statistical Analysis

Monthly means were calculated from the daily total column ozone data, and these are used throughout this work. To examine trends, a time series line plot of the monthly means of total ozone was created (Figure 4), revealing the presence of strong seasonal cycles and resulted in a low coefficient of determination ($r^2=0.033$). A low $r^2$ value indicates that the regression line can account for only a small percentage of the variations in total ozone.
To illustrate larger time scale trends, the seasonal variations were minimized using two separate methods. The first method was the use of a 13 month running mean. The ozone value for every month was calculated as a mean of the data six months before and after. The running mean method is a helpful graphical aid for visualizing any long term patterns or apparent trends (Hill 1982). Afterward, a time series spectral analysis was performed on the running mean data in order to observe any possible long term variations other than the obvious seasonal cycles.

The second method that was used to minimize the data variability is a method suggested by Hill (1982), where the average of all values corresponding to the same month is subtracted from that month; e.g., total monthly ozone for January 1982 minus the mean of monthly ozone for all months of January, from 1960 to 1998. To compare the results of these two methods, a basic statistical analysis was performed on the data obtained from each method.

**Results**

Figure 4 is a time series line plot of monthly total column ozone for Toronto, from 1960 to 1998. One gross feature is an apparent decrease in total ozone with time. As the regression line indicates, the slope is 0.053. Every month, on average, there is a 0.053 percent decrease in total ozone (0.64 percent per year, or 6.4 percent per decade). Another feature is the reduction of seasonal amplitude with time, which appears to be tied to the absolute value of the ozone concentration, a point explored in more detail in Hosseinian (2000).

Figures 5a and 6 are the line plots of monthly total column ozone for Toronto for the same time period as Figure 4, applying the two trend analysis methods described above. In Figure 5a, the running mean method of de-trending is used and in Figure 6, the second method is used. Using a linear regression fit, the same decreasing trend observed in Figure 4 is found in Figures 5a and 6. In these two figures, however, the seasonal variations have been reduced.
Figure 5: Monthly total column ozone over Toronto for 1960 - 1998. Thirteen month running mean trend analysis has been applied. a) Linear regression fit. b) Polynomial fit.
A comparison of Figures 5a and 6 reveals that the 13 month running mean trend analysis method (Figure 5) is a more effective way of removing the seasonal cycles (high frequency variation) from the data. This is further substantiated by Table 1 where some basic statistical results of the three data sets (i.e. original monthly total ozone, monthly total ozone with 13 month running average applied, and monthly total ozone with seasonal cycles removed) are summarized: The coefficient of determination \( r^2 \) increases from three percent to 57 percent for the first method and to 19 percent for the second method. Other methods for removing the seasonal cycle are reviewed in Hosseinian (2000).

In Figure 5(b) a polynomial fit is also included. The polynomial fit indicates that most of the decrease in total ozone that was evident in Figure 4 took place between 1979 and 1992, with a recent increasing trend in ozone concentration beginning in 1993. The influence of volcanism can also be seen as there is a significant decrease in total ozone concentration at or shortly after 1991 and a similar, albeit muted, pattern is also apparent after 1982. This is coincident with the eruption of Mt. Pinatubo in 1991 and El Chichón in 1982.

Figure 7 is a time series spectral analysis for the mean monthly total column ozone data with the 13 month running mean applied. This graph summarizes some of the mechanisms that can result in variations in total ozone concentration at different time scales. The three distinct peaks that are highlighted in this figure correspond to long period waves that are responsible for causing variations in the total ozone at Toronto. Peak one has a period of 12 months, and it simply represents the seasonal variation caused due to meridional circulation which was not entirely suppressed by the 13 month running mean. Peak two, which is not as sharp as the other peaks (representing a wider range of periods), has a period of approximately 2.7 to 3.0 years, which qualitatively matches the quasi biennial oscillation (QBO) described in Figure 3. To further substantiate that the period of QBO from 1960 to 1998 matches the period of peak 2 in Figure 7, a cospectral density analysis was performed on the QBO
**Table 1 Regression Analysis of Mean Monthly Ozone Data**

<table>
<thead>
<tr>
<th></th>
<th>Original Data</th>
<th>Thirteen month running mean applied</th>
<th>Seasonal cycles removed</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Regression line</strong></td>
<td>y = 359.8 - 0.053x</td>
<td>y = 360.158 - 0.0x</td>
<td>y = 12.97 - 0.053x</td>
</tr>
<tr>
<td><strong>Slope</strong></td>
<td>-0.053</td>
<td>-0.053</td>
<td>-0.053</td>
</tr>
<tr>
<td><strong>Coefficient of Determination ($r^2$)</strong></td>
<td>0.033</td>
<td>0.57</td>
<td>0.16</td>
</tr>
<tr>
<td><strong>Variance</strong></td>
<td>1347</td>
<td>93</td>
<td>308</td>
</tr>
</tbody>
</table>

Data from 1960 to 1998 and annual ozone concentration data from 1960 to 1998, as seen in Figure 8. As Figure 8 shows, there is a strong peak with a period of 2.5 years (frequency = 0.034) suggesting the source of the second peak is the zonal tropical wind in the stratosphere. The extremes in the prevailing winds vary from cycle to cycle, but the peak easterly usually exceeds 30 metres/second (m/s), while the westerly extreme is usually between 10 to 20 m/s (Hamilton 1998). Hence, it is deduced that easterlies are generally stronger and capable of transporting more ozone from the equatorial region to higher latitudes, thereby contributing to variations in the total ozone concentration over Toronto. The third peak in Figure 7 has a period of approximately 9.5 years and this clearly matches the solar sunspot cycle period (Figure 2) (Wilson 1994).

To further examine this, a cospectral density analysis was performed on the solar activity data from 1960 to 1998 and annual ozone concentration data from 1960 to 1998 (Figure 9). As Figure 9 shows, there is a strong peak with a period of 9.52 years (frequency = 0.105) confirming that the source of the third peak is the solar sunspot cycle activity consistent with other results (Haigh 1994).

The final peak occurs at the low frequency end of the spectrum and represents the secular trend of ozone for the entire span of the data. This information is already contained in the regression analysis. Thus, the variations in total ozone in the Greater Toronto Area, aside from seasonal cycles, can also be related to quasi biennial oscillations, to sun spot activity and to a long term secular trend, likely the result of anthropogenic emissions of CFCs.

It is important to note that these cycles coexist and at any given time, depending on their relative phase, they can amplify or mitigate ozone variability. For example, the recent rise in ozone since 1993 (Figure 5) can be attributed to a solar activity maximum in 1996 (Figure 2), the dominance of easterlies in tropical winds in the stratosphere since 1996 (Figure 3), and likely the decline in CFCs due to emission restrictions resulting from the 1987 Montreal Protocol. Knowledge of these cycles provides the basis for a realistic ozone forecast.

**Discussion**

The 38 years of ozone data that were analyzed in this study revealed that the total ozone over the Greater Toronto Area over the period of record showed an overall decrease of 0.64 percent per year or 6.4 percent per decade. This regional estimate is consistent with the results obtained by others. Miller et al. (1995), using data covering the period between 1968 to 1991, found ozone trends in both the lower stratosphere (15-20 km) and the upper stratosphere (35-50 km), of about -6 percent per decade. Similarly, Randel et al. (1999), for the period between 1979 to 1996, showed trends in total ozone concentration at all altitudes between 10 to 45 km, of about approximately -7 percent per decade. Chen and Nunez (1998) studied the temporal and spatial variability of ozone in Southwest Sweden for the period 1988 to 1997, and found that the long term total ozone trend has been decreasing at a rate of 0.79 percent per year (or 7.9 percent per decade).

As discussed previously, seasonal variations of ozone are due to the presence of meridional circulation as illustrated in the Brewer Dobson circulation model (Figure 1). Two separate statistical procedures were used to minimize seasonal variations from the ozone data. The running mean method resulted in an effective mitigation of seasonal variation and therefore, the adjusted total ozone data obtained using this method, was used in the subsequent analysis.
Figure 7: Spectral analysis of monthly total column ozone data for Toronto from 1960 to 1998 with 13-month running mean applied.

Figure 8: Cospectral analysis of annual ozone data and QBO variations.
The smoothed data showed four spectral peaks which were linked to a residual seasonal variation, quasi-biennial oscillation (QBO), solar sun-spot variation and a longer term secular trend likely the results of anthropogenic influences (CFCs). The solar variability provided a precise match to a spectral peak in the ozone data. The QBO provided a close match with another spectral peak, however, the spectral period was slightly longer than the tropical QBO data. It is possible that only the stronger QBO episodes (with longer periods) influence ozone distant from the equator. On-going work on the spatial variability of the QBO influence will decide this issue. It should be noted, however, we are making inferences about causal relationships based solely on statistical analysis. Although the results are consistent with proposed physical mechanisms, this does not constitute direct evidence of causality.

The analysis in this paper illustrates the difficulty in predicting future ozone levels. Although a decreasing trend was found for the 38 year period, there is considerable variability on a variety of time scales. Thus, a prediction for a specific year needs to consider not only this long term trend but also the state of the QBO and the sun spot cycle.

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References


