Long-term Changes in Tropospheric Ozone

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Abstract: Tropospheric ozone changes are investigated using a selected network of surface and ozonesonde sites to give a broad geographic picture of long-term variations. The picture of long-term tropospheric ozone changes is a varied one in terms of both the sign and magnitude of trends and in the possible causes for the changes. At mid latitudes of the S.H. three time series of ~20 years in length agree in showing increases that are strongest in the austral spring (August-October). Profile measurements show this increase extending through the mid troposphere but not into the highest levels of the troposphere.

In the N.H. in the Arctic a period of declining ozone in the troposphere through the 1980s into the mid 1990s has reversed and the overall change is small. The decadal-scale variations in the troposphere in this region are related in part to changes in the lowermost stratosphere.

At mid latitudes in the N.H., continental Europe and Japan showed significant increases in the 1970s and 1980s. Over North America rises in the 1970s are less than those seen in Europe and Japan, suggesting significant regional differences. In all three of these mid latitude, continental regions tropospheric ozone amounts appear to have leveled off or in some cases declined in the more recent decades. Over the North Atlantic three widely separated sites show significant increases since the late 1990s that may have peaked in recent years.

In the N.H. tropics both the surface record and the ozonesondes in Hawaii show a significant increase in the autumn months in the most recent decade compared to earlier periods that drives the overall increase seen in the 30 year record. This appears to be related to a shift in the transport pattern during this season with more frequent flow from higher latitudes in the latest decade.

Key words: trends, surface ozone, ozonesondes, tropospheric chemistry, ozone transport

Introduction

Ozone in the troposphere is a key ingredient in a number of atmospheric physical and chemical processes. These include radiative forcing as ozone is an infrared absorber (greenhouse gas). It is also a precursor to the formation of the hydroxyl radical which affects the oxidizing (cleansing) capacity of the atmosphere. Tropospheric ozone is an effective absorber of solar ultraviolet (UV) radiation that on a per molecule basis is more effective than stratospheric ozone in filtering UV-B (Bruhl and Crutzen, 1989). The larger tropospheric column ozone amounts in the N.H. as compared to the S.H. may be an important contributor to the larger surface UV amounts recorded in the S.H. (McKenzie et al., 2003). In addition human health, terrestrial ecosystems, and materials degradation are impacted by poor air quality resulting from high ozone levels caused by photochemical ozone production of human-emitted precursors. Tropospheric ozone changes may also come about from climate changes, such as an increase in stagnation episodes or other altered transport patterns. While air quality concerns are focused near ground level, the climatic and oxidizing impacts of tropospheric ozone are significant through the entire depth of the troposphere.

Determination of the long-term changes in tropospheric ozone on a global or hemispheric basis is hampered by the relative scarcity of representative observing locations with observational records of 15 years or more. With a lifetime of several days to several weeks, ozone is not a globally or even hemispherically well-mixed constituent of the troposphere. Representative observations on geographic scales of 500-1000 km (Prinn, 1988) are required for characterizing ozone behavior in background air on a regional basis. While surface ozone is extensively observed at sites in N.H. continental regions as part of air quality monitoring networks, these sites are often only representative of local conditions. Profile measurements that include the troposphere are very limited spatially and are carried out relatively infrequently (in most cases weekly). In the S.H. measurements are limited but with fewer continental regions with large precursor emissions, the tropospheric ozone distribution may present a more homogeneous picture than in the N.H. Even with these notable limitations it is useful to examine the available time series to get as broad a picture as possible of changes that are occurring. It is changes on these larger scales that may play the biggest role in climate forcing and oxidizing capacity by tropospheric ozone. Several earlier studies have addressed changes in

tropospheric ozone with the focus on developing as broad a picture as possible of the geographic distribution of these changes (Logan, 1994; Logan et al., 1999a; Oltmans et al., 1998; Vingarzan, 2004). This work builds on the analysis of Oltmans et al. (1998) by extending many of the time series, supplementing with additional locations, and using several new statistical tools to do this analysis.

The approach taken in this study is to focus on tropospheric ozone time series with relatively long records (mostly 15 years or longer) and locations (Table 1) that are representative of large geographic regions not immediately influenced by nearby precursor sources. We designate these sites as "background" stations. This designation is somewhat arbitrary but considers distance from precursor sources and the character of ozone variation at the site. In some cases a degree of compromise is made in these criteria because of the longevity of a record at a key location. In discussing the record from a particular site, the potential departure from background characteristics is considered. Data from surface measuring sites are drawn primarily from two sources. Most of the remote or high altitude sites are part of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) network and data are available from the World Data Centre for Greenhouse Gases (WDCGG). Several North American sites are located in U.S. National Parks and the data come from the U.S. EPA Air Quality System (AQS) data archive. The vertical profile measurements are from balloon-borne ozonesondes. These observations are some of the longest records of tropospheric ozone. Many of these sites are also part of the GAW network and the data are available from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC). Investigators associated with most of the surface and ozonesonde data sets are part of this study. The following sections will discuss the measurement methods and data sets to be used in the analysis, the statistical models used in the treatment of the observations, a presentation of the trend results, and a discussion of the pattern of long-term changes and in some cases possible keys to understanding tropospheric ozone changes. Tropospheric ozone changes are investigated using a selected series of surface and ozonesonde sites to give a broad geographic picture of longer-term variations. The longest time series are nearly 40 years in length with the majority of records extending back about 20 years.

The Measurements

Surface Observations

Most of the surface measurements used in this study were obtained using continuously operating analyzers that are based on the absorption of ultraviolet radiation (UV) at 254 nm in a cell of known length (Meyer et al., 1990). For the most part the ozone analyzers are referenced to a standard instrument also employing the UV absorption technique. These references are traceable to the Standard Reference Photometer (SRP) maintained by the U.S. National Institute of Standards and Technology (NIST). In recent years this standard has been propagated in the GAW network through the Swiss operated WMO World Calibration Centre for Surface Ozone, which also maintains an SRP. The U.S. National Park instruments as well as other data sets in the U.S. EPA archive are linked to the NIST standard through EPA maintained SRPs. The traceability of the calibration of the data sets is not likely as well documented in the 1970s as in more recent years. The long-term stability of these time series has in most cases been maintained at a level of ~±2%.

Ozonesondes

Ozone profile measurements are obtained using balloon-borne ozonesondes that obtain a snapshot of the atmosphere, usually on a weekly schedule. A notable exception is the sounding program at Hohenpeissenberg in southern Germany where soundings were made once per week beginning in the late 1960s, but have been made 2-3 times per week since 1978. In the records considered here, three different types of ozonesondes were used, all employing some variation of the reaction of ozone with potassium iodide. At Hohenpiessenberg the Brewer-Mast ozonesonde (Brewer and Milford, 1960) has been used throughout the measurement period using procedures (Claude et al., 1987) that have produced a high quality time series. At the Japanese station the KC type sonde was used that was converted in 1979 from a two-chamber electrochemical concentration cell to a single cell instrument (SPARC, 1998). The time series at the Japanese stations have significant periods with infrequent soundings particularly in the late 1970s and through the 1980s. The other locations used in this study employed the electrochemical concentration cell (ECC) ozonesonde (Komhyr, 1969) that has been extensively evaluated (Johnson et al., 2002; Smit and Straeter, 2004). The measurement uncertainties influencing trends for tropospheric observations with ozonesondes is of the order of 2%/decade (SPARC, 1998).

Back trajectories

To help identify the role that changing transport patterns may play on long-term ozone changes, clustered air parcel trajectories were examined. In this study 3-dimensional (3-D) back trajectories were calculated using the European ERA-40 Reanalysis Data Set (http://www.ecmwf.int/research/era). The characteristics, including the strengths and weaknesses, of various trajectory formulations are discussed in Harris et al. (2005).

Treatment of the Data

Several approaches have been used to analyze the time-varying characteristics of the tropospheric ozone time series. The seasonal dependence of the trends has been deduced by separately analyzing calendar monthly averages of the data records. In addition, to highlight the decadal changes in these seasonally dependent trends, the trends have been examined for three decadal periods: 1995-2004, 1985-1994 and 1975-1984, the last of which may have a different start year depending on the data record analyzed. For Hohenpeissenberg the segment from the beginning of the record in 1966 to 1974 was also considered.

To examine the linear trend in each of the 12 calendar monthly mean time series, the following equation is used

$$\text{Ozone} = \tau \times t + \beta + \text{residual} \qquad (1)$$

where τ is the monthly trend parameter and β is the monthly intercept parameter. An autoregressive process of order two (AR(2)) error structure for the residual term was used (Tiao et al., 1990).

The monthly change in the distribution of hourly average concentrations for each monitoring site was investigated by characterizing the median difference between each 10 ppb increment in absolute frequency except at the South Pole background site where increments of 5 ppb were used. These median differences for each increment (10 or 5 pbb) are plotted as histograms. To test for statistical significance, Kendall's tau test (Lefohn and Shadwick, 1991) was used to determine significance at the 10% level for the specified increments. The overall ozone trend is computed in a two-step process (Harris et al., 2001). The first step uses an autoregressive model that incorporates explanatory variables and a cubic polynomial fit

rather than a straight line for better representation of the long-term variations. The model accounts for serial correlation in the ozone data and minimizes the residual variance of the model fit by regressing to known sources of ozone variability. The second step determines the ozone tendency (trend line) and growth rate curves (Thoning et al., 1989). A bootstrap method (Efron and Tibshirani, 1993) produces 100 statistical realizations of the population from which the original data were drawn by combining the tendency curve with randomly selected residuals from the curve according to month (Harris et al., 2001). The growth rate curve is obtained by numerical differentiation of the tendency curve with the 95% confidence limits determined using the standard deviation of the growth rate curves from the 100 bootstrap samples. The average ozone growth rate is a measure of the overall change.

Results and Discussion

Changes in tropospheric ozone are presented for the N.H. and S.H. In the N.H. because of the greater availability of data and the heterogeneous character of the changes, individual consideration is given to various regions.

Changes in the Northern Hemisphere

Developing a picture of longer-term variations of ozone in the N.H. troposphere requires consideration of several significant factors including the influence of anthropogenic emissions of ozone precursors from densely populated regions in Europe, Asia, and North America. There are also differences between N.H. regions in the extent to which precursor emissions are regulated. The influence of the continents in the N.H. also leads to varying conditions such as those seen in warm conveyor belts (Cooper et al., 2004) that are effective in mixing precursors from the boundary layer into the free troposphere. It might be expected that under these conditions a good deal of heterogeneity should exist in the long-term behavior of tropospheric ozone among individual station locations. That this is indeed the case is illustrated in Figure 1. These six sites cover a range of conditions that represent several regional patterns. The results for the N.H. are presented by considering changes at high and mid latitudes (including the subtropics - locations north of 25N) and the tropics where the station in Hawaii is the only available N.H. tropical station with a longer-term time series.

High Latitudes

At high latitudes of the N.H. the longest observational series are in the North American sector. Surface measurements at Barrow (70N) since 1973 and Alert (82N) since 1992 are significantly influenced by boundary layer, springtime ozone depletion related to bromine chemistry (Barrie et al., 1988; Oltmans, 1991). Ozonesonde records at Resolute (75N) beginning in 1979 and Alert beginning in 1987 also show the signature of springtime depletion in the low-level observations but are unaffected above the boundary layer (Oltmans, 1993). The site at Denali National Park (64N) in the interior of Alaska is not influenced by the springtime depletion. The long record at Barrow shows a significant 4.8 (1.7) %/decade increase. The winter months of November-January and May (statistically significant individual monthly increases in December and May) are the primary contributors to the overall increase (Figure 2). In the late summer months there was an increase from the early period (1973-1984) to the middle decade (Figure 2). The early period was the time of the development of, and maximum in, petroleum extraction activities on the North Slope of Alaska that peaked in the late 1980s. The Prudhoe Bay facility was a major source of NO_x emissions, equivalent to those of Washington, D.C. at the time (Jaffe, 1991). Surface ozone at Barrow also peaked at this time (Figure 1) and though there have been fairly large interannual variations since then, there has been little overall change in the last 15 years (Figure 1). During the most recent decade, August and September values have dropped back to near those of the early period (Figure 2). This may reflect the decline in petroleum production in the recent decade.

The ozonesonde record at Resolute beginning in 1980 shows a very small overall decline. The record shows a significant decline during the first half of the record followed by an increase to levels near those at the beginning of the record (Figure 3). This is a pattern seen at all the Canadian stations north of 50N with records going back to 1980 (Churchill, Goose, Edmonton). At Alert both the ozonesonde record, which begins in December 1987, and the surface measurements that began in 1992 show significant increases. This period corresponds to the time of increasing tropospheric ozone at the longer-term Canadian ozonesonde stations. The increases at Alert in both the surface and ozonesonde records occur during the winter and spring months with significant individual monthly trends in January, April, and June. The long-term change at the high latitude Canadian ozonesonde stations has been shown to be strongly related to the wintertime frequency of occurrence of ozone lamina in the lowest part of the

stratosphere (Tarasick et al., 2005). There is a strong correlation between the interannual variability of these lamina and ozone amount in the lower stratosphere as well as in the long-term pattern of change (Tarasick et al., 2005). The correlation between ozone changes in the lower stratosphere and in tropospheric ozone is also very significant leading to the conclusion that at least a portion of the changes in troposphere results from changes in the lower stratosphere (Tarasick et al., 2005). At Denali NP, where the period of surface measurements corresponds in length with the ozonesonde record at Alert, the pattern of change is remarkably similar with winter and spring increases in the most recent decade. This increase is also seen in the shorter Alert surface record (8.7 (± 5.0) %/decade). In assessing the long-term changes in the Arctic it is important to be cognizant of the period being considered since there have been extended periods of both declining and increasing ozone amounts. The longest surface and ozonesonde records show varying patterns of change on multi-decadal time scales.

Mid latitudes and Subtropics

1. Changes over Europe and the North Atlantic

One of the largest changes in tropospheric ozone is seen at Zugspitze (48N), a continental European location (Figure 1) with an overall increase of 12.6(±0.8) %/decade. While ozone increased significantly during all months over the observational record, the largest increase was during the spring and summer months during the earliest portion of the record (Figure 4). This is in contrast with the smaller summer increases during the most recent period (1995-2004) compared to the previous period (1985-1994). The change between the later two segments shows increases that are primarily in the autumn and winter. This pattern with both the strong increase during the warmer months in the early period and an increase in the cooler months during the later period suggests the influence of changing ozone precursor emissions on the ozone trend (Scheel, 2003). This results from less production in the summer and less titration by NO in the winter as NO emissions have declined over Europe (Lindskog et al., 2003; Lovblad et al., 2004; Jonson et al., 2005).

The ozonesonde record at Hohenpeissenberg (Claude et al., 2004), also located in southern Germany, extends back to 1966. The pattern of long-term change in the 700-500 hPa layer (Figure 5) shows many of the characteristics seen at Zugspitze (Figure 1) with large increases in the early period (including the period from the mid 1960s to the mid 1970s) into the mid 1980s and smaller changes, even declines, thereafter. The small declines seen in the most

recent decade at Hohenpeissenberg, although not seen at Zugspitze, have also been noted at the nearby Alpine site of Wank and result primarily from summer decreases (Scheel, 2003). The trends at the Zugspitze and Hohenpeissenberg also follow a similar seasonal pattern (Figures 4 and 6). The overall agreement between the surface measurements at the high altitude Zugspitze site and the vertical profile measurements at Hohenpeissenberg lend confidence to these results and suggest that they are indicative of the pattern over continental western Europe.

Two stations in the eastern North Atlantic, Izaña and Mace Head, also show significantly increasing ozone amounts over their period of record, which begin in 1987 (Figure 1). The high altitude site at Izaña, Canary Islands (26N) is influenced by flow from both the mid latitudes and the subtropics. While increases are seen in most months, the statistically significant changes are during winter and spring months (Figure 7). At Mace Head, Ireland there is a preponderance of flow from the north Atlantic sector, especially during the winter and spring months when increases are the largest. Simmonds et al. (2004) found that there was a significant increase in baseline ozone in clean oceanic air masses reaching Mace Head. On the other hand declines were found in photochemically produced ozone in summertime, regionally polluted air masses. The mid Atlantic station in Bermuda (32N) began measurements in 1988 and operated until May 1998 and resumed measurements in 2003. Comparison of monthly average values prior to 1995 with those since, show higher amounts in the winter and spring months in the later period (Figure 7). The significant data gap makes a rigorous statistical testing of this difference impractical, but Bermuda appears to fit the pattern of the other two North Atlantic sites. Lelieveld et al. (2004) presented results from a longer series of measurements in the Atlantic and found increases up to about 40N, but not further north.

2. Changes over Japan

In East Asia the primary source of information on longer-term tropospheric ozone changes are the ozonesonde records from three Japanese locations. The most complete record is at Tsukuba (36N), which is located within 50 km of Tokyo. It can be expected that data in the lowest portion of the profile are strongly influenced by regional pollution (Logan et al., 1999b; Oltmans et al., 2004). The long-term record at Tsukuba shows an overall increase through the troposphere (Figure 8). This increase comes during the period into the late 1980s and encompasses most of the troposphere. The other two Japanese stations with long records, Sapporo (40N) and Kagoshima (32N), show a similar overall pattern. Flow from regionally

polluted air masses from China appears to be the major contributor to the long-term change at Tsukuba and Kagoshima (Naja and Akimoto, 2004). At Sapporo the change is associated with longer-range flow from the Eurasian continent at higher latitudes (Naja and Akimoto, 2004). Since the beginning of the 1990s, the overall trend has been weakly downward at all of the Japanese locations with perhaps somewhat stronger declines in the most recent years. It should be noted that during the late 1970s, there are very few observations and during the 1980s there are almost no soundings in the summer months. The subtropical site at Naha (26N) began measurements in 1989 and like the other Japanese stations during this period shows no significant change (Figure 9). This lack of change comes in spite of the rapid industrialization in China and the documented rise in NO_x emissions in East Asia (Naja and Akimoto, 2004 and references therein; Richter et al., 2005). This lack of congruence between recent emission increases in East Asia and relatively flat ozone changes over Japan remains largely unexplained (Naja and Akimoto, 2004).

3. Changes over North America

Over the mid latitudes of North America, there are several longer-term records both at the surface and from ozonesondes. At more northerly mid latitudes the three Canadian ozonesonde stations at Churchill (59N), Edmonton (54N), and Goose (53N) have a pattern of change similar to that described earlier for the high Arctic station at Resolute with a correspondingly similar, though a bit weaker, relationship between lower stratospheric phenomena and tropospheric ozone change (Tarasick et al., 2005). The result is that after a period of decline followed by an increase, the overall trend is small in the troposphere for these locations (Figure 10).

The longest tropospheric ozone time series in North America is the ozonesonde record at Wallops Island, Virginia that begins in 1970 (Figure 11). The primary feature of this record is the anomalously high values in the late 1980s centered on 1988 with relatively small changes during other periods. This is in contrast to the pattern seen over continental Europe and Japan (Figure 11). Overall the change is rather small at all tropospheric altitudes. There has been a slight tendency for summer months to decline and winter months to increase. The longest continuous surface record in the U.S. is at Whiteface Mountain, New York (Figure 1). This site is impacted by regional pollution but is not located in close proximity to an urban area. It is also at an elevated altitude (1480 m) and can be considered representative of a broader scale

regional pattern. There have been significant declines during May and August and increases during December and January. These changes have not been dramatic, but represent a shift away from the highest values during the warmer months when the seasonal maximum occurs and from lower values during the winter months at the time of the seasonal minimum (Figure 12). This appears to be in keeping with the pattern seen for reductions in NO_x (Jonson et al., 2005) and similar to that seen in the profile measurements at Wallops Island.

Several National Park sites in the western U.S. have surface ozone measurements starting in the mid to late 1980s. These sites (Yellowstone, Wyoming; Glacier, Montana; and Olympic, Washington) are generally remote from significant urban and most regional pollution influences. For the approximately 15 year data records at each site, only Olympic shows a single month (February increase) with a significant change indicating that for these more remote sites there have not been important recent changes, related to either local or distant sources. At the ozonesonde site at Boulder, Colorado scattered profile measurements began in 1979 and a regular sounding program started in 1985. The longer record shows modest declines overall while the more robust record beginning in 1985 also shows a small decline through the troposphere that took place almost exclusively in the earliest portion of the record.

Two contrasting sites in northern California point out the difference in change recorded at locations that are not separated geographically by a large distance. The Lassen Volcanic National Park record, which has been described by Jaffe et al. (2003), shows marked increases during the warm months (April-August) for the period 1988-2003. On the other hand, the site at Yreka, near the northern border of California, shows no overall change for 1981-2003 with small increases in September and decreases in January. It has been suggested that the spring increases seen at Lassen may be the result of trans-Pacific transport of enhanced ozone from Asia emissions (Jaffe et at., 2003). The Yreka record suggests that longer-range effects may not be playing a major role, however, since no spring increases are noted. Lassen is located downwind of the rapidly expanding northern portion of the central valley of California where there are numerous air quality violations in locations in the vicinity of cities such as Redding. The spring increases at Lassen could result from the more immediate upwind population centers that would also contribute to the summer rise.

Tropics

The only long-term record of tropospheric ozone at lower latitudes of the N.H. is from Hawaii in the Pacific Ocean. The continuous monitoring site at the 3400 meter altitude Mauna Loa Observatory (MLO) began measurements in 1973 (Figure 1). Ozonesonde observations from Hilo (20N) began in 1982. The Hawaiian location sees transport events that may have their origin in East Asia. These events occur most frequently in the spring and are occasionally accompanied by higher ozone amounts (Oltmans et al., 2004). Transport from continental regions and higher latitudes brings higher ozone amounts to Hawaii than air masses that remain over the ocean for extended periods of time or come from lower latitudes (Harris et al., 1998). However, the long-term increase in Hawaii (3.5 ± 1.5 %/decade) has occurred during the autumn and winter, which is the seasonal minimum in tropospheric ozone, with the largest changes coming in September and October (Figure 13). In September and October the distribution of the hourly values has changed dramatically with occurrences in the 20-30 ppb range declining while hourly values in the 40-50 ppb and 50-60 ppb have increased significantly (Figure 14). This shift has occurred primarily in the most recent decade (Figure 14) and is corroborated in the ozonesonde record (Figure 13) that shows that this change extends through the mid troposphere (850-500 hPa). The similar behavior of the independent continuous monitoring data at MLO and the weekly profile data from Hilo indicates that this is a very robust result.

It is likely that the change in the autumn months is associated with a shift in transport characteristics of air masses reaching the island of Hawaii. Back trajectories to MLO computed for the 10-year periods 1985-1994 and 1995-2004 (Figure 14) show that in the earlier period 13% of the 10-day back trajectories fall in a cluster (Moody, 1986; Harris and Kahl, 1990) whose mean trajectory originated north of 30N, while in the most recent period 42% fall in a cluster whose mean originated north of 30N. Given the latitudinal gradient with higher ozone amounts to the north of Hawaii (Logan, 1999b; Oltmans et al., 2004), this change in the transport is likely the primary factor in producing the shift to higher ozone amounts in the autumn months.

The MLO observations for the month of May show a noticeable decline (though not significant at the 95% confidence level) between the most recent decade and earlier 10-year intervals (Figure 13). This difference is even more noticeable in the ozonesonde data (Figure

13) and has a large vertical extent (850-300 hPa) that includes much of the troposphere. Even though this is still a month of significant transport from Asia, this change is not likely related to changing precursor emissions, which have increased over this time (Naja and Akimoto, 2004). As with the autumn change, it appears that the May decline is a result of a shift in transport characteristics. Clustered back trajectories for the pre and post 1994 periods for the month of May demonstrate a decline in the most rapid flow from the west that extends back to Asia declined from about 34% of trajectories in the earlier period to only 20% in the most recent period. Flow from the east that seldom reaches a continent in 10 days increased from 30% of all cases to 50% of the trajectories. A decline in the number of trajectories with a significant westerly component will generally mean reduced ozone amounts at Hawaii (Oltmans et al., 1996).

Ozone Changes in the Southern Hemisphere

Because the S.H. has much smaller land area and lower population than the N.H., it might be expected that human activity plays a smaller role in tropospheric ozone changes in the S.H. On the other hand, extensive biomass burning, particularly in Africa and South America during the austral winter and spring, is unique to the S.H. This burning in the absence of other strong anthropogenic inputs should play a significant role in overall tropospheric ozone levels in the S.H. and should influence the seasonal pattern as well. The difference in the level of anthropogenic influence between the S.H. and N.H. is reflected in the gradient between the hemispheres in carbon monoxide (Novelli et al., 2003) and likely in ozone as well (Fabian and Pruchniewicz, 1977; Fishman and Seiler, 1983; Winkler, 1988; Oltmans and Levy II, 1994).

Significant surface ozone changes have occurred on decadal time scales at background S.H. sites (Figure 16). At the South Pole, surface ozone amounts declined through the 1980s into the early 1990s with a recovery in the most recent decade. At the mid latitude sites at Cape Grim, Australia and Cape Point, South Africa, ozone amounts have increased since the early 1990s with the increase at Cape Point being the largest. At Samoa there have been large multi-year variations and an overall decline.

Consideration of the seasonal cycle at these locations, as well as at the coastal Antarctic site at Arrival Heights (with a shorter record than the other sites), provides some insight into the longer-term changes and their relationship to each other. The mid latitude site at Cape Grim

serves as something of an anchor point for comparison purposes for changes at the locations to the north and south. The time series at this site has benefited from the use of simultaneous measurements from two well-calibrated UV ozone monitors throughout the entire record (Meyer et al., 1990).

Figure 17 shows the time series at five S.H. stations for a four-year period from 2000-2003. This figure illustrates the relationship between the low latitude, low altitude site at Samoa (with correspondingly low ozone amount) to the high latitude, high altitude South Pole location. Apparent is the near synchronization of the seasonal cycle at all latitudes with high ozone in the austral winter and strong draw down in the summer (Ayers et al., 1992). All of the non-tropical sites show similar minimum values with the exception of South Pole, which has a secondary peak in the austral summer so that the minimum never dips down to the lower values seen at Cape Point, Cape Grim, and Arrival Heights. The coastal Antarctic site at Arrival Heights is more similar to Cape Grim than to the inland Antarctic South Pole location. To get a picture of the change in the seasonal pattern with time, the data are divided into two time periods with the break between 1994 and 1995. In addition at South Pole and Samoa, where data are available from 1975, the period 1975 – 1984 is considered.

At Cape Point and Cape Grim there are clear differences between the two time periods and the two sites (Figure 18). At Cape Grim there has been essentially no change during the summer seasonal minimum, but a significant increase during the late winter and early spring. There has been some increase throughout the year at Cape Point, but the largest increase is again in the late winter and spring. In the later period the Cape Point values have risen nearer to those seen at Cape Grim. The large change seen at Cape Point is very consistent with results from shipboard measurements in the eastern South Atlantic (Lelieveld et al., 2004) that cover the same period as the Cape Point observations. These changes were the largest of any of the latitude bands surveyed.

The seasonal increase at Cape Grim occurs during a time of the year when biomass burning in the S.H. is very active. However, trends in this activity on a decadal time scale have not been reported. It might also be expected that if burning were driving the ozone changes at Cape Grim and Cape Point that this would be reflected in long-term changes in carbon monoxide. Both of these sites have CO records similar in length to the surface ozone measurements, but neither of these sites has seen a long-term increase in CO (Langenfels et al., 2003; Brunke et

al., 1995). The absence of an increase in CO at these sites is reflected in the results from hemisphere-wide measurements as well (Novelli et al., 2003). A preliminary analysis of back trajectories to Cape Point during the two different time periods does not reveal a significant shift in the transport patterns. Since Cape Grim represents the highest amounts in the hemispheric gradient (Figure 17), changes in horizontal transport cannot explain the increase at Cape Grim. Because the amount of ozone in the troposphere generally increases with altitude, changes in air mixed down from above could play a role in the change seen at the surface. The ozone profile record at Lauder, New Zealand (45S) from ozonesondes also shows increases in the middle and lower troposphere (Figure 19). The changes in the free troposphere at Lauder also follow the seasonal pattern seen at the surface sites with the largest increases during the spring (Figure 18). This record does not, however, show a long-term change in the upper troposphere that could be indicative of enhanced fluxes from the stratosphere. Both the record at Cape Point and at Cape Grim indicate that there may have been a leveling off of the increases in the most recent years.

The seasonal pattern at Samoa (Figure 20) shows no change in the seasonal maximum between the early period (1975-1984) and the 1985-1994 period and only small changes at other times of the year. The primary change from the earlier to the latest period is in the seasonal maximum (July-August). While there is a relatively complete ozonesonde record in the most recent decade at Samoa, ozonesondes were only flown between 1986-1990 in the previous decade. The representativeness of the record in this earlier period needs to be kept in mind, but the pattern seen in the surface data is reproduced in the ozonesondes (Figure 20). This pattern is seen into the mid troposphere but not at higher altitudes. As with other locations in the S.H., there has not been a long-term increase in CO (Novelli et al., 2003) in the S.H. tropical belt. During the seasonal maximum at Samoa a greater proportion of transport is from higher latitudes and higher altitudes than during the time of the seasonal minimum (Harris et al., 1997), however, trajectories do indicate that a shift in transport to Samoa during July-August has occurred.

In Antarctica the South Pole station represents a unique environment in the S.H. located at high altitude on the extensive Antarctic plateau. The observational record with long periods of both declining and increasing amounts (Figure 16) is a somewhat anomalous pattern compared with the other S.H. records and coastal Antarctic locations (Figure 17). Although the overall

trend at South Pole during the most recent period is increasing, all months from March-August for the most recent period (Figure 21) have lesser amounts than the two earlier periods (1975-1984, 1985-1994). Although these changes are fairly small, they are statistically significant and represent a shift in the distribution (Figure 22) during these months, indicating that larger values are getting smaller rather than low values getting even lower. Significant fluctuations at South Pole between the time periods take place in the late spring and summer (November-February). It is this season that appears to be contributing to the increasing ozone amounts seen in the overall trend (Figure 16) during the latter period since other months have continued to decline in the most recent period. At Syowa (69S) there is very little change in the long-term ozonesonde record. Although the Syowa record began in 1966, the measurement series is very sparse during most years up to the 1980s. Comparing the record at Syowa over the same period during which South Pole ozonesondes have been flown (1986-2004), reveals that the Syowa record does not have the tendency for higher values during the summer months in the most recent decade. This indicates that the processes controlling the summertime ozone behavior at these two sites is different. The unique behavior at South Pole is tied to ozone production in a very shallow layer (<500 m in thickness) over the Antarctic plateau (Helmig et al., 2006) resulting from nitric oxide liberated photochemically from nitrate deposited in the snow surface (Crawford et al., 2001). During the period of strongly declining surface ozone amounts (~1985-1994), the November-February period had uniformly lower ozone amounts than the earlier and later periods.

Conclusions

The picture of long-term tropospheric ozone changes is a varied one in terms of both the sign and magnitude of trends and in the possible causes for the changes. In several geographical regions the changes in time are broadly consistent with the expected behavior from changes in precursor emissions. In Hawaii a strong link to decadal variability in transport patterns could be identified. Especially for the most recent 10-15 year period, there are a number of locations such as the ozonesonde stations in Japan and Hohenpeissenberg, and both surface and ozonesonde sites in the U.S., where ozone has remained relatively unchanged or declined compared to earlier periods.

At high latitudes of the S.H. the surface and ozonesonde data at South Pole, which are in very good agreement with each other, indicate that some of the decadal scale changes seen in the surface record are related to the changing pattern of photochemical ozone production in the summer due to strong NO emissions from the surface snow layer (Crawford et al., 2001). This behavior is confined to a thin layer and it is not clear to what extent this phenomenon influences the broader Antarctic region.

At mid latitudes of the S.H. three time series of moderate length (~20 years) agree in showing increases that are strongest in the austral spring (August-October). Cape Point, South Africa (32S) shows the largest change. This is in keeping with the results of (Lelieveld et al., 2004) that found the largest increases from shipboard measurements in the eastern Atlantic in the 20-40S latitude band. The agreement in the magnitude of the change is also good (3.6 %/decade for the shipboard data and 4.9 %/decade at Cape Point) considering that the ship data are over a wide latitude band. The magnitude of the change in the ozonesonde record at Lauder, New Zealand (45S) falls between that seen at Cape Point and at Cape Grim, Australia (40S). The profile measurements at Lauder show this increase extending through the mid troposphere but not into the highest levels of the troposphere. The lack of a trend in the CO record in the S.H. makes a link to changes in biomass burning less likely. At Cape Point, where the change is largest, there is also no clear link to changing transport patterns.

At Samoa (14S), a tropical Pacific location, the most recent decade shows declines during July and August in the surface observations relative to the previous two decades. These changes are corroborated in the ozonesondes though the ozonesonde record prior to 1995 only encompasses a portion of the earlier decade (1986-1990). As at Cape Point and Cape Grim, neither the CO record nor changes in transport as determined from trajectory analysis provide ready clues as to the cause for this decline.

In the N.H. in the Arctic, a period of declining ozone in the troposphere through the 1980s into the mid 1990s has reversed and the overall change is small. Sites with shorter records mostly reflect the period of recovering ozone and hence show some increase that may not reflect the longer-term pattern. The decadal-scale variations in the troposphere in this region have been related, at least in part, to changes in the lowermost stratosphere by Tarasick et al. (2005).

At mid latitudes in the N.H., continental Europe and Japan showed significant increases in the 1970s and 1980s that appear to have leveled off or in some cases declined in the more recent decades. Over North America increases in the 1970s, as reflected in the Wallops Island ozonesondes and Whiteface Mountain surface data are less, suggesting significant regional differences. Time series, beginning in the 1980s at sites located in the mid latitudes of North America, generally confirm the modest changes in the most recent two decades. However, even at stations in relatively close proximity to each other, such as those in southern Germany, some differences in detail are seen. There is strong confirmation of the increase in the 1970s with a slowdown at both German sites thereafter. The high altitude mountain site at Zugspitze suggests continuing smaller increases in recent decades while the ozonesondes at Hohenpeissenberg show declines through the troposphere. The variation in ozone trends over Europe and their relationship to precursor emissions is also seen in modeling studies (Jonson et al., 2005) and observations (Schuepbach et al., 2001) In particular changes over Europe cannot be fully explained based on precursor changes alone (Jonson et al., 2005). Over the North Atlantic three widely separated sites show significant increases since the late 1990s that may have peaked in recent years. The source of these changes are not considered here, but are discussed in Simmonds et al. (2004). The results at mid latitudes can be compared to a recent model study of the evolution of tropospheric ozone in the twentieth century (Lamarque et al., 2005). The earliest time series considered here, beginning in the 1970s, are included in the most recent two decades (1970-1990) in the modeling study. The increases seen in the model over Europe and Japan are seen in the observations. Over eastern North America the three plus decade observational record considered here does not show much overall change. However, when considering the shorter overlapping time period studied in the model, both Wallops Island ozonesondes and the Whiteface Mountain surface record show significant increases primarily because of low values through the mid 1970s and relatively high ozone amounts in the late 1980s. The increase seen by the model in the 1970-1990 period is a result of increases in precursor emissions (Lamarque et al., 2005). The subsequent period of a leveling off and declines seen in the observational record beginning in the 1990s in all three regions is not considered in the modeling work. The changes in tropospheric ozone seen in the observations in the most recent 30-40 year period over Europe can also be viewed in the context of the observations extending further back in time (Staehelin et al., 1994). The large increases in

ozone over Europe that are captured in the long records at Hohenpeissenberg and the Zugspitze appear to have begun in the 1950s with much more gradual changes prior to the 1950s (Staehelin et al., 1994).

In the N.H. tropics the only long record is from Hawaii (20N). In both the surface record at the high altitude Mauna Loa Observatory and the ozonesondes at Hilo there has been a significant increase in the autumn months in the most recent decade compared to earlier periods that drives the overall increase seen in the 30+ year record at Mauna Loa. This appears to be related to a shift in the transport pattern during this season with more frequent flow from higher latitudes in the latest decade.

Although still not numerous, an increasing number of ozone monitoring sites and the lengthening of a number of time series resulting from continuing observations should provide additional insight on tropospheric ozone changes over the next decade. In addition the improved capability of models to simulate long-term tropospheric ozone behavior will make it beneficial to carry out a study such as that by Lamarque et al. (2005) that includes the most recent time period. It appears from the records considered here that there has been a leveling off of recent increases in the tropospheric ozone burden, particularly at mid latitudes of the N.H. that have been most affected by anthropogenic changes.

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Figure Captions:

Figure 1: Ozone trend curves (determined from the fit to the difference between the modeled data and the observations) in percent deviation at six selected N.H. surface ozone sites (Barrow – magenta, Mace Head – red, Zugspitze – green, Whiteface Mountain – black, Izana – blue, Mauna Loa – gray).

Figure 2: Average monthly surface ozone at Barrow, Alaska for three time periods.

Figure 3: Monthly average ozone amounts at Resolute in the 850-700 hPa layer (diamonds), the modeled values (gray solid line), and the fit (black solid curve) to the residuals (the difference between the data and the model) with the 95% confidence interval (black dashed curves).

Figure 4: Average monthly surface ozone at Zugspitze for two time periods.

Figure 5: Monthly average ozone amounts at Hohenpeissenberg in the 700-500 hPa layer (diamonds), the modeled values (gray solid line), and the fit (black solid curve) to the residuals (the difference between the data and the model) with the 95% confidence interval (black dashed curves).

Figure 6: Average monthly 850-700 hPa layer average ozone at Hohenpeissenberg for three time periods.

Figure 7: Average monthly surface ozone for three sites in the North Atlantic for two time periods (MHD = Mace Head, IZA = Izana, BER = Bermuda).

Figure 8: Monthly average ozone amounts at Tsukuba in the 850-700 hPa layer (diamonds), the modeled values (gray solid line), and the fit (black solid curve) to the residuals (the difference between the data and the model) with the 95% confidence interval (black dashed curves).

Figure 9: Trend with altitude of the ozonesonde layer averages at four Japanese stations. Sapporo, Tsukuba and Kagoshima data are for the period 1970-2004 while Naha only includes the period 1990-2004.

Figure 10: Trend with altitude of the ozonesonde layer averages at three Canadian stations for the period 1980-2004.

Figure 11: Ozone trend curves (determined from the fit to the difference between the modeled data and the observations) in percent deviation for Hohenpeissenberg, Tsukuba, and Wallops Island for the 850-700 hPa layer.

Figure 12: The distribution of changes in surface ozone concentrations at Whiteface Mountain, New York by month for months with significant changes in the distribution. The mass in the histogram for each month sums to one. The changes (pluses and minuses) add approximately to zero. A change in the frequency per year can be translated into hours by multiplying the plotted number by the total number of hours in the month. For example a month with 720 hours and a frequency of 0.01 per year represents a shift from one concentration bin to another of 7 hours

per year. The median difference is computed by differencing between individual years (for example 1982-1983, 1982-1984, 1982-1985 … 1983-1984, 1983-1985, 1983-1986 …). The plotted value is the median of these differences for each month and each concentration bin with a significant change.

Figure 13: Seasonal variation in surface ozone (filled symbols) at Mauna Loa Observatory (MLO) and in the 700-500 hPa layer ozone (open symbols) at Hilo, Hawaii for different 10-year time periods.

Figure 14: The monthly change in the distribution of hourly average concentrations of Mauna Loa surface ozone expressed as the median difference of occurrence of hourly averages in each concentration bin for each month with a significant change.

Figure 15: Clustered trajectories for Mauna Loa Observatory for the months of September and October for the (a) 1986-1994 and (b) 1995-2004 time periods.

Figure 16: Ozone trend curves (determined from the fit to the difference between the modeled data and the observations) in percent deviation at four selected S.H. surface ozone sites (South Pole – green, Cape Grim – blue, Cape Point – red, Samoa – magenta)

Figure 17: Time series of monthly mean surface ozone at five sites in the S.H. for the period 2000 – 2003.

Figure 18: Average seasonal cycle of surface ozone at Cape Point (CPT) and Cape Grim (CPG) and the 850-700 hPa layer average ozone at Lauder (LAU) for two time periods.

Figure 20: Trend in altitude layers from ozonesonde data at Lauder, New Zealand.

Figure 21: Average monthly surface ozone at South Pole for three time periods.

Figure 22: The monthly change in the distribution of hourly average concentrations of South Pole surface ozone expressed as the median difference of occurrence of hourly averages in each concentration bin for each month with a significant change.

Table 1: Locations, period of observation, and type of observation (surface or ozonesonde) for stations used in this study.

Station	Lat.	Lon.	Elev(m)	Period	Type
Alert, Nunavut, Canada	82.5N	62.3W	62	1992-2004	surface
				1987-2004	ozonesonde
Resolute, NWT, Canada	74.7N	95.0W	64	1980-2003	ozonesonde
Barrow, Alaska, USA	71.1N	156.6W	11	1973-2004	surface
Denali NP, Alaska, USA	63.7N	149.0W	661	1987-2003	surface
Churchill, Manitoba, Canada	58.8N	94.1W	35	1980-2004	ozonesonde
Edmonton, Alberta, Canada	53.6N	114.1W	766	1979-2004	ozonesonde
Goose, Newfndlnd, Canada	53.3N	60.3W	44	1979-2004	ozonesonde
Mace Head, Ireland	53.2N	9.54W	25	1987-2003	surface
Glacier NP, Montana, USA	48.5N	114.0W	976	1989-2003	surface
Olympic NP, Wash., USA	48.1N	123.3W	125	1987-2003	surface
Hohenpeissenberg, Germany	47.8N	11.0E	975	1966-2004	ozonesonde
Zugspitze, Germany	47.4N	11.0E	2962	1978-2004	surface
Whiteface Mtn., NY, USA	44.4N	73.9W	1484	1973-2004	surface
Sapporo, Japan	43.1N	141.3E	19	1967-2004	ozonesonde
Yreka, California, USA	41.7N	122.6W	800	1981-2003	surface
Lassen NP, Calif., USA	40.5N	121.6W	1756	1987-2003	surface
Boulder, Colorado, USA	40.0N	105.0W	1745	1979-2004	ozonesonde
Wallops Isl., Virginia, USA	37.9N	75.5E	13	1970-2003	ozonesonde
Tsukuba (Tateno), Japan	36.1N	140.1E	31	1968-2004	ozonesonde
Tudor Hill, Bermuda	32.3N	64.9W	30	1988-2004	surface
Kagoshima, Japan	31.6N	130.6E	31	1968-2004	ozonesonde
Izaña, Tenerife, Spain	28.3N	16.5W	2800	1988-2004	surface
Naha, Japan	26.2N	127.7E	27	1989-2004	ozonesonde
Hilo, Hawaii, USA	19.7N	155.1W	11	1982-2004	ozonesonde
Mauna Loa, Hawaii, USA	19.5N	155.6W	3397	1973-2004	surface
Matatula Pt., Am. Samoa	14.3S	170.6W	82	1975-2004	surface
Pago Pago, American Samoa	14.5S	170.5W	10	1986-2004	ozonesonde
Cape Point, South Africa	34.4S	18.5E	230	1983-2004	surface
Cape Grim, Australia	40.7S	144.7E	104	1982-2004	surface
Baring Head, New Zealand	41.4S	174.9E	85	1991-2003	surface
Lauder, New Zealand	45.0S	169.7E	370	1986-2004	ozonesonde
Syowa, Antarctica	69.0S	39.6E	21	1966-2004	ozonesonde
South Pole, Antarctica	90.0S	----	2840	1975-2004	surface
				1986-2004	ozonesonde

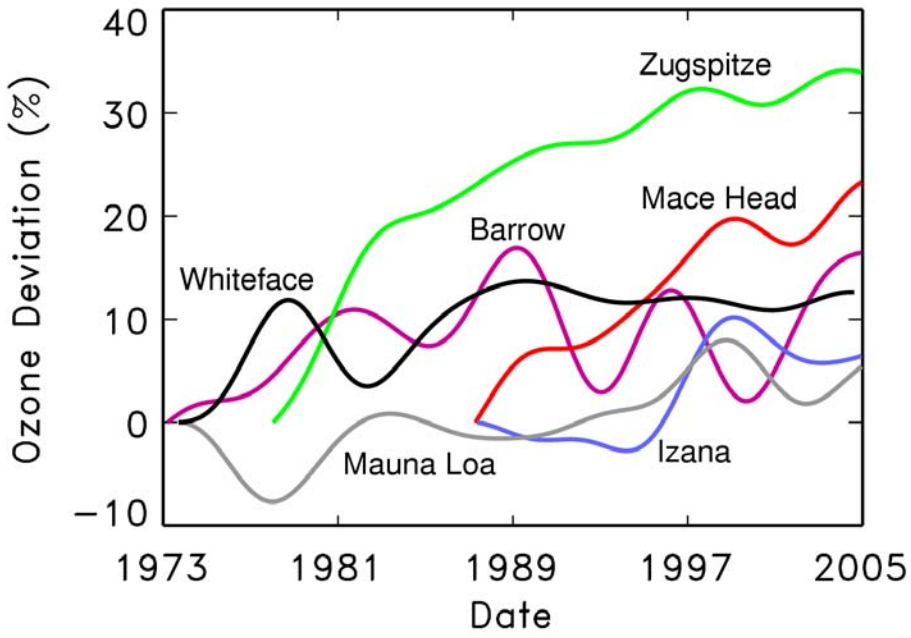

Figure 1: Ozone trend curves (determined from the fit to the difference between the modeled data and the observations) in percent deviation at six selected N.H. surface ozone sites (Barrow – magenta, Mace Head – red, Zugspitze – green, Whiteface Mountain – black, Izana – blue, Mauna Loa – gray).

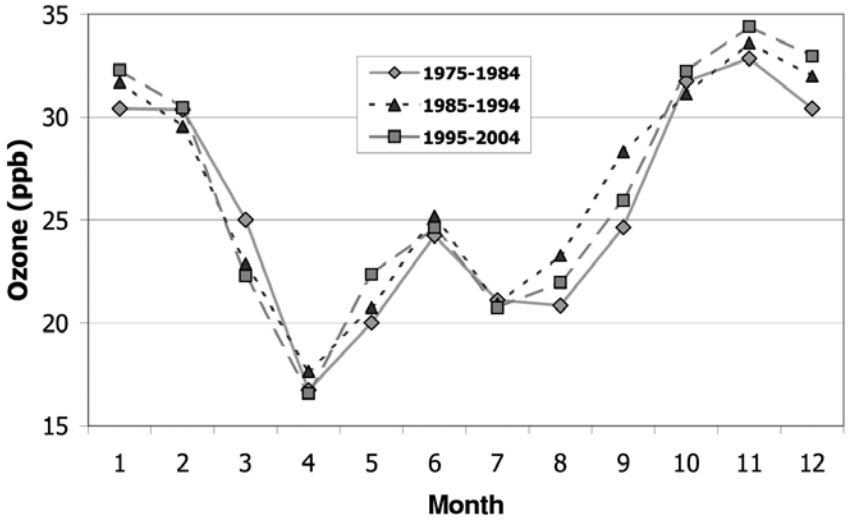

Figure 2: Average monthly surface ozone at Barrow, Alaska for three time periods.

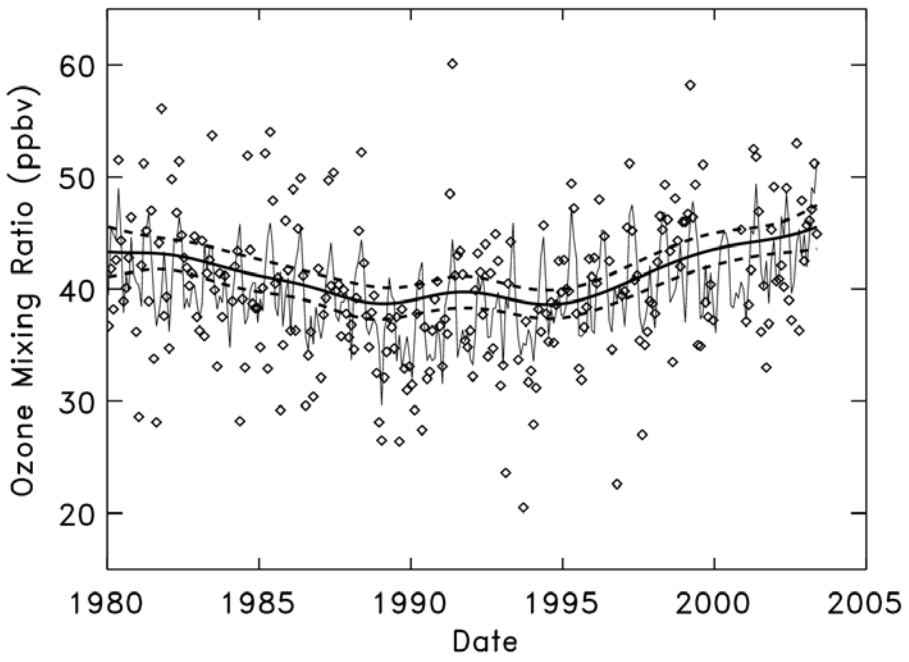

Figure 3: Monthly average ozone amounts at Resolute in the 850-700 hPa layer (diamonds), the modeled values (gray solid line), and the fit (black solid curve) to the residuals (the difference between the data and the model) with the 95% confidence interval (black dashed curves).

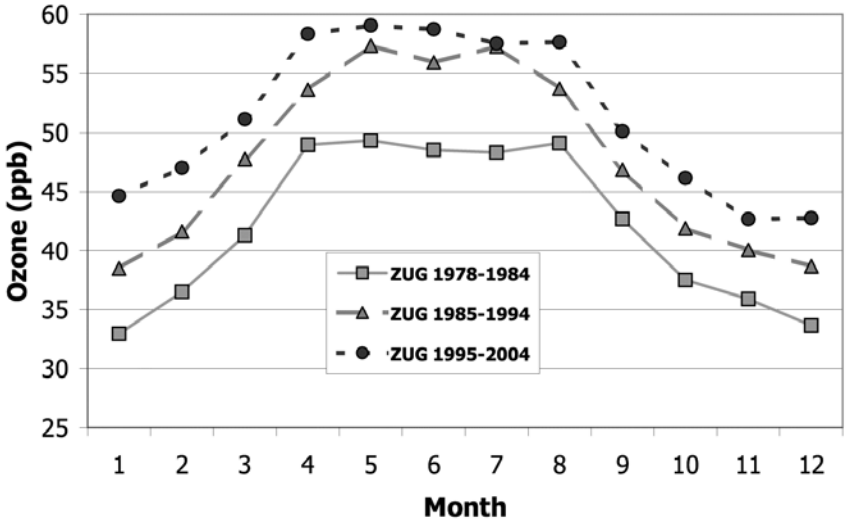

Figure 4: Average monthly surface ozone at Zugspitze for three time periods.

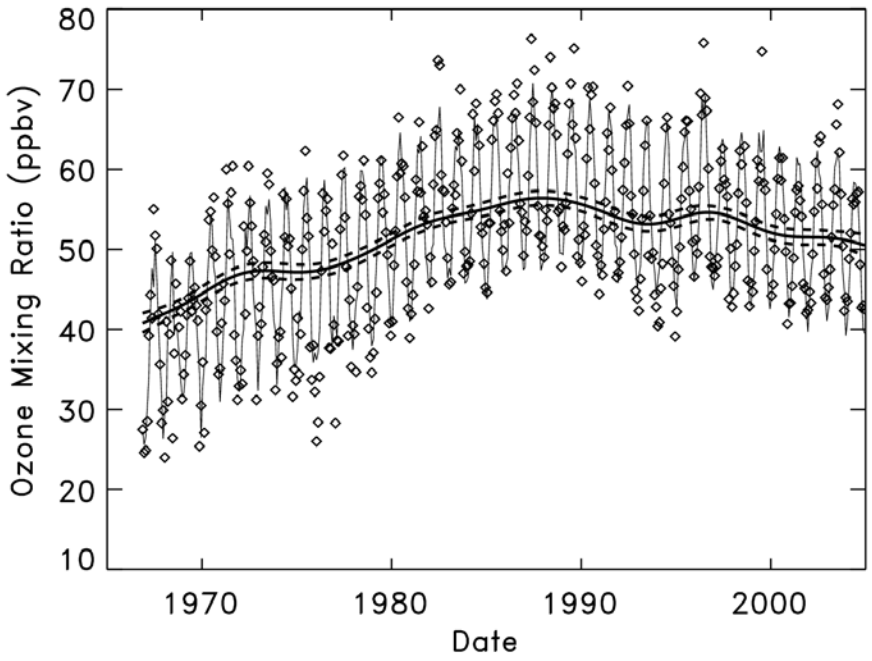

Figure 5: Monthly average ozone amounts at Hohenpeissenberg in the 700-500 hPa layer (diamonds), the modeled values (gray solid line), and the fit (black solid curve) to the residuals (the difference between the data and the model) with the 95% confidence interval (black dashed curves).

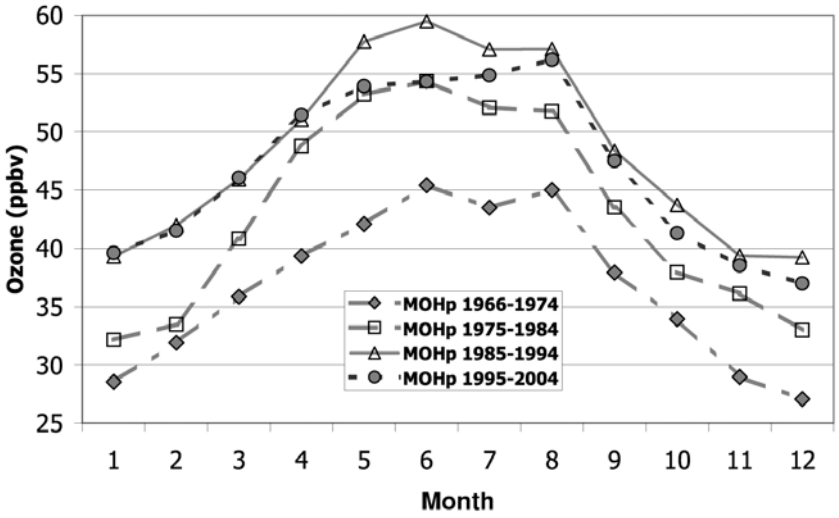

Figure 6: Average monthly ozone in the 850-700 hPa layer at Hohenpeissenberg for four time periods.

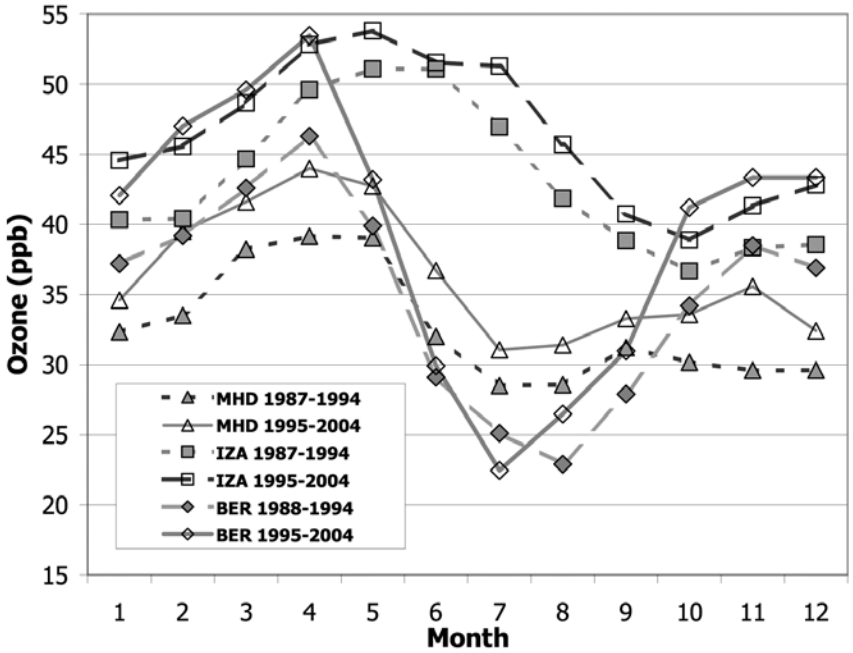

Figure 7: Average monthly surface ozone for three sites in the North Atlantic for two time periods (MHD = Mace Head, IZA = Izana, BER = Bermuda).

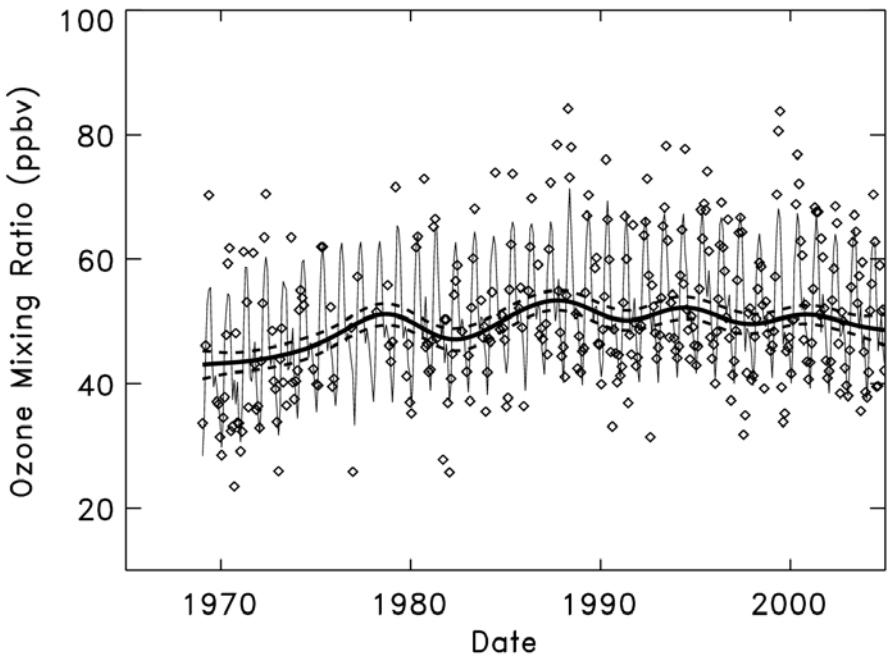

Figure 8: Monthly average ozone amounts at Tsukuba in the 850-700 hPa layer (diamonds), the modeled values (gray solid line), and the fit (black solid curve) to the residuals (the difference between the data and the model) superimposed on the model with the 95% confidence interval (black dashed curves).

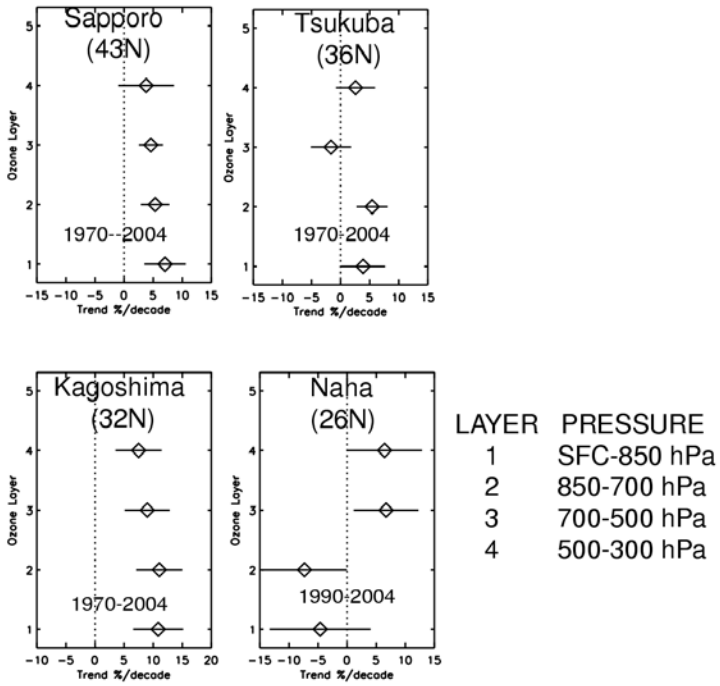

Figure 9: Trend with altitude of the ozonesonde layer averages at four Japanese stations. Sapporo, Tsukuba and Kagoshima data are for the period 1970-2004 while Naha only includes the period 1990-2004.

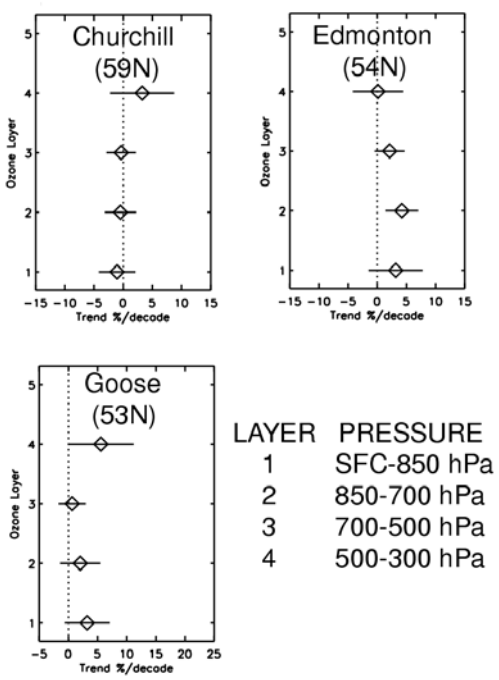

Figure 10: Trend with altitude of the ozonesonde layer averages at three mid latitude Canadian stations for the period 1980-2004.

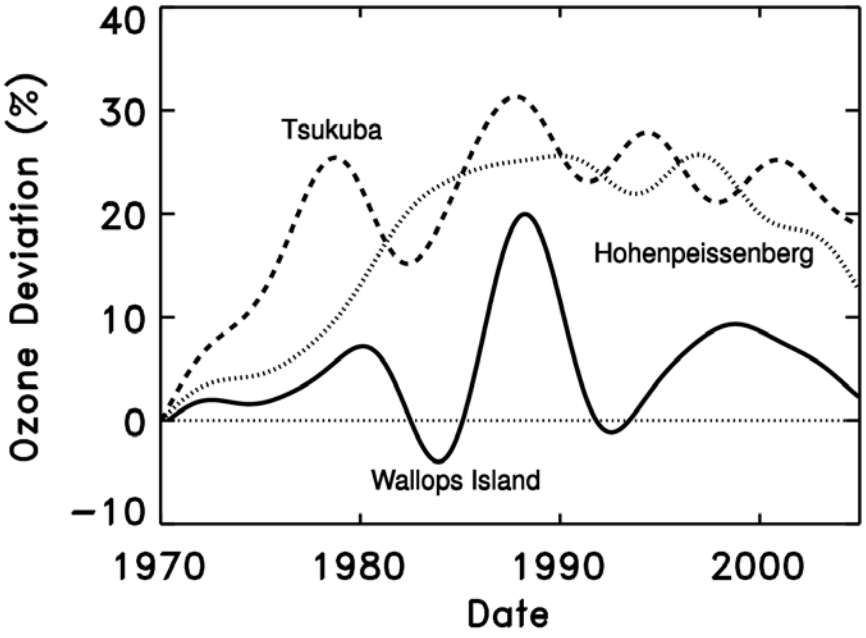

Figure 11: Ozone trend curves (determined from the fit to the difference between the modeled data and the observations) in percent deviation for Hohenpeissenberg, Tsukuba, and Wallops Island for the 850-700 hPa layer.

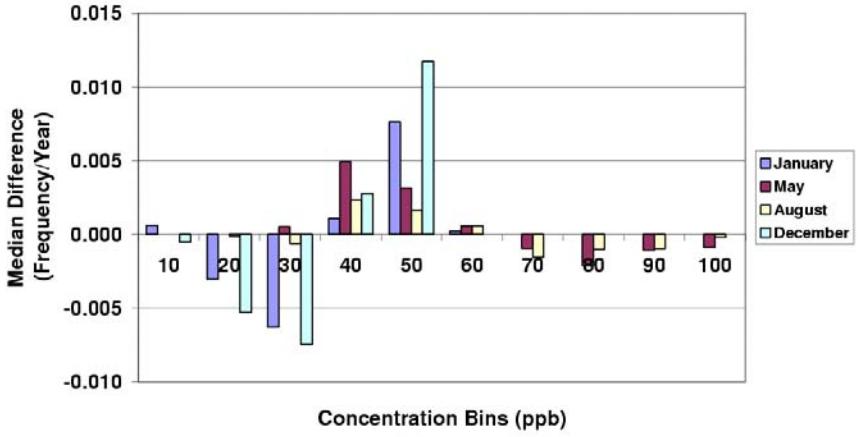

Figure 12: The distribution of changes in surface ozone concentrations at Whiteface Mountain, New York by month for months with significant changes in the distribution. The mass in the histogram for each month sums to one. The changes (pluses and minuses) add approximately to zero. A change in the frequency per year can be translated into hours by multiplying the plotted number by the total number of hours in the month. For example a month with 720 hours and a frequency of 0.01 per year represents a shift from one concentration bin to another of 7 hours per year. The median difference is computed by differencing between individual years (for example 1982-1983, 1982-1984, 1982-1985 … 1983-1984, 1983-1985, 1983-1986 …). The plotted value is the median of these differences for each month and each concentration bin with a significant change.

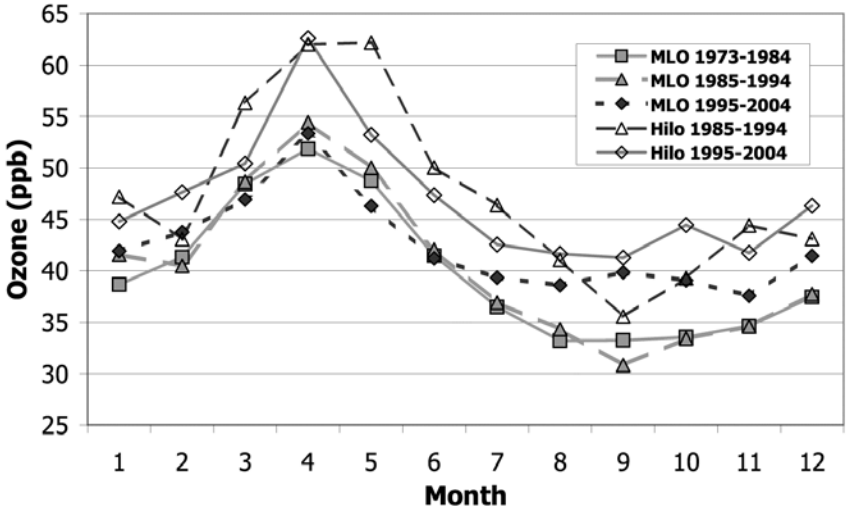

Figure 13: Seasonal variation in surface ozone (filled symbols) at Mauna Loa Observatory (MLO) and in the 700-500 hPa layer ozone (open symbols) at Hilo, Hawaii for different 10-year time periods.

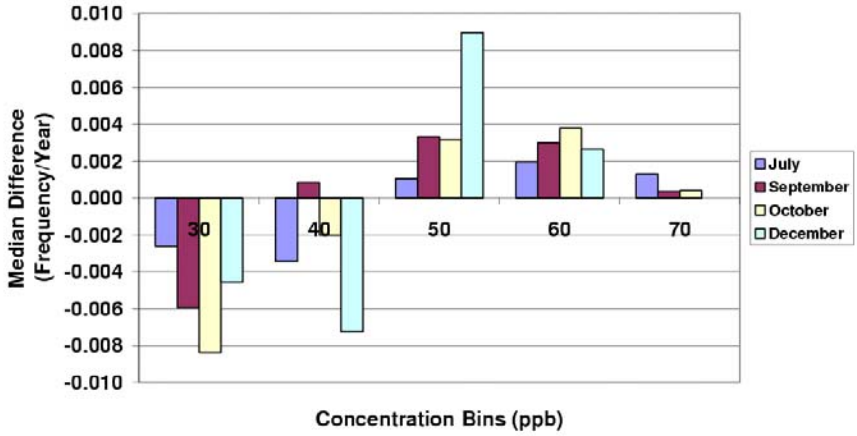

Figure 14: The monthly change in the distribution of hourly average concentrations of Mauna Loa surface ozone expressed as the median difference of occurrence of hourly averages in each concentration bin for each month with a significant change.

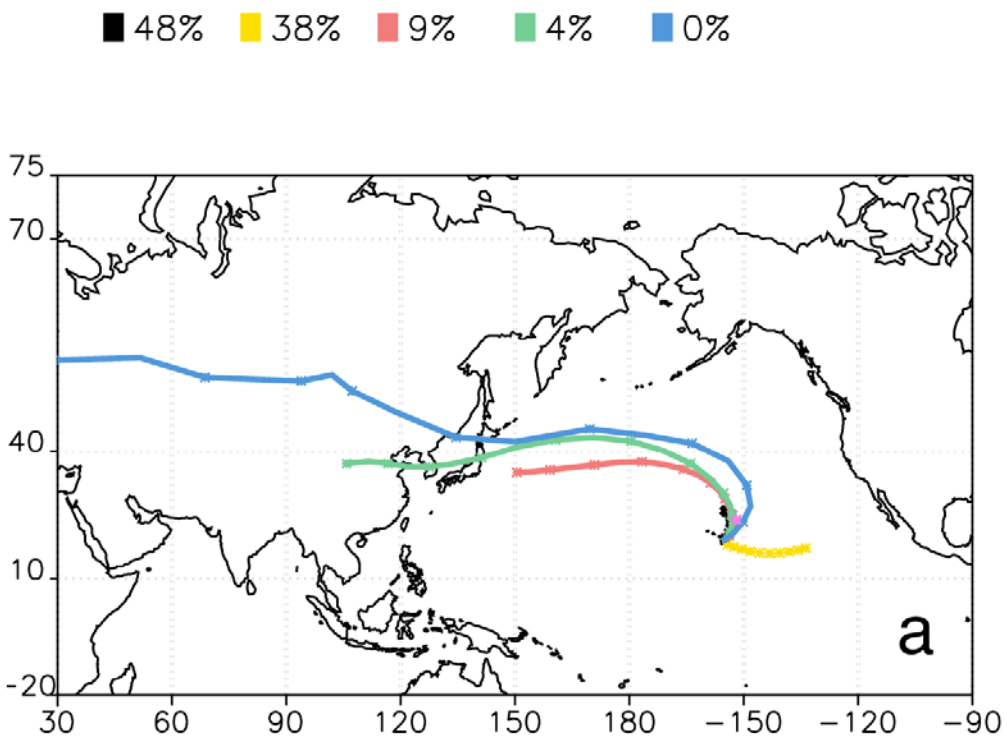

Figure 15a: Clustered trajectories for Mauna Loa Observatory for the months of September and October for the period 1986-1994.

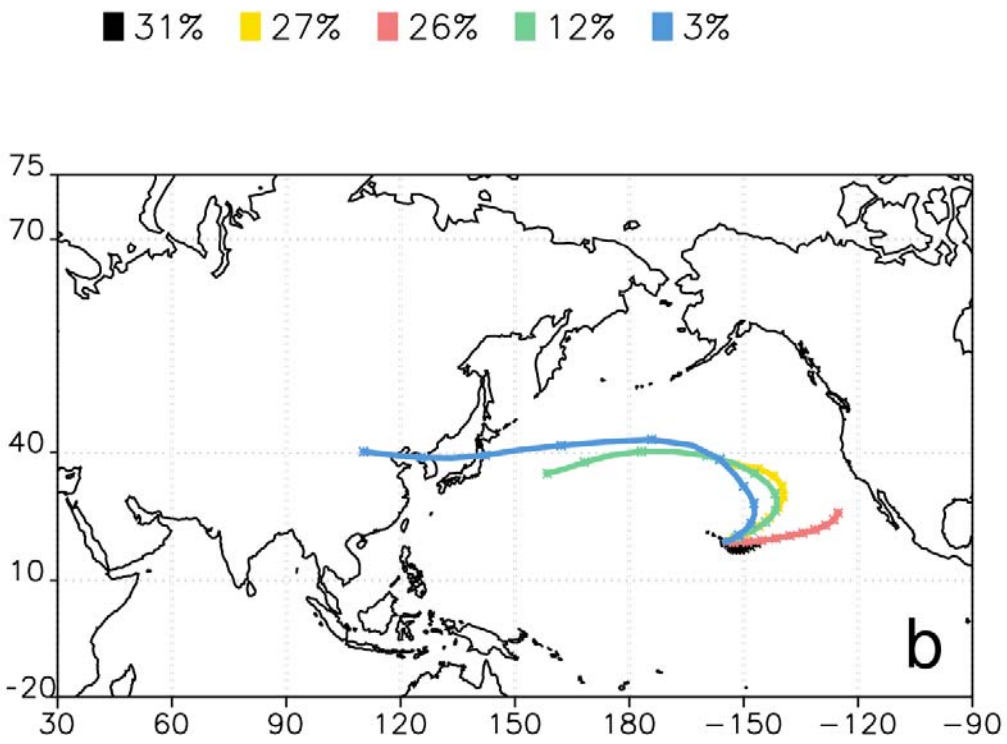

Figure 15b: Clustered trajectories for Mauna Loa Observatory for the months of September and October for the period 1995-2004.

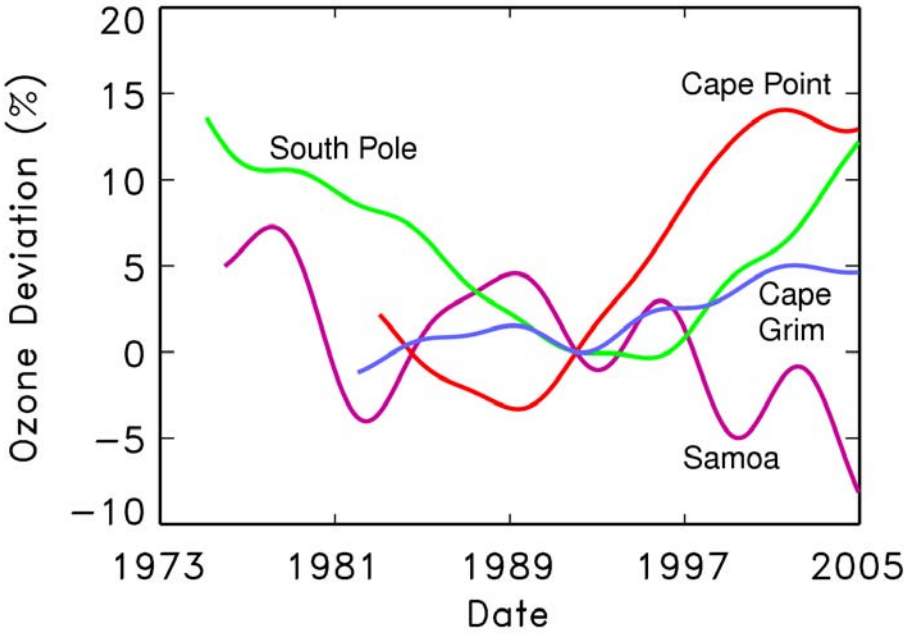

Figure 16: Ozone trend curves (determined from the fit to the difference between the modeled data and the observations) in percent deviation at four selected S.H. surface ozone sites (South Pole – green, Cape Grim – blue, Cape Point – red, Samoa – magenta).

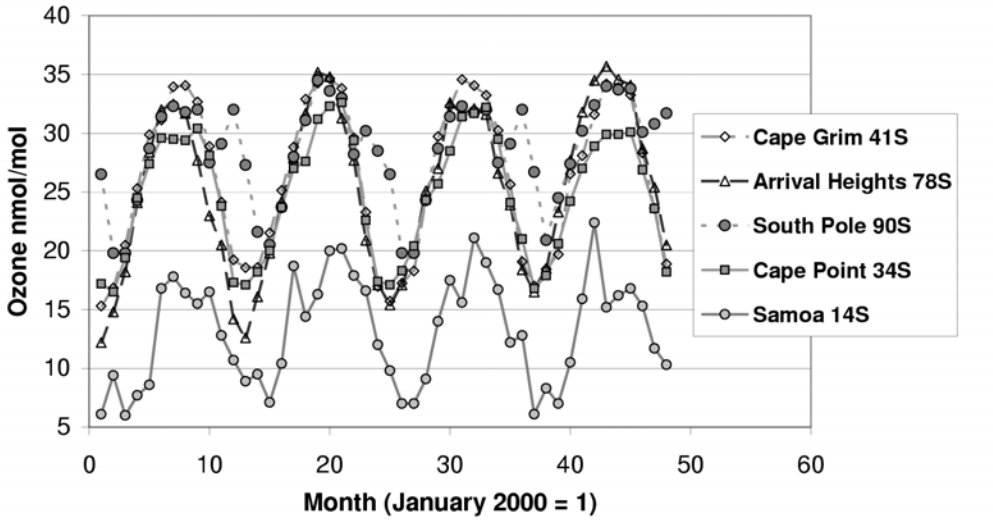

Figure 17: Time series of monthly mean surface ozone at five sites in the S.H. for the period 2000 – 2003.

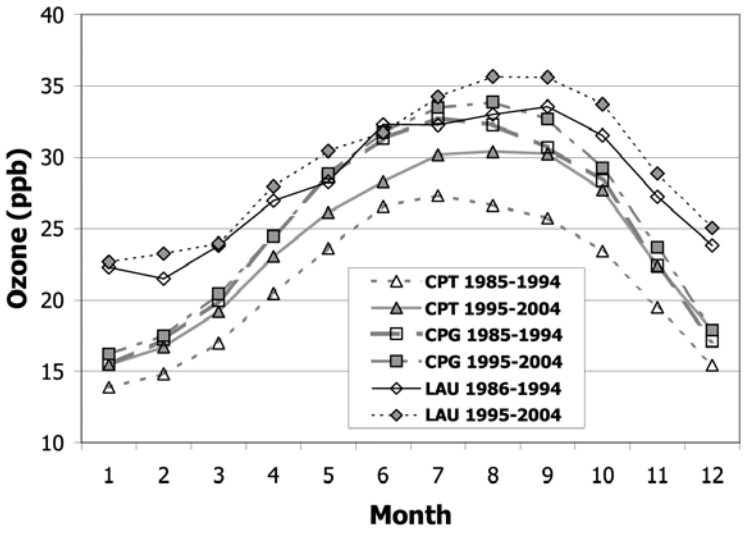

Figure 18: Average seasonal cycle of surface ozone at Cape Point (CPT) and Cape Grim (CPG) and the 850-700 hPa layer average ozone at Lauder (LAU) for two time periods.

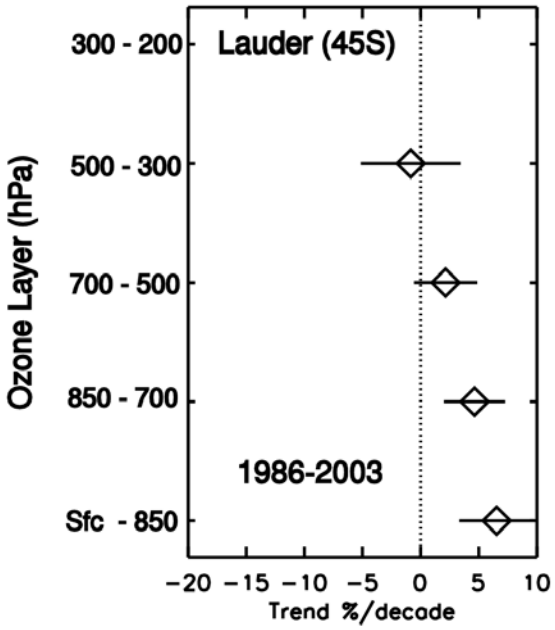

Figure 19: Trend in altitude layers from ozonesonde data at Lauder, New Zealand

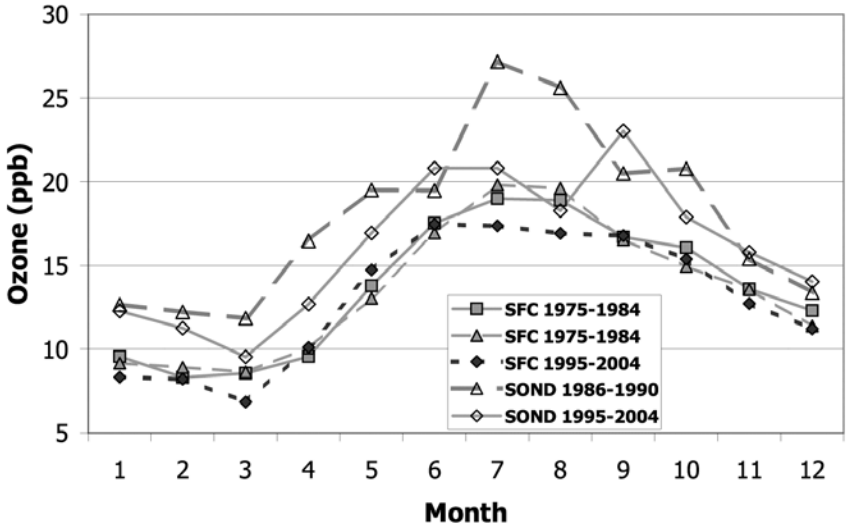

Figure 20: Seasonal cycle in surface ozone (SFC) for three time periods and the Surface-850 hPa layer ozone (SOND) for two time periods at Samoa.

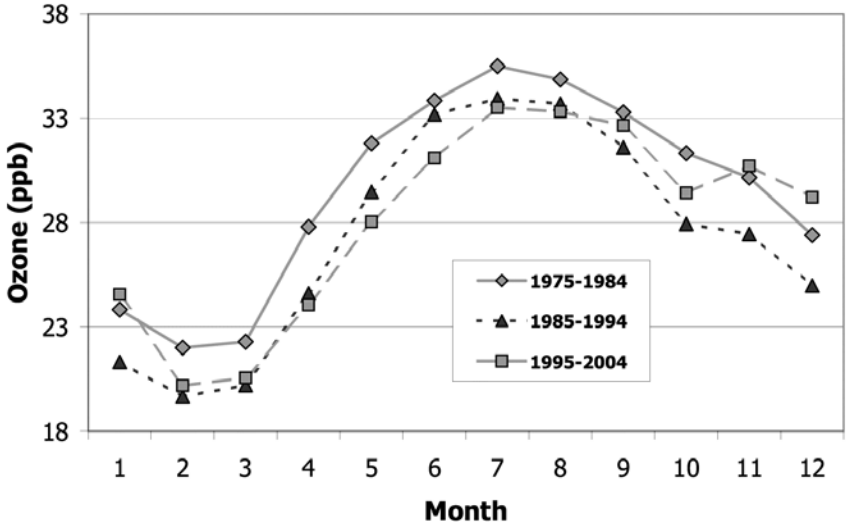

Figure 21: Average monthly surface ozone at South Pole for three time periods.

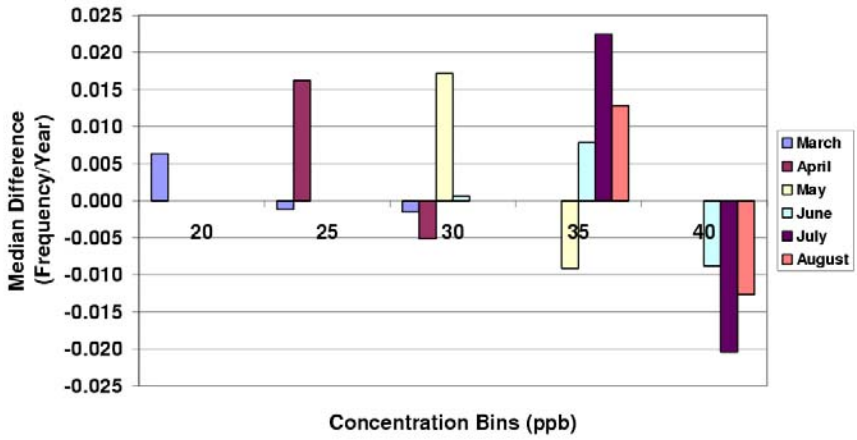

Figure 22: The monthly change in the distribution of hourly average concentrations of South Pole surface ozone expressed as the median difference of occurrence of hourly averages in each concentration bin for each month with a significant change.