CHAPTER 1

Ozone Measurements

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CHAPTER 1

OZONE MEASUREMENTS

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SCIENTIFIC SUMMARY

The quality of the total ozone measurements made by ground-based and satellite systems has been assessed and trends calculated where appropriate.

- Trends in total ozone since 1979 have been updated through early 1994:
  - Northern Hemisphere middle latitude trends are significantly negative in all seasons, but are much larger in winter/spring (about 6%/decade), than in summer/fall (about 3%/decade).
  - Tropical (approx. 20°S – 20°N) trends are slightly negative, but not statistically significant when suspected drift in the satellite data is incorporated into the uncertainty.
  - Southern midlatitude trends are significantly negative in all seasons, and increase in magnitude for high latitudes.

- Representative trends (annual averages, in % per decade) for north and south midlatitudes and the tropics are as follows.

		Latitude		
		Mid South	Equatorial	Mid North
Recent:				
1/79 to 5/94	SBUV+SBUV/2	-4.9 ± 1.5	-1.8 ± 1.4	-4.6 ± 1.8
1/79 to 2/94	Dobson network	-3.2 ± 1.3	-1.1 ± 0.6	-4.8 ± 0.8
1/79 to 2/94	Ozonometer (former USSR)	na	na	-4.9 ± 0.8
Pre-Pinatubo:				
1/79 to 5/91	SBUV+SBUV/2	-4.9 ± 2.3	-0.8 ± 2.1	-3.3 ± 2.4
1/79 to 5/91	TOMS	-4.5 ± 2.1	+0.4 ± 2.1	-4.0 ± 2.1
1/79 to 5/91	Dobson network	-3.8 ± 1.3	+0.2 ± 1.2	-3.9 ± 0.7
1/79 to 5/91	Ozonometer (former USSR)	na	na	-3.8 ± 1.0

Note: Uncertainties (±) are expressed at the 95% confidence limits (2 standard errors).

- The corresponding ozone loss (in %) accumulated over 15.3 years for trends calculated through 1994 are:

	Latitude		
	Mid South	Equatorial	Mid North
SBUV+SBUV/2	-7.4 ± 2.3	-2.7 ± 2.2	-7.0 ± 2.7
Dobson network	-4.8 ± 2.1	-1.7 ± 0.9	-7.3 ± 1.3
Ozonometer (former USSR)	na	na	-7.5 ± 1.3

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- There was a statistically significant increase (about 2%/decade) in the average rate of ozone depletion at the Dobson stations north of 25°N in the period 1981-1991 compared to the period 1970-1980.

- We have confidence in the trends deduced from the ground-based network, particularly in the Northern Hemisphere. The record is longer than for the satellite instruments, although the geographic coverage is patchy, with most stations situated in the Northern Hemisphere midlatitudes. The absolute calibration of the International Standard Dobson spectrophotometer has been maintained at ± 1%/decade. The quality of the data from the ground-based network has improved since the last assessment, partly as a result of improvements to the existing records and partly as a result of the improving quality control in the ground-based network.

- An extensive revision and reanalysis of the measurements made using the filter ozonometer data from the vast area of the former USSR has recently been performed. Trend estimates from these revised data substantiate those made at similar latitudes by Dobson and satellite instruments.

- During the 1980s, the Total Ozone Mapping Spectrometer (TOMS) total ozone calibration drifted by 1-2% relative to the Dobson instruments, depending on latitude. In addition, a systematic bias of 1-2%/decade may be present in measurements made at high solar zenith angles (and so is most important at high latitudes in winter). Our confidence in the trends presented in the 1991 Ozone Assessment, which covered the period through March 1991, is unchanged.

- However after this time, a problem developed in the TOMS instrument that lasted until the instrument became inoperative in May 1993. This problem resulted in systematic errors dependent on both season and latitude, and caused, on average, a drift of 1-2% between 1991 and 1993. TOMS satellite measurements made after May 1991 were, therefore, not used for trend analyses. A TOMS instrument was launched on the Meteor-3 satellite in August 1991. The satellite orbit is not ideal and the measurements from this instrument have not yet been sufficiently assessed to allow use in trend analyses.

- The drift in the calibration of total ozone by the Solar Backscatter Ultraviolet (SBUV) instrument from January 1979 to June 1990 was 1% or less relative to Dobson instruments, and any seasonal differences in the Northern Hemisphere were less than 1%. The SBUV/2 instrument on board the NOAA-11 satellite has measurements available from January 1989. The drift relative to Dobson instruments in the Northern Hemisphere has been less than 1%. However, there is an apparent seasonal cycle in the differences of about 1-2% (minimum to maximum).

- Nearly all ground-based instruments are now on the calibration scale of the World Standard Dobson Instrument #83. The quality of the measurements made at individual stations is tested using satellite data; any revision of the data is based on available instrumental records. Satellite measurements are independently calibrated by checking the internal consistency. However, the satellite record is tested for possible drift by comparison with the collection of station data. Thus, the ground-based and satellite records are not completely independent from one another.

Trends in the Vertical Distribution of Ozone

The state of knowledge about the trends in the vertical distribution of ozone is not as good as that about the total ozone trends. The quality of the available data varies considerably with altitude.

- At altitudes of 35-45 km, there is reasonable agreement between the Stratospheric Aerosol and Gas Experiment I/II (SAGE I/II), SBUV, and Umkehr, that during 1979-1991, ozone declined 5-10% per decade at 30-50°N and slightly more at southern midlatitudes. In the tropics, SAGE I/II gives larger trends (ca. -10% per decade) than SBUV (ca. -5% per decade) at these altitudes.

- At altitudes between 25 and 30 km, there is reasonable agreement between SAGE I/II, SBUV, Umkehr, and ozonesondes that, during the 1979-1991 period, there was no significant ozone depletion at any latitude. The agreement continues down to about 20 km, where statistically significant reductions of 7 ± 4% per decade were observed between 30 and 50°N by both ozonesondes and SAGE I/II. Over the longer period from 1968-1991, the ozonesonde record indicates a trend of -4 ± 2% per decade at 20 km at northern midlatitudes.

- There appear to have been sizeable ozone reductions during the 1979-1991 period in the 15-20 km region in midlatitudes. There is disagreement on the magnitude of the reduction, with SAGE indicating trends as large as -20 ± 8% per decade at 16-17 km and the ozonesondes indicating an average trend of -7 ± 3% per decade in the Northern Hemisphere. The trend in the integrated ozone column for SAGE is larger than those found from SBUV, TOMS, and the ground-based network, but the uncertainties are too large to evaluate the consistency between the data sets properly. For 1968-1991 the ozonesonde record indicates a trend of -7 ± 3% per decade at 16 km at northern midlatitudes.

- In the tropics, trend determination at altitudes between 15 and 20 km is made difficult by the small ozone amounts. In addition, the large vertical ozone gradients make the trends very sensitive to small vertical displacements of the profile. The SAGE I/II record indicates large (-20 to -30% (± 18%) per decade) trends in the 16-17 km region (-10% (± 8%) at 20 km). Limited tropical ozonesonde data sets at Natal, 6°S and Hilo, 20°N do not indicate significant trends between 16 and 17 km or at any other altitude for this time period. With currently available information it is difficult to evaluate the trends below 20 km in the tropics, as the related uncertainties are large. The effect on the trend in the total column from any changes at these altitudes would be small.

- In the free troposphere, only limited data (all from ozonesondes) are available for trend determination. In the Northern Hemisphere, trends are highly variable between regions. Upward trends in the 1970s over Europe have declined significantly in the 1980s, have been small or non-existent over North America, and continue upward over Japan. The determination of the size of the change over North America requires a proper treatment of the relative tropospheric sensitivities for the type of sondes used during different time periods.

- Surface measurements indicate that ozone levels at the surface in Europe have doubled since the 1950s. Over the last two decades there has been a downward trend at the South Pole, and positive trends are observed at high altitude sites in the Northern Hemisphere. When considering the latter conclusion, the regional nature of trends in the Northern Hemisphere must be borne in mind.

Observations of Ozone and Aerosols in 1991-1994

- Global total ozone values in 1992/93 were 3-4% lower than the 1980s average. If the trend, solar cycle, and quasi-biennial oscillation (QBO) effects inferred from the 1980s record are extrapolated, an additional global anomaly of between -1 and -2% remains.

- The most negative anomalies were observed in the Northern Hemisphere springs in 1992 and 1993, with peak deviations of 6-10% in February-April 1993.

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- A reduction of 3-4% occurred in the tropics in the six months following the eruption of Mt. Pinatubo.

- Overall the smallest effects were observed in the extra-tropical Southern Hemisphere, where total ozone amounts were at the low end of the range observed in the 1980s, as would be expected from the long-term downward trend observed in that region.

- In 1994, global ozone levels are also at the low end of the 1980s range, again in line with expectations of a continuation of the observed long-term trend.

- Following the June 1991 eruption of Mt. Pinatubo, stratospheric aerosol levels increased globally, with northern midlatitude peak particle surface areas increasing by factors of 30-40 above pre-eruption values about one year after the eruption. Since that time, they have been decreasing.

- Several mechanisms have been suggested as causes of the total ozone anomalies, though the relative importance is not yet clear. The possible influences include: radiative, dynamical, and chemical perturbations resulting from the Mt. Pinatubo volcanic aerosol; and global and regional dynamical perturbations, including the El Niño-Southern Oscillation.

Antarctic Ozone Depletion

- Record low mean values for October were observed at three Antarctic ground-based stations with continuous records since the late 1950s and early 1960s. There is no evidence of major springtime ozone depletion in Antarctica at any of the four Dobson stations prior to 1980.

- In early October 1993, a record low daily value of total ozone of 91 $\pm$ 5 Dobson units was observed with an ozonesonde at the South Pole. During this flight (and in several others), no detectable ozone (less than 1%) was found over a 5 km range from 14 to 19 km, implying that complete chemical destruction of ozone had occurred. The geographical extents of the ozone holes in 1992 and 1993 were the two largest on record.

- A comparison of ozonesonde measurements made at the South Pole from 1967-1971 with those made between 1986 and 1991 reaffirms that the Antarctic depletion that has developed since the early period occurs at altitudes between 14 and 20 km, and that the largest changes occur in September, October, and November.

1.1 INTRODUCTION

Ozone in the atmosphere is easy to detect. Several techniques have been successfully used: most are optical, using absorption or emission of light in many regions of the spectrum; others are chemical; and some are a mixture of the two. However, while it is relatively easy to detect ozone in the atmosphere, it has proved difficult to make sufficiently precise and numerous measurements to determine credible changes of a few percent on a decadal time scale. Difficulties include: knowing what the absolute calibrations of the instruments are and how they change with time; assessing how much variability in any set of measurements is caused by the instrument and how much by the natural variability in the atmosphere; and making meaningful comparisons of measurements made by different instruments, especially when different techniques are used. Detailed descriptions of the major techniques and instruments were given in the report of the International Ozone Trends Panel (IOTP) (WMO, 1990a) and are not repeated here.

We first consider the quality of total ozone measurements, particularly those made by the ground-based observing network, the Total Ozone Mapping Spectrometer (TOMS), and the Solar Backscatter Ultraviolet spectrometers (SBUV). The ground-based and satellite instruments have proven invaluable in assessing each others' data quality. Nearly all ground-based instruments are now on the calibration scale of the World Standard Dobson Instrument #83. The quality of the measurements made at individual stations is tested using satellite data; any revision of the data is based on available instrumental records. Satellite measurements are independently calibrated by checking the internal consistency. However, the satellite record is tested for possible drift by comparison with the collection of station data. Thus, the ground-based and satellite records are not completely independent from one another.

Given this perspective, we next present the trends in total ozone calculated to May 1994. Special attention is paid to how the trends are affected by the record low ozone values that were observed in 1992 and 1993. This theme is taken up again later, in Section 1.4, where we describe the ozone changes seen in this period. The evolution of stratospheric aerosol following the eruptions of Mt. Pinatubo in June 1991 and Volcán Hudson in August 1991, and possible links with the low ozone values, are briefly discussed, along with other potentially important influences on ozone at this time.

In Section 1.3 we discuss the quality of the various techniques (remote and *in situ*) that measure the vertical distribution of ozone in the atmosphere. Although progress has been made, a good deal of work remains before a clear picture can emerge, especially in the region near the tropopause, which is so important in determining the impact of ozone changes on climate.

Last, the development of the Antarctic ozone hole in 1992 and 1993 is described in Section 1.5, together with some new analyses of some old measurements.

1.2 TOTAL OZONE

1.2.1 Total Ozone Data Quality

Total column ozone has been measured using Dobson instruments since the 1920s. The number of monitoring stations has increased through the years, and since the 1960s a large enough network has existed to monitor ozone over most of the world with particularly good coverage in the northern midlatitudes and in Antarctica. Truly global monitoring has been possible only since the introduction of satellite-based instruments. The 1988 IOTP (WMO, 1990a) examined the quality of ozone measurements from both ground-based systems (Dobson, M83, M124) and satellite systems. They reported great variability in the quality of the data from ground-based instruments and found large calibration drifts in the SBUV and TOMS instruments caused by imperfectly corrected degradation of the on-board diffuser plates. When the 1991 assessment of ozone trends was made (WMO, 1992a), improvements in the quality of ozone data were noted. The re-evaluation of historical Dobson data records initiated by Bojkov *et al.* (1990) had been carried out at a small number of stations. Similarly, the quality of the satellite data had improved, though unresolved problems were still apparent. The entire TOMS ozone data record had been reprocessed using the version 6 algorithm, which improved the instrument calibration through the requirement that ozone amounts measured by different wavelength pairs maintain relative stability (Herman *et al.*, 1991). Comparison with the World Standard Dobson instrument number 83

(I83) at Mauna Loa indicated that good, long-term precision had been achieved (McPeters and Komhyr, 1991).

1.2.1.1 Ground-Based Observations

Since January 1992, all ground-based measurements have been reported using the Bass and Paur (1985) ozone cross sections. This change should increase the accuracy of the ozone record for direct comparison with other measurement systems, but should have no effect on the core time series of observations made with the AD wavelength pairs since the conversion from the old Vigroux (1953) scale is defined (Komhyr *et al.*, 1993). Since the last assessment the number of Dobson stations at which the historical records have been reanalyzed by the responsible personnel has increased to over 25, with many more in the process of reanalysis.

In a full re-evaluation, the station log books and lamp calibration records are carefully examined and corrections are made where appropriate (WMO, 1992b). Measurements are treated on an individual basis, in contrast to the "provisionally revised" data described and used in IOTP and subsequent assessments where monthly averages are treated. Comparisons with external data sets (total ozone records in the same synoptic region, meteorological data and, since 1978, satellite overpass data) are made to identify periods where special attention should be paid. The data are only corrected if a cause is found based on the station records. The goal of re-evaluation is to produce a high quality, long-term total ozone record. Increasingly frequent international intercomparisons of ground-based instruments bring more consistency to the global network. Recent intercomparisons were made at Arosa (Switzerland) in 1990, at Hradec Kralove (Czech Republic) in 1993, and at Izaña (Canary Islands) in 1994. In addition, the practice of using traveling standard lamps to check the calibration of individual instruments has become more frequent in recent years, with a consequent reduction in the observed scatter (Grass and Komhyr, 1989; WMO, 1994a).

Several important concerns about the quality of the ground-based data remain – in particular, how reliable are trends determined from Dobson data in the 1960-1980 period? While the program to reanalyze Dobson records is important, there are limits to what can be achieved. Not only is sufficient information not available in many cases, particularly in the early years, but, even in recent TOMS overpass comparisons, apparent calibration shifts are identified for which no cause has been found. Another issue of concern is whether uniform data quality can be maintained when a Dobson instrument is replaced by a Brewer. Brewer instruments replaced Dobsons at 4 Canadian sites (Churchill, Edmonton, Goose Bay, and Resolute) in the mid-1980s. During the changeover at each site, both instruments were operated for a period of at least 3 years in order to quantify possible biases and differences in seasonal response. In order to ensure continuity, a simulated Dobson AD direct sun measurement is reported for these sites (Kerr *et al.*, 1988). The data records for these sites must be monitored for possible biases and differences in seasonal response that might affect trend analyses.

In Section 1.2.2, trend analyses of the measurements from 43 stations are reported. The records from many more were examined for possible inclusion, but were not used for a variety of reasons. First, only records starting before 1980 were considered sufficiently long for meaningful analyses to be made. Second, a minimum of 12 days of observation were required for a monthly mean to be included. In the case of three high latitude stations, all midwinter monthly means were missing, a situation that cannot be handled by the current, well-documented statistical technique, at least as far as computation of seasonal average trends is concerned. For this assessment, no analysis of data from such stations is made. Third, some station records show large variations against nearby stations or satellite overpasses that cannot be explained in terms of any natural phenomena. These records are few and were not used. A number of points requiring corrections have been identified in the measurements submitted to the World Ozone Data Center. The re-evaluations used in the records used here for trend analysis will be documented in WMO Report No. 35 (appendix by Bojkov). About half of these corrections result from the WMO intercomparison program and individual instrument's calibration procedures, and most of the remainder are made from information made available from the instrument log books by the operating agency (Bojkov, private communication). A few obvious calibration shifts for which no instrumentally derived correction can be found are treated in the statistical analysis (see Section 1.2.2). An empirical technique has been used to correct the air mass dependencies at a few stations, as insufficient instrumental information

exists in these cases (see appendix by Bojkov in WMO, 1994b).

The chief instrument used in the former USSR was a filter ozonometer. Various improvements have been made over the years, and the record of the M-83 and M-124 versions since 1973 has been assessed by Bojkov *et al.* (1994) using recently available information on the individual instruments' performance and calibration histories. The errors associated with these instruments are larger than those of Dobson or Brewer instruments, and Bojkov *et al.* combine the individual station data into regional averages.

Sulfur dioxide (SO_2) absorbs ultraviolet at the wavelengths used by Dobson and Brewer instruments to measure total ozone. The presence of SO_2 causes a false increase of total ozone measured by Dobson instruments for both the AD and CD wavelengths. As part of a detailed revision of the total ozone record at Uccle, Belgium, De Muer and De Backer (1992) considered the effect of the locally measured reduction in surface SO_2 on the total ozone record from 1972 to 1991. Over this period, surface SO_2 levels dropped by a factor of about 5. The size of the downward correction to the observed total ozone was found to be 3-4% in 1972 and just under 1% in 1990, a change of similar size to the trend calculated in IOTP (WMO, 1990a). The trends calculated using the revised data for 1978-1991 are in reasonable agreement with TOMS version 6 overpass measurements (WMO, 1992).

This analysis clearly raises the question as to how many records might be similarly affected (De Muer and De Backer, 1993). Most North American stations are in unpolluted areas and measurements made there will not have been influenced by tropospheric SO_2. In Canada, surface SO_2 measurements made since 1974 are reported by Environment Canada in the National Air Pollution Surveillance Series for sites in Toronto, the worst affected station in Canada. In 1974 the average surface SO_2 concentration in Toronto was 42 $\mu g\ m^{-3}$, about 40% that measured near Uccle in the same year. A review of these data indicates that about 1% (3-4 Dobson units, DU) false total ozone may have occurred at Toronto in the early part of the record. This dropped to 0.3% (1.2 DU false ozone) in the early to mid-1980s and has remained level since then, in good agreement with Kerr *et al.* (1985, 1988). There is greater uncertainty in the earlier data made by wet chemical instruments (which may be sensitive to other pollutants besides SO_2) than there is in the later data made by pulse fluorescence techniques. Similar measurements made at Edmonton indicate that interference due to SO_2 is less than 0.2% throughout the record (in good agreement with Kerr *et al.*, 1989). The effects of SO_2 on the three other non-urban sites in Canada are thought to be negligible. In the United States, anthropogenic emissions of SO_2 decreased by 27-29% from 1970 to 1988 (Placet, 1991). None of the U.S. stations is in as heavily populated a region as Uccle and so should not have been as affected.

A model study of SO_2 concentrations in Europe, based on emission estimates, indicated that the largest changes in SO_2 concentrations since 1970 have occurred over Belgium, Holland, and Northern France, and that in 1960 the SO_2 concentrations calculated for Belgium were among the highest in Europe (Mylona, 1993). Decreases by a factor of 50-75% were calculated for this region, while elsewhere in Europe and Scandinavia the reductions since 1970 seem to have been 50% at most and are often less. Thus while some Dobson measurements in Europe were affected by the decreasing SO_2 concentrations, it is likely that Uccle is one of the most heavily influenced.

Elsewhere, stations are in polluted regions where the SO_2 trends are different from those in Europe and parts of North America. Work still needs to be done to assess the impact of SO_2 on O_3 measurements at many individual stations.

In June of 1991 the eruption of Mt. Pinatubo resulted in the injection of large amounts of material into the stratosphere. The plume included large amounts of SO_2, but this had decreased to low levels by the end of July (Bluth *et al.*, 1992). Of greater concern is the high level of stratospheric aerosol that spread over the globe and produced large aerosol optical depths for more than a year. But Komhyr (private communication) notes that the data record from the World Standard Dobson instrument I-83 shows little apparent disturbance when the initial, dense aerosol cloud passed over Mauna Loa Observatory in early July. The initial error appeared to be only a tenth of a percent or so. A small change (<1%) in the calibration of I-83 was seen in June 1992. In June 1993, when the stratosphere over Mauna Loa was much cleaner, the calibration of I-83 was the same as in 1991. Thus ozone measurement errors due to Mt. Pinatubo aerosols most likely did not exceed ±1%, for direct sun

observations made by a well-maintained Dobson instrument using the fundamental AD wavelength pairs. This result should be expected, as the wavelength pairs were originally chosen to minimize the effect of aerosol on the measurement (Dobson, 1957).

1.2.1.2 Satellite-Based Observations

Total ozone data are now available from a number of satellite systems. The Nimbus 7 TOMS produced global ozone maps (except in polar night) on nearly every day from November 1978 until May 6, 1993, when the instrument failed. Another TOMS instrument was launched on the Russian Meteor 3 spacecraft in August of 1991 and continues to operate, so a continuous TOMS data record has been maintained, although, because of its drifting orbit, the geographic coverage of the Meteor 3 TOMS is not as extensive as that of Nimbus 7 TOMS.

TOMS has been used as the "most reliable" satellite-based monitor of total ozone because it gives daily global coverage and has a 14.5-year record of observations. The version 6 TOMS data were produced using a calibration based on data up through May 1990, and there is concern that its calibration may have drifted since then. This issue will be addressed through comparisons with other instruments. There is a known error at large solar zenith angles (>70°) demonstrated by comparison with Système d'Analyse par Observation Zénithale (SAOZ) spectrometers (Pommereau and Goutail, 1988), which make zenith sky measurements of ozone at sunset and sunrise and thus avoid the concerns about airmass or temperature dependencies that arise with the shorter wavelengths used in the Dobson, Brewer, TOMS, and SBUV instruments. This error in TOMS is caused by a dependence on the shape of the ozone profile when the ultraviolet light, used to measure the ozone, no longer penetrates well to the ground. For the Nimbus 7 TOMS, this problem is only important at high latitudes in the winter hemisphere. Wellemeyer *et al.* (1993) estimate that the 60° latitude winter trend will be in error by less than 1-2% per decade; errors at lower latitudes should be insignificant.

The sensitivity of TOMS to volcanic aerosol has been analyzed in detail (Bhartia *et al.*, 1993). There are systematic errors depending on scan angle, but on a zonal mean basis the errors largely cancel. Aerosol-related effects on the TOMS observation were only observed in the tropics for a few months, so there should not be a significant effect on trends.

Data from Meteor 3 TOMS have been available since its launch in August 1991, but the consistency of the data from the two TOMS instruments (Nimbus 7 TOMS and Meteor 3 TOMS) has not been properly assessed yet. The comparison is complicated by the orbit of Meteor 3, which drifts from near-noon observations to near-terminator observations every 53 days. Periodically, all data from Meteor 3 TOMS are collected at very large solar zenith angles, so that the problems connected with high latitude measurements occur at all latitudes. In the light of these problems and the lack of a more detailed assessment of the data quality, no use is made of the Meteor 3 TOMS measurements for the trends presented in this assessment.

The SBUV instruments also measure total ozone, viewing directly below the orbital track of the spacecraft. The SBUV instrument on Nimbus 7 operated from November 1978 to June 1990. While SBUV and TOMS were separate instruments, they shared the diffuser plate measuring the extraterrestrial solar flux and so did not have completely independent calibrations. The same basic algorithm is used to calculate both the TOMS and the SBUV total ozone measurements. Data are also available from the NOAA-11 SBUV/2 beginning in January 1989 through May 1994. The SBUV/2, which has suffered much less degradation than SBUV, maintains calibration using on-board calibration lamps and comparison with periodic flights of the Shuttle SBUV instrument (Hilsenrath *et al.*, 1994), and so its data record is truly independent of the other systems. There is a concern that, as the NOAA-11 orbit has drifted from an initial 1:30 PM equator crossing time to a 4:30 PM equator crossing time in 1994, zenith angle dependent errors could be aliased into the ozone trend from SBUV/2.

The TOVS (TIROS Operational Vertical Sounder) instruments (flown on a number of platforms) monitor total ozone using the 9.6 μm channel, which makes them most sensitive to ozone near the ozone maximum. This fact and the unresolved problem of possible calibration differences between the series of TOVS instruments limit the current usefulness of TOVS for trend analysis.

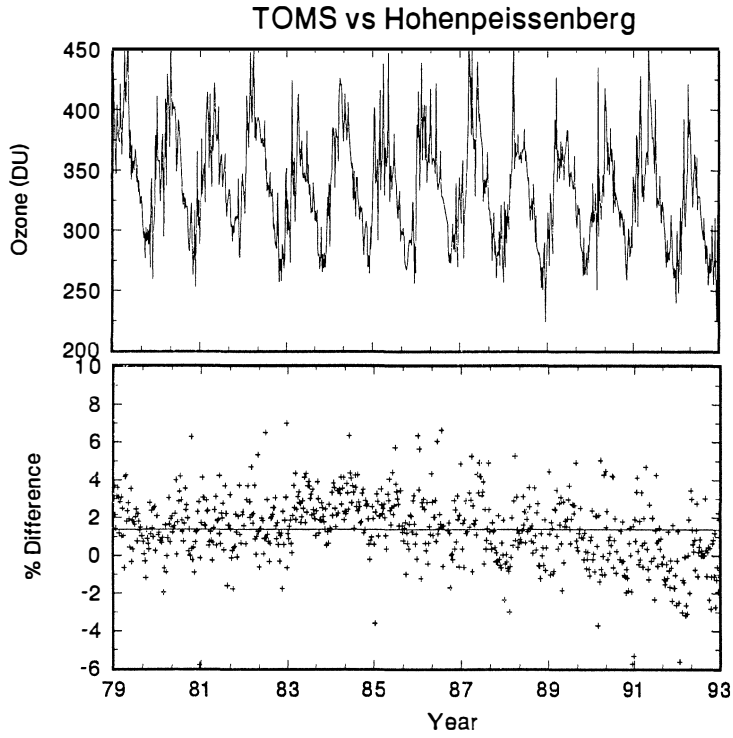

Figure 1-1. Time series of weekly average TOMS ozone overpasses at Hohenpeissenberg (top) and of the percent difference between TOMS and Hohenpeissenberg total ozone amounts (bottom). (The Hohenpeissenberg data were taken from the World Ozone Data Center in December 1993; some minor revisions have since been made.)

1.2.1.3 Data Quality Evaluation

The large natural variations in ozone complicate the evaluation of the quality of total ozone measurements. The comparison of simultaneous measurements of the same quantity by independent instruments is an effective means of checking the quality of the individual instruments. For the early Dobson record there are no independent, simultaneous measurements of total ozone except during rare intercomparisons. (An exception occurred at Arosa, where two instruments have been operated simultaneously since 1968). The quality of the early record thus depends on how well the individual instruments and their calibrations were maintained. Evaluations of the early Dobson records are based on comparisons with data from other stations in the same synoptic region, with meteorological data such as the 100 hPa temperature series, and critical examination of available log books. Such methods were discussed at length in the IOTP (WMO, 1990a) and have been described further in WMO Report No. 29 (1992b). Details of the calibration histories at individual stations will be published in WMO Report No. 35 (1994b).

Since the launch of TOMS in 1978, a total ozone measurement has been made almost daily from space within 1° of every Dobson station. Figure 1-1 shows an example of a TOMS-Dobson comparison for Hohenpeissenberg, Germany. Similar comparisons have been made for each of 142 ground-based stations (Dobson, Brewer, and M-124) with relatively complete records over the life of TOMS (Ozone Data for the World, 1993). A single such comparison shows the relative differences between the two measurement systems; examination of many such plots can reveal the cause for differences between the systems. Changes relative to TOMS that occur at one station but not at other nearby stations can be presumed to be caused by that one station, but a change that is seen at most stations can be presumed to be caused by TOMS. Two simple indicators of data

quality that can be derived from these plots are the average bias and drift relative to TOMS. Figure 1-2 shows the first-year bias and trend relative to TOMS of 18 Dobson stations, including I83 in its measurements at Mauna Loa each summer. The average offset of TOMS relative to Dobson of 3-4% is almost certainly due to small prelaunch calibration errors in TOMS. The scatter in this diagram is noticeably less now that revised total ozone records are used, indicating an improvement in the quality of these measurements. The average drift of TOMS relative to the Dobson network of about -2% per decade is discussed below.

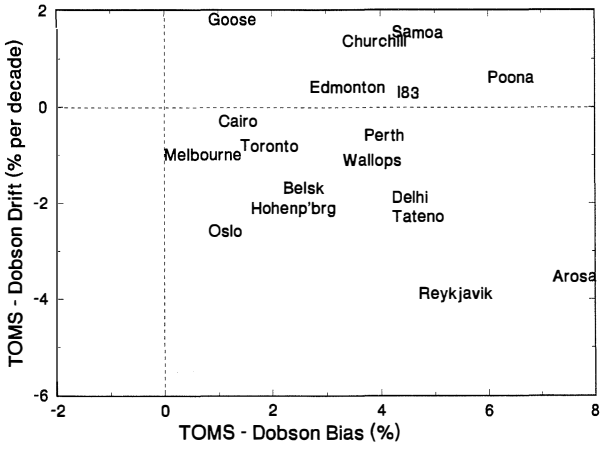

Figure 1-2. The average bias relative to TOMS in the first year (usually 1979) and the drift relative to TOMS over 14 years for a sample of 18 Dobson stations. The Dobson station data were taken from the World Ozone Data Center in December 1993. I83 at Mauna Loa and the regular Mauna Loa record are shown separately.

Despite the variability of individual Dobson stations, random errors should largely cancel in a network of Dobson stations, so that conclusions can be made about the performance of TOMS. Figure 1-3 shows comparisons of TOMS with ground-based measurements, including I83 both at Mauna Loa and at Boulder, a network of 30 Northern Hemisphere (25-60°N) Dobson stations that have complete data records through May 6, 1993, and summer-only averages for the same stations. TOMS is stable relative to I83 over its life. The error bars shown for the I83 comparisons are statistical uncertainties (95% confidence limits) for each summer's

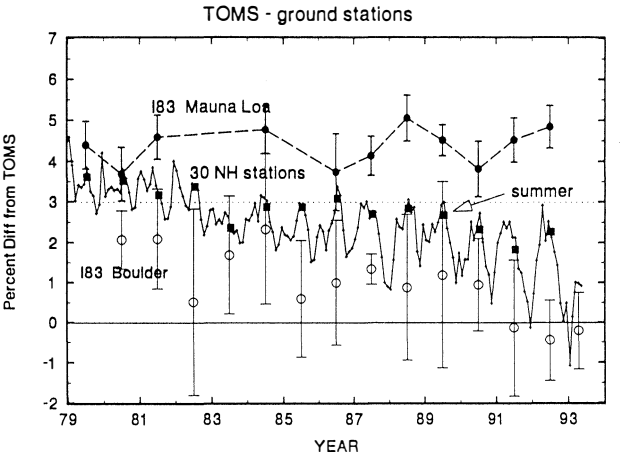

Figure 1-3. Percent difference between TOMS and World Standard Dobson #83, at both Mauna Loa (solid circles) and at Boulder (empty circles); monthly average differences for an average of 30 Northern Hemisphere Dobson stations; and summer only (JJA) differences for the same stations (squares). The uncertainties shown are 95% confidence limits for the mean value.

set of match-ups; the ±0.5% or so year-to-year variation represents the limit of accuracy for a single site comparison, since many errors are systematic and not random as the statistical error calculation assumes. A preliminary comparison of I83 observations made in Boulder, where fewer measurements were made with I83, shows a drift relative to TOMS that is very similar to that seen in the 30-stations average, which implies a TOMS latitude (or zenith angle) dependent drift. The comparison with the ensemble of 30 Northern Hemisphere Dobson stations was made using monthly averages. There is a seasonal cycle in the TOMS-Dobson difference of about 1% amplitude in 1985 and increasing thereafter.

An initial decline of TOMS ozone relative to Dobson (or increase in Dobson ozone relative to TOMS) between 1979 and 1984 is followed by a period of apparent lesser drift between 1984 and 1990 and, after 1990, a significant decline of about 2½%. Evidence of this decline beginning in about 1989 can also be seen in Figure 1-1, the comparison with Hohenpeissenberg. The initial decline of TOMS relative to Dobson could be caused by an error in TOMS not resolved by the internal calibration method or, possibly, it could be partly due to a change in the average calibration of the Dobson network in the

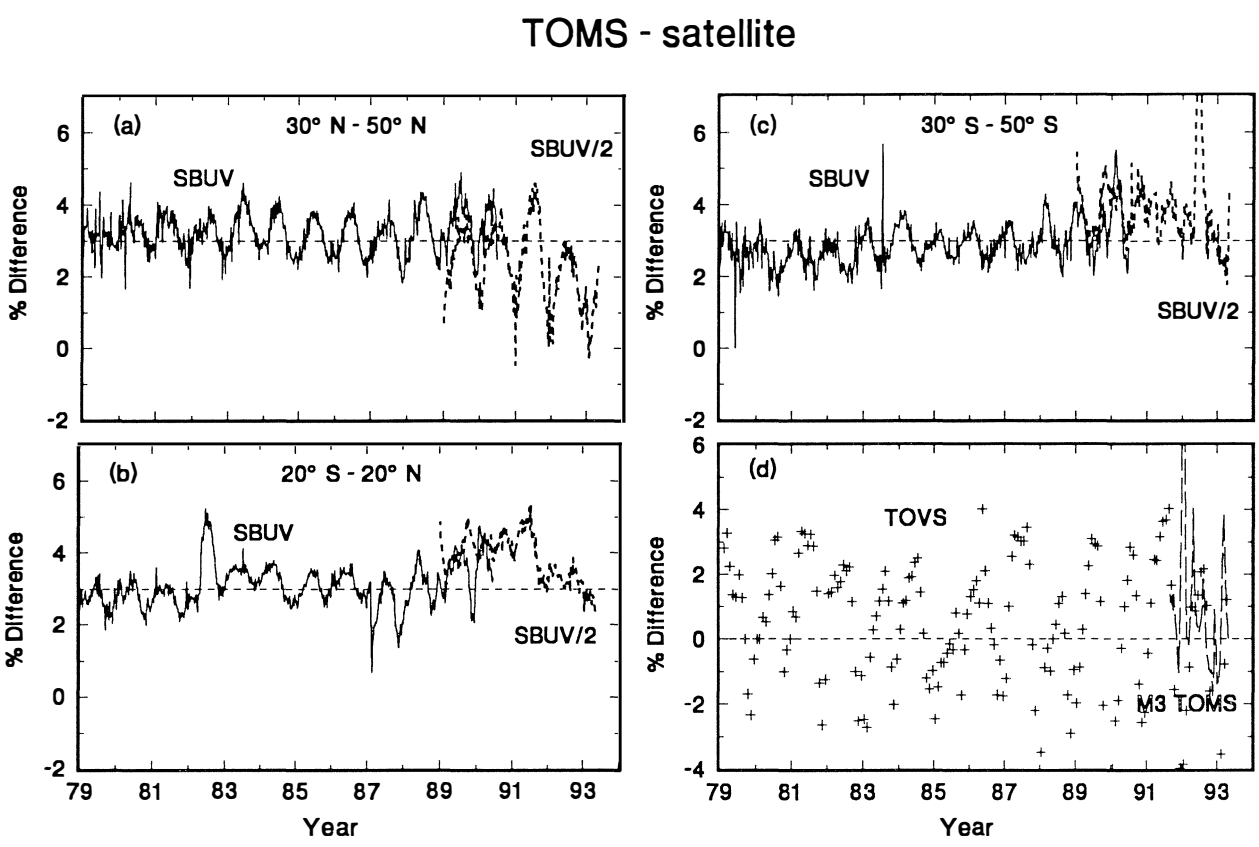

Figure 1-4. Weekly average differences between TOMS and SBUV, NOAA-11 SBUV/2, and Meteor 3 TOMS, and monthly average differences between TOMS and TOVS.

early 1980s before the strong program of intercomparison was extended. Figure 1-3 shows that such a decline is common to the Dobson records for most stations. Possible solar zenith angle dependent errors (in either Dobson or TOMS) can be minimized by comparing summer average values (where summer is defined as June-July-August). There is a similar time dependence, though of lesser magnitude (1-1.5%). Most of the seasonal cycle must then be due to TOMS. The decline of TOMS relative to I83 at Boulder, coupled with the stability relative to I83 at Mauna Loa, indicates a TOMS error that depends on the signal level, because UV signal levels are generally lower at Boulder (more ozone) than at Hilo. It is most likely that the TOMS photomultiplier has developed a small nonlinearity in its response that has increased with time. If true, the equatorial and summer midlatitude trends from TOMS should be accurate, but the high and winter midlatitude trends could be too large by 1-2% per decade.

Comparisons with TOMS have been done with an average of 9 Brewer stations (not shown). The data record is simply not long enough for definitive comparisons, but the seasonal dependence is larger, probably because the Brewers tend to be at high latitude sites. There is a decline between 1990 and 1992 that is consistent with the Dobson results.

Figure 1-4 is a comparison of Nimbus 7 TOMS with other satellite instruments: Nimbus-7 SBUV, NOAA-11 SBUV/2, TOVS, and Meteor 3 TOMS. Comparisons have been done of weekly zonal mean ozone, except for TOVS, where monthly means are used. The comparisons for the 30°-50°N, 30°-50°S, and 20°S-20°N zones are shown. Although 3% higher than SBUV, TOMS is quite stable relative to SBUV, not surprising since both were recalibrated using similar techniques and the two instruments use the same diffuser plate, albeit with different viewing geometries. There is a seasonal variation of about 1% magnitude that again is

likely caused by nonlinearity in the TOMS photomultiplier. There is no evidence for nonlinearity in the SBUV photomultiplier. The NOAA-11 SBUV/2 calibration is completely independent and is maintained through use of on-board calibration lamps. There is a decline of TOMS relative to SBUV/2 of 1% or so between 1989 and 1993. A comparison of SBUV/2 with an ensemble of ground-based stations between 20° and 60°N indicates that there has been little drift and that there is an apparent seasonal cycle of about 1-2% (minimum to maximum).

Finally, comparisons with monthly average TOVS zonal means for 30°-50°N are shown (Figure 1-4). The TOVS data show significant variance, presumably resulting from the sensitivity to stratospheric temperatures, and cannot currently be used for trend analysis.

1.2.2 Trends in Total Ozone

Trends in total ozone were reported in the last assessment (WMO, 1992a; see also Stolarski *et al.*, 1992), using TOMS satellite data from November 1978 through March 1991, and ground-based data through March 1991 where available. A number of recent studies have examined the available records, either on large scales (Krzyścin, 1992, 1994a; Reinsel *et al.*, 1994a) or at individual stations (Degórska *et al.*, 1992; Henriksen *et al.*, 1992, 1993; Kundu and Jain, 1993; Lehmann, 1994). In addition, a number of studies investigated the effects of interannual variability, and its various causes, on total ozone trends (Hood and McCormack, 1992; Shiotani, 1992; Marko and Fissel, 1993; Krzyścin, 1994b, c; Randel and Cobb, 1994; Zerefos *et al.*, 1992, 1994). In general, the conclusions of these studies agree well with those presented in WMO (1992a) and here. One exception is the analysis by Henriksen *et al.* (1992, 1993) of the total ozone record from Tromsø (70°N). Measurements have been made there using a Dobson spectrophotometer that show no long-term change from 1939 to 1989. Two difficulties arise in the interpretation of this record. First, there is a gap between 1969 and 1984 during which the instrument was overhauled. Unfortunately the amount of adjustment caused by this overhaul cannot be given (Henriksen *et al.*, 1992). Second, the natural variability of ozone is such that there are geographic differences in the trends (WMO, 1992a), so that one would expect the trends measured at some individual stations to be zero.

For this assessment, trends have been updated through the most recent available data. The trend update is complicated by the failure of the Nimbus 7 TOMS instrument on May 6, 1993, and concerns about the correction of its calibration after 1990 (see Section 1.2.1.3). However, SBUV data have been re-evaluated since the 1991 assessment, and are now suitable for trend analysis when combined with the SBUV/2 data from the NOAA-11 satellite. In the following section, trend analyses of SBUV data extended with SBUV/2 after 1988, abbreviated SBUV(/2), are updated through May 1994.

Trends from the Dobson network are updated through February 1994 at the majority of stations, and several new stations have been added. In addition, since the 1991 assessment, a number of Dobson stations have revised data for part or all of their historical records based on detailed re-evaluations. These data have been used if submitted to the World Ozone Data Center or directly to the chapter authors. In addition, at some stations, revisions were made by R. Bojkov (private communication) from the WMO intercomparison program results or from information in the station log books (see Section 1.2.1.1). Furthermore, data from 45 filter ozonometer stations in the former USSR have been thoroughly assessed and revised by Bojkov *et al.* (1994). Regional average data for the four regions discussed in that paper have been obtained from the authors and trends calculated using the same statistical fit as for the Dobson stations; the trends calculated for this report are close to those tabulated by the authors.

As discussed in detail in Section 1.4, ozone levels declined a few months after the eruption of Mt. Pinatubo in June 1991, and at northern midlatitudes they remained abnormally low through the fall of 1993 (Gleason *et al.*, 1993; Herman and Larko, 1994; Bojkov *et al.*, 1993; Kerr *et al.*, 1993; Komhyr *et al.*, 1994a). Whatever the cause of these low values, the calculation of trends with abnormally low data at the end of the time period may lead to substantially more negative values for the calculated trend. This presents difficulties in interpretation of the results, since the use of the word "trend" implies a generally consistent, continuing change over a given period. By the inclusion of very recent data in late 1993 and the first half of 1994, this effect is lessened, except in the Jun-Jul-Aug season where the very low 1993 data are at the end of the series. Section 1.2.2.3 compares SBUV(/2) trends through May 1991 versus trends

through May 1994 as an analysis of the effect of including this period of anomalous ozone.

1.2.2.1 Statistical Models for Trends

As discussed in previous reports (WMO 1990a; WMO 1990b; WMO 1992a), proper trend analysis of ozone series uses a statistical regression model that fits terms for seasonal variation in mean ozone, seasonal variation in ozone trends, and the effects of other identifiable variables such as the 11-year solar cycle, quasi-biennial oscillation (QBO), and atmospheric nuclear tests (if data from the early 1960s are used). The residuals from the model are autocorrelated, and this autocorrelation should be fitted as part of the statistical estimation procedure to ensure reliable standard errors for the calculated trends (see, for example, Reinsel *et al.*, 1987; 1994a; Bojkov *et al.*, 1990). Also, proper error analysis requires a weighted regression technique, since ozone levels are much more variable in winter months than in summer. For the long-term Dobson analyses, the trend fitted for each month was a "hockey stick," with a level baseline prior to December 1969 and a linear trend after 1970. For series beginning after 1970, including all satellite data, the trend is a simple linear monthly trend. As in previous reports, the other explanatory variables used are: 10.7cm radio flux for the effect of the solar cycle; and 50 mbar winds in the tropics (average of Ascension, Balboa, and Singapore) for the QBO with an appropriate latitude-dependent lag. For a given monthly ozone series, individual monthly means in Dobson units (DU) are calculated from the model for the beginning of the time period, and monthly trends are calculated in DU/year. For compactness in presentation, these are averaged over four seasons, DJF, MAM, JJA, SON (December-January-February, etc.), together with a summary year-round trend. The trends are expressed in % per decade, with the average DU/decade trends given as a percent of the seasonal mean ozone in DU. Note that the seasonal definitions are slightly different from those used in previous assessments (DJFM, MJJA, SON, with April not reported).

Mean level shifts ("intervention terms") can be used in the statistical model to account for instrument calibrations or changes, and other sudden shifts in observed mean ozone, for which the calibration information necessary for direct adjustment is not available. Reinsel *et al.* (1994a) describe the methodology and give the dates at each station where intervention terms are necessary if the publicly available data from the World Ozone Data Center are used. In most cases in this report, direct adjustment using known calibration information was used, except in the sensitivity analysis presented in Section 1.2.2. An additional intervention term not used in Reinsel *et al.* was calculated in the analysis here for Mauna Loa at June 1976 to adjust for an unexplained but clear drop in mean ozone of several percent.

It is necessary to ensure correct intercalibration between the SBUV and SBUV/2 satellite records, and the following procedure was used to estimate a possible shift between records for each latitude zone. The standard statistical model was fit to the combined records beginning 1/79, and ending in 5/91 to avoid the anomalous ozone period after that time. There is an overlap of eighteen months in the SBUV and SBUV/2 satellite records (1/89 to 6/90), and each series was given one-half weight in the overlap period. Intervention terms were fit to estimate any difference in calibration between the satellites, and these were typically found to be less than 1% (in two zones, $1^1/_2$%). These same shifts were used to adjust SBUV/2 data to the level of SBUV for analyses through 1994, the fit then being done giving each series one-half weight in the overlap period, but without further intervention terms.

1.2.2.2 Total Ozone Trends Updated through 1994

This section presents a comparison of trends from ground-based data through February 1994 and SBUV(/2) satellite data through May 1994. The analysis of ground-based data gives both long-term (using data from 1/64) and short-term (1/79 to 2/94) trends for direct comparison to SBUV(/2) results. As noted in the 1991 assessment, the short-term, more recent trends are more negative than the long-term trends; an analysis of this apparent trend acceleration is presented in Section 1.2.2.4.

The ground-based trend analysis uses a set of 43 Dobson stations, the majority of which are in Northern Hemisphere mid- to high latitudes. The station set is a subset (see Section 1.2.1.1) of the 56 stations used in Reinsel *et al.* (1994a), together with the addition of Lisbon, now with revised data. The trends at individual stations are tabulated only in one case (Table 1-1); otherwise the individual station trends have been averaged

Table 1-1. Set of 43 Dobson stations used for the trend analyses, with dates of usable data (although the earliest analysis in this report begins at 1/64). Stations are grouped by the latitude zones used in Figures 1-5 through 1-9. Seasonal trend estimates by station are shown for the period 1/79 through 2/94; these are plotted in Figure 1-5 (zonal averages in Figure 1-6). The columns labeled "2se" give 95% uncertainty limits (two standard errors). The "Src" column indicates the source of the data used here, with codes: WODC = data from World Ozone Data Center, Sta = data supplied by the station authorities, Rev = revised as discussed in Section 1.2.1.1.

				Dec-Feb		Mar-May		Jun-Aug		Sep-Nov		Year		
Station	Latitude	First	Last	est	2se	est	2se	est	2se	est	2se	est	2se	Src
St. Petersburg	60.0 N	68-08	94-02	-7.4	5.5	-7.4	4.2	-4.7	2.7	-3.8	3.1	-6.0	2.3	Sta
Churchill	58.8 N	65-01	93-10	-5.7	4.2	-6.9	3.4	-4.5	2.3	-2.4	3.2	-5.0	1.8	Sta
Edmonton	53.6 N	58-03	94-02	-5.6	4.7	-7.6	3.3	-5.5	2.2	-3.4	3.2	-5.6	1.9	Sta
Goose	53.3 N	62-01	94-02	-2.8	5.4	-5.7	4.4	-7.6	3.0	-3.4	2.8	-4.9	2.4	Sta
Belsk	51.8 N	63-04	93-12	-9.1	5.4	-6.7	4.0	-4.0	2.4	-1.4	3.2	-5.5	2.3	Rev
Uccle	50.8 N	71-07	94-02	-5.9	5.4	-7.4	3.8	-1.3	2.4	-0.3	3.4	-4.0	2.2	WODC
Hradec Kralove	50.2 N	62-03	94-02	-7.3	5.3	-6.4	3.8	-4.4	2.4	-0.8	2.9	-4.9	2.2	WODC
Hohenpeissenberg	47.8 N	68-05	94-02	-8.4	4.7	-6.1	4.6	-3.6	2.6	-2.0	3.1	-5.2	2.4	Sta
Caribou	46.9 N	62-09	94-02	-5.3	4.4	-6.5	2.7	-2.6	2.2	-3.1	3.3	-4.5	1.8	Sta
Arosa	46.8 N	57-07	94-02	-5.9	4.7	-4.5	3.8	-2.2	2.0	-1.1	2.6	-3.6	2.1	Sta
Bismarck	46.8 N	62-12	94-02	-1.9	3.5	-6.8	2.9	-2.1	2.3	-1.8	2.1	-3.3	1.5	Sta
Sestola	44.2 N	76-11	94-02	-5.4	4.7	-6.8	4.0	-4.3	2.2	-0.9	3.0	-4.6	2.0	Rev
Toronto	43.8 N	60-01	94-02	-4.5	3.7	-5.9	2.8	-2.7	1.8	-0.5	3.1	-3.6	1.6	Sta
Sapporo	43.1 N	58-02	94-02	-6.8	3.7	-5.6	3.1	-4.0	2.6	-2.2	2.6	-4.8	1.8	WODC
Vigna Di Valle	42.1 N	57-07	94-02	-8.0	4.3	-5.5	5.1	-3.8	2.4	-4.8	2.7	-5.6	2.4	Rev
Boulder	40.0 N	76-09	94-02	-2.5	3.2	-7.5	3.2	-1.7	1.6	-1.7	2.6	-3.6	1.6	Sta
Shiangher	39.8 N	79-01	93-08	-5.1	3.2	-3.8	3.6	-0.4	2.7	-1.0	2.8	-2.7	1.8	WODC
Lisbon	38.8 N	67-08	94-02	-1.3	3.4	-6.7	2.8	-4.1	1.7	-1.5	2.7	-3.6	1.4	Sta
Wallops Island	37.9 N	57-07	94-02	-6.5	3.5	-5.4	3.5	-4.4	2.2	-3.0	3.3	-4.9	1.9	Sta
Nashville	36.3 N	62-08	94-02	-5.0	3.3	-4.4	3.9	-2.9	2.6	-1.3	3.1	-3.5	1.9	Sta
Tateno	36.1 N	57-07	94-02	-3.6	3.7	-1.2	3.3	-0.8	2.2	0.5	2.3	-1.3	1.7	Sta
Kagoshima	31.6 N	63-02	94-02	-2.6	3.1	-1.8	3.1	-0.6	1.9	0.3	2.0	-1.2	1.6	Sta
Quetta	30.2 N	69-08	93-02	-5.3	4.3	-1.6	4.2	0.7	2.7	-0.2	2.5	-1.6	2.5	Rev
Cairo	30.1 N	74-11	94-02	-1.7	4.0	-3.1	3.0	-0.2	1.6	-0.9	1.6	-1.5	1.7	Sta
New Delhi	28.7 N	75-01	94-02	-2.2	3.3	-2.0	3.2	0.3	2.9	-0.4	1.5	-1.1	1.9	WODC
Naha	26.2 N	74-04	94-02	-2.3	3.0	-2.0	2.9	-0.3	1.7	-1.0	2.0	-1.4	1.5	WODC
Varanasi	25.3 N	75-01	94-02	-2.2	2.4	-1.4	2.5	-0.2	2.5	-1.2	1.9	-1.2	1.5	Rev
Kunming	25.0 N	80-01	94-02	-0.5	2.6	-1.8	3.5	0.2	1.8	-1.2	1.7	-0.8	1.6	Rev
Ahmedabad	23.0 N	59-01	92-12	-1.1	2.7	-1.6	3.4	-4.3	1.7	1.2	2.5	-1.5	1.7	Rev
Mauna Loa	19.5 N	64-01	94-02	-0.6	3.4	0.2	3.1	-0.1	2.3	-0.4	1.9	-0.2	1.8	Sta
Kodaikanal	10.2 N	76-08	94-02	1.1	2.6	0.2	2.6	-0.8	2.8	-1.0	2.9	-0.2	2.1	WODC
Singapore	1.3 N	79-02	93-10	1.0	3.1	-0.4	4.0	-1.1	3.0	-1.1	3.3	-0.4	2.9	Rev
Mahe	4.7 S	75-11	93-10	-0.7	1.8	-1.0	2.4	-2.0	2.5	-1.7	2.3	-1.4	1.6	Rev
Natal	5.8 S	78-12	94-02	-0.3	2.5	1.6	2.0	-1.6	2.4	-1.1	2.4	-0.4	1.6	Rev
Huancayo	12.1 S	64-02	92-12	-0.7	1.7	-1.4	2.0	-3.4	2.8	-0.5	2.1	-1.5	1.5	Rev
Samoa	14.3 S	75-12	94-02	-1.6	1.9	-2.5	1.8	-1.3	3.1	-1.9	2.5	-1.8	1.7	Sta
Brisbane	27.4 S	57-07	93-07	-2.2	1.8	-2.1	1.7	-1.8	3.6	-1.9	2.4	-2.0	1.5	Rev
Perth	31.9 S	69-03	94-02	-0.4	1.4	-1.7	2.0	-1.4	3.4	-0.9	2.0	-1.1	1.3	Rev
Buenos Aires	34.6 S	65-10	94-02	-2.1	1.5	-1.4	2.4	-4.2	3.3	-2.0	3.4	-2.5	1.6	Sta
Aspendale	38.0 S	57-07	93-07	-2.9	1.6	-3.5	1.6	-3.2	2.8	-2.1	2.4	-2.9	1.2	Rev
Hobart	42.8 S	67-07	92-04	-4.4	2.1	-5.2	2.7	-5.2	3.4	-2.7	2.7	-4.3	1.6	Rev
Invercargill	46.4 S	70-07	94-02	-5.2	1.6	-2.0	2.1	-1.2	2.6	-3.2	2.6	-2.9	1.2	Rev
MacQuarie Island	54.5 S	63-03	93-06	-6.8	2.6	-3.4	3.0	-6.5	4.8	-6.0	3.2	-5.7	1.9	Rev

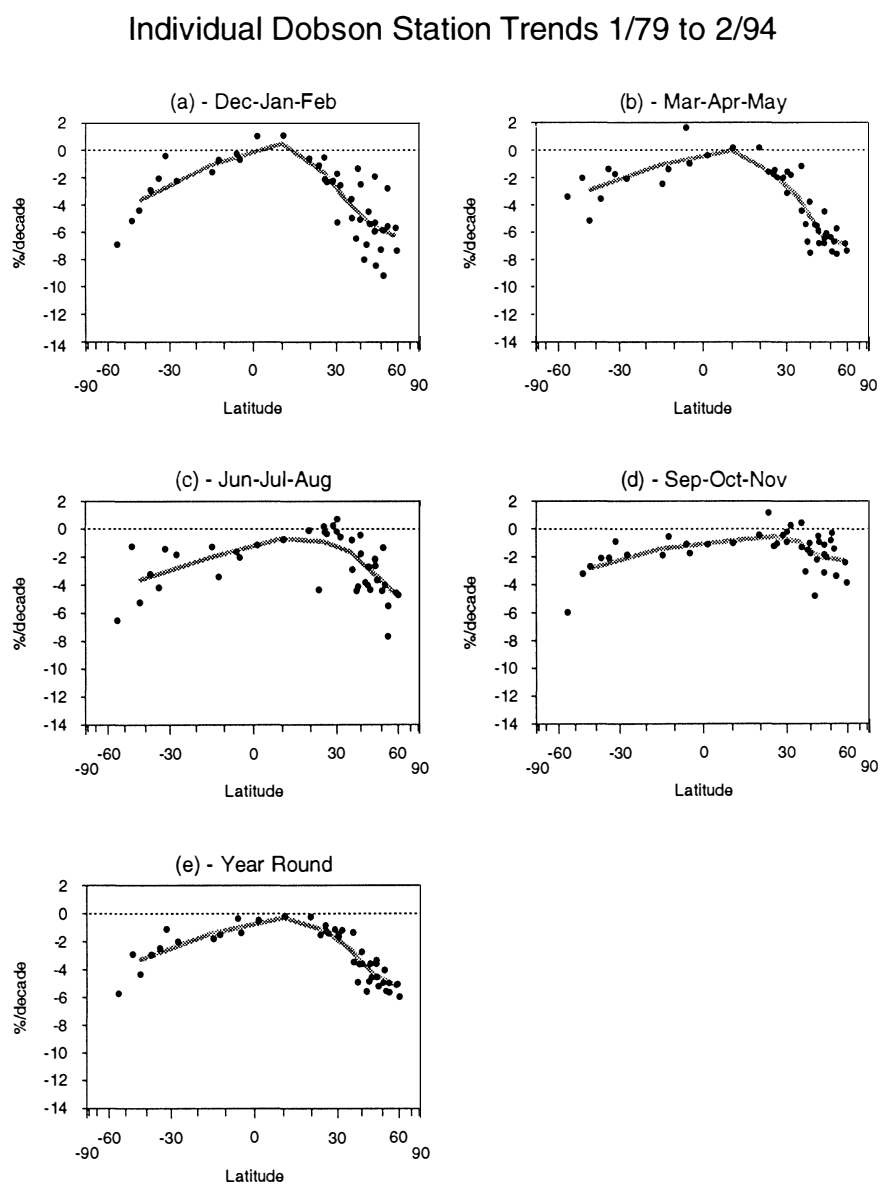

Figure 1-5. Individual Dobson station seasonal trends in total ozone in %/decade against latitude, over the period 1/79 through 2/94 (where data are available). The gray curves are the averages of the individual stations' trends in the following latitudinal zones: 55-30°S, 30°S-0, 0-20°N, 20-30°N, 30-40°N, 40-50°N, and 50-60°N. These averages (plus standard errors) are tabulated in Table 1-3.

within the following latitudinal zones: 55°S-30°S, 30°S-0, 0-20°N, 20-30°N, 30°N-40°N, 40°N-50°N, and 50°N-65°N. Figure 1-5 shows the individual station trends together with the zonal averages for the period 1/79 through 2/94. Although there is substantial scatter among individual stations, the latitudinal pattern is clearly represented by the zonal averages, which will be used in the following analyses for comparison to satellite trends. Seasonal trends from the reassessed filter ozonometer in four large regions of the former USSR are plotted as separate points in Figure 1-6; they are consistent with and support the Dobson data analysis.

SBUV(/2) trends through May 1994 are given by season and latitudinal zone in Table 1-2. Ground-based

Table 1-2. SBUV(/2) trends in %/decade by season and latitudinal zone over the period 1/79 to 5/94, with 95% uncertainty limits (two standard errors, labeled 2se).

Zone	Dec-Feb	2se	Mar-May	2se	Jun-Aug	2se	Sep-Nov	2se	Year	2se
65N	-5.6	4.2	-6.3	2.9	-3.5	1.4	-4.3	1.6	-5.0	2.0
55N	-6.0	3.4	-6.1	2.6	-3.0	1.6	-3.7	1.5	-4.8	1.9
45N	-6.4	2.9	-5.7	2.3	-2.8	1.5	-3.1	1.5	-4.6	1.8
35N	-4.9	2.4	-4.5	2.5	-3.1	1.5	-2.9	1.5	-3.9	1.8
25N	-3.2	2.0	-2.7	2.5	-2.7	1.6	-3.0	1.3	-2.9	1.6
15N	-2.0	1.6	-1.8	1.8	-2.0	1.9	-2.6	1.4	-2.1	1.4
5N	-1.3	1.8	-1.7	2.2	-1.8	1.5	-1.6	1.8	-1.6	1.6
5S	-1.5	1.3	-1.8	1.7	-2.5	1.3	-2.1	1.5	-2.0	1.2
15S	-0.7	1.1	-0.3	1.1	-1.5	1.8	-1.0	1.5	-0.9	1.1
25S	-3.1	0.9	-2.7	1.3	-3.6	2.6	-2.7	1.8	-3.0	1.4
35S	-4.4	1.0	-5.3	1.8	-6.5	2.6	-3.9	2.0	-5.0	1.5
45S	-4.4	1.4	-5.0	1.7	-6.6	2.5	-3.5	2.2	-4.9	1.5
55S	-4.6	1.6	-6.3	1.9	-10.7	3.0	-6.3	3.3	-7.0	2.1
65S	-5.8	1.4	-7.6	2.1	-14.3	3.8	-13.6	5.2	-10.4	2.4

Table 1-3. Short-term Dobson trends in %/decade using data from 1/79 to 2/94. Tabled numbers are averages of individual trends within latitude zones, with 95% uncertainty limits (two standard errors, labeled 2se).

Zone	N	Dec-Feb	2se	Mar-May	2se	Jun-Aug	2se	Sep-Nov	2se	Year	2se
50-65 N	7	-6.2	1.5	-6.9	0.5	-4.6	1.4	-2.2	1.1	-5.2	0.5
40-50 N	9	-5.4	1.5	-6.1	0.6	-3.0	0.6	-2.0	0.9	-4.3	0.5
30-40 N	8	-3.9	1.3	-3.5	1.4	-1.6	1.4	-0.9	0.8	-2.5	1.0
20-30 N	5	-1.7	0.7	-1.8	0.2	-0.9	1.7	-0.5	0.9	-1.2	0.2
0-20 N	3	0.5	1.1	-0.0	0.4	-0.7	0.6	-0.8	0.4	-0.3	0.2
30- 0 S	5	-1.1	0.7	-1.1	1.4	-2.0	0.7	-1.4	0.5	-1.4	0.6
55-30 S	6	-3.6	1.9	-2.9	1.2	-3.6	1.7	-2.8	1.4	-3.2	1.3

Table 1-4. Long-term Dobson trends in %/decade using data from 1/64 to 2/94 (trends from 1/70). Tabled numbers are averages of individual trends within latitude zones, with 95% uncertainty limits (two standard errors, labeled 2se).

Zone	N	Dec-Feb	2se	Mar-May	2se	Jun-Aug	2se	Sep-Nov	2se	Year	2se
50-65 N	7	-4.0	1.0	-3.4	0.5	-1.4	0.4	-1.2	0.5	-2.6	0.4
40-50 N	9	-3.7	0.8	-3.6	0.9	-1.8	0.6	-1.3	0.4	-2.7	0.5
30-40 N	8	-2.4	1.0	-1.8	0.7	-0.6	0.5	-0.7	0.5	-1.4	0.6
20-30 N	5	-1.5	0.8	-1.1	0.5	0.0	0.3	-0.4	0.7	-0.7	0.4
0-20 N	3	0.4	0.8	-0.0	0.4	-0.8	0.7	-0.7	0.9	-0.3	0.3
30- 0 S	5	-1.2	0.7	-1.2	1.5	-1.7	0.3	-1.4	0.7	-1.4	0.7
55-30 S	6	-1.8	1.0	-1.9	0.8	-2.5	0.6	-1.6	0.8	-2.0	0.7

-7%/decade. In the Southern Hemisphere, extremely large ozone depletion is seen in the southern winter (Jun-Aug) and spring (Sep-Nov).

The agreement between SBUV(/2) satellite and Dobson ground-based trends is not as good as seen in the 1991 assessment between TOMS satellite and ground-based trends. In the 1991 assessment, TOMS trends averaged slightly more negative than the Dobson trends, but only by 1%/decade or less. As seen in Figure 1-6, the SBUV(/2) trends average 1 to 2%/decade more negative than the short-term Dobson trends in all seasons and at all latitudes except mid- to high northern latitudes. In the case of the mid- to high northern latitudes, the agreement is much better. In the equatorial regions, while the Dobson network shows essentially no trend in total ozone in concurrence with previous assessments, the SBUV(/2) analysis indicates a seasonally independent trend of about -2%/decade; these are just statistically significant in many cases, since two standard errors of the trend estimates are about 2%/decade in low latitudes. This is particularly so in the Jun-Jul-Aug period; however, due to the timing of this assessment, we cannot update trends in that period beyond the extremely low 1993 values discussed in Section 1.2.2.4.

In order to check the consistency of the SBUV(/2) trends versus both Dobson and TOMS, Figure 1-7 shows seasonal trends in total ozone using data through May 1991 for all three. The TOMS trends through May 1991 are similar to those reported in the 1991 assessment (only an additional two months of data are used), although the seasonal definitions were different in the 1991 assessment (Dec-Jan-Feb-Mar, May-Jun-Jul-Aug, Sep-Oct-Nov, with April not reported). The Dobson and TOMS curves in Figure 1-7 are close to those given in Reinsel *et al.* (1994a) for the period 11/78 through 12/91; slight differences in the recent Dobson results are primarily due to use of Dobson station revisions.

Over the same time period, SBUV(/2) trends tend to be consistently more negative than both TOMS and Dobson at low latitudes, say 30°S to 30°N. TOMS trends are also slightly more negative than Dobson trends on the average, as noted above and in the previous assessment. SBUV(/2) trends average close to -2%/decade in the tropics, even when data from the low 1992-1993 period are excluded.

Reinsel *et al.* (1994a) used a set of 56 Dobson station records, publicly available from the World Ozone Data Center, to analyze trends through 1991. Figure 1-8 shows the year-round trends calculated for this report as discussed above compared to the year-round trends from the 56 Reinsel *et al.* stations records, updated with publicly available data. The data used for the comparison analysis were obtained from the World Ozone Data Center, except that newly revised data for the U.S. stations and Arosa were used as obtained directly from the stations. The same statistical interventions as used in Reinsel *et al.* were also used in the comparison analysis, with an additional one at Mauna Loa as discussed above. The results from the larger Reinsel *et al.* set of stations, using in many cases data that have not yet been processed using current quality control procedures (WMO, 1992b), show much more variation in the trends; however the average across stations within each latitude zone is close to the analogous average for the 43-station analysis discussed here.

1.2.2.3 The Effect of the 1992-1994 Data

As discussed in the preamble to Section 1.2.2, it is desirable to update trend estimates through the most recently available data. However, interpretation of these trends that include the recent period must be made with caution, since global total ozone was low over the period late 1991 through late 1993.

Figure 1-9 shows the effect of using data over the period 1992-1994, compared to stopping the trend analyses at December 1991, for SBUV(/2) and Dobson data. The comparison is not made for TOMS, because of the concerns about the TOMS calibration in the last couple of years of the instrument's life, and because of difficulties in extending the TOMS data beyond May 1993.

The effect of excluding the 1992-1994 data from the trend calculations is less than one might expect, given the size of the 1992-1993 anomaly, although certainly on the average the updated trends are slightly more negative. The largest consistent effects are in the Jun-Jul-Aug period in the tropics (note the latest Jun-Jul-Aug data in this analysis are from 1993) seen in both SBUV and Dobson analyses; the effect is to make the trends about 1%/decade more negative. The Dobson data show about a 2%/decade effect in winter and spring in the mid- to high north latitudes, which is not so clear from SBUV except in the high northern latitudes. In other seasons/latitudes, the effects are typically less than about 1%/decade.

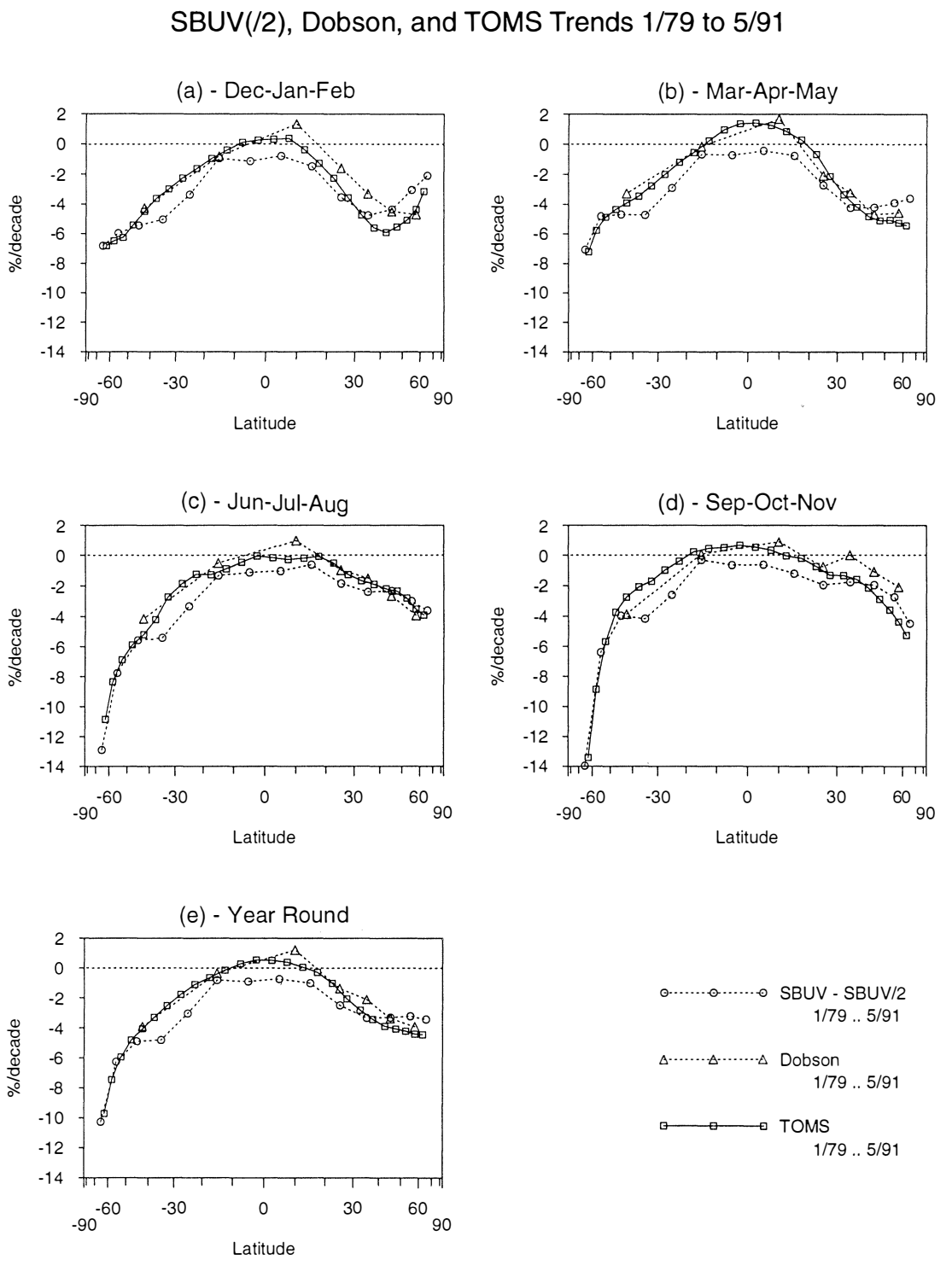

Figure 1-7. SBUV(/2), Dobson, and TOMS seasonal total ozone trends in percent per decade by latitude through 5/91. Open circles are SBUV(/2) trends over 1/79 to 5/91; open triangles are Dobson trends over 1/79 to 5/91; open squares are TOMS trends over 1/79 through 5/91. The Dobson trends are averages within latitudinal zones of individual trends at 59 Dobson stations.

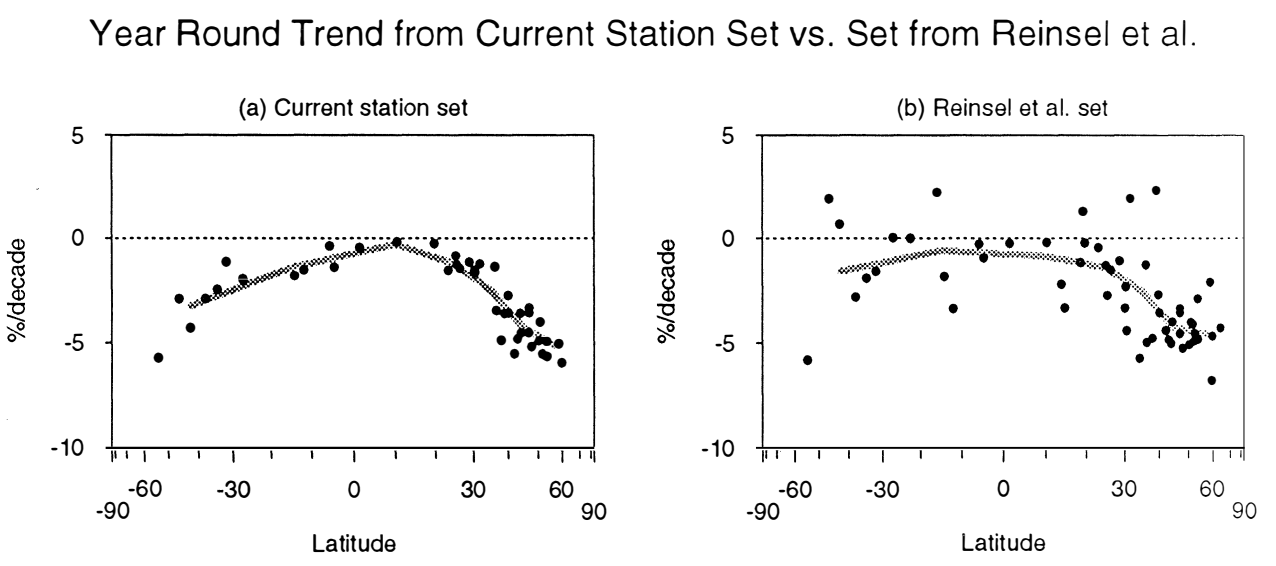

Figure 1-8. Comparison of year-round trends 1/79 through 2/94 from the 43-station set of revised data used in this report (plot (a)) with trends from the station set of Reinsel *et al.* (1994a) using data from the World Ozone Data Center together with updates for the U.S.A. stations and Arosa obtained from the stations (plot (b)). The gray curves are averages within latitudinal zones as in Figure 1-5.

1.2.2.4 Acceleration of Ozone Trends

It was commented upon in the 1991 assessment (WMO, 1992a) that trends in the 1979-1991 period from the Dobson network tended to be larger (more negative) than trends calculated over the longer period 1970-1991. This is also seen in Figure 1-6, comparing the short-term (1/79 to 2/94) trends with the long-term (1/70 to 2/94) trends. This phenomenon has led to speculation that ozone trends have accelerated in recent years compared to the trends in the 1970s.

To test this, a double trends model was used to analyze data from 34 Dobson stations whose records begin by January 1975, but utilizing data from January 1964 where available, as for the long-term trend analysis in Table 1-4. The time trend fitted was a "double jointed hockey stick," with a level base before 1970, a trend beginning in January 1970, and a possibly different trend from January 1981 through December 1991 (the date of the trend change was chosen for convenience to divide the 22-year period 1970-1991 into two equal 11-year segments). Interest focuses on the difference in the trends over 1981-1991 vs. 1970-1980. This model was fitted to the 34 Dobson stations, and the trend difference calculated at each station for each season. The year-round average differences are shown in Figure 1-10.

There is an indication of an acceleration in the annual trends in northern mid- to high latitudes and in all seasons except Sep-Oct-Nov (seasonal results not shown in plot). The largest number of Dobson stations are in mid- to high north latitudes where trends, especially in winter and spring, are large. Table 1-5 shows the mean trend difference for the 24 Dobson stations in this analysis north of 25° north latitude, together with the standard error of the mean. The largest trend acceleration appears in the spring, followed by the winter and summer seasons. The average trend differences are statistically significant in the spring, summer, and year-round average, and very nearly so in winter.

1.2.3 Discussion

As a result of efforts to reanalyze the historical ground-based data record and of a continuing program of instrument intercomparisons relative to the World Standard Instrument, the quality of the Dobson (and M-124) record has improved since the last report (WMO, 1992a). We can thus have greater confidence in the derived trends. There is still a great deal of station-

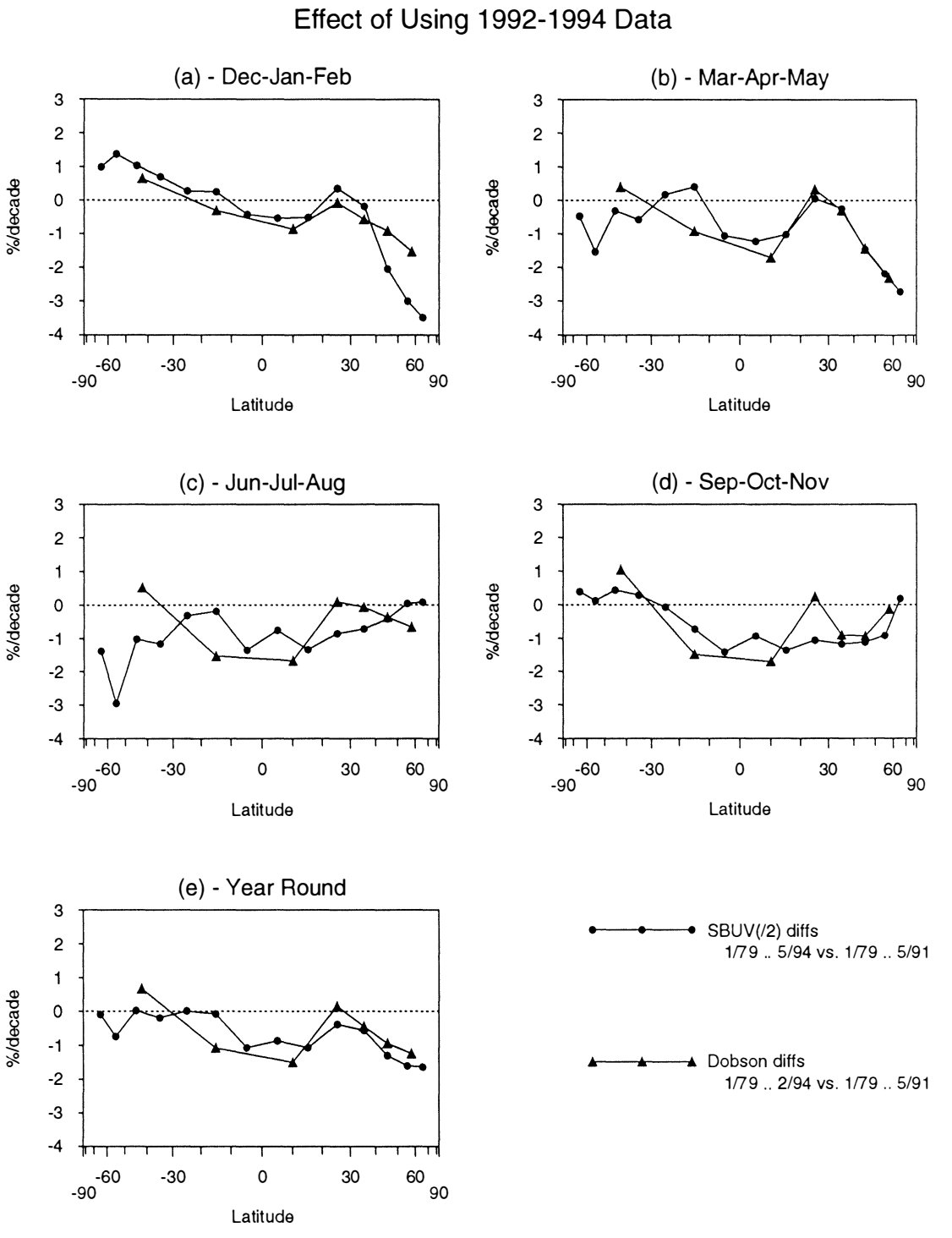

Figure 1-9. Effect on trends of using 1992-1994 data. Triangles denote the difference in the trends calculated from Dobson data (1/79 to 2/94 minus 1/79 to 5/91). Circles denote the difference in the trends (1/79 to 5/94 minus 1/79 to 5/91) calculated from SBUV(/2) data.

Table 1-5. Difference in trends 1981-1991 vs. 1970-1980 from the double trends model, averaged over 24 Dobson stations north of 25°N. The column labeled 2se represents 95% uncertainty limits (two standard errors) for the difference in trend.

Season	Average Trend Difference	2se
Dec-Jan-Feb	-2.0	1.5
Mar-Apr-May	-2.8	1.1
Jun-Jul-Aug	-1.9	1.5
Sep-Oct-Nov	-0.4	1.2
Year round	-1.8	0.7

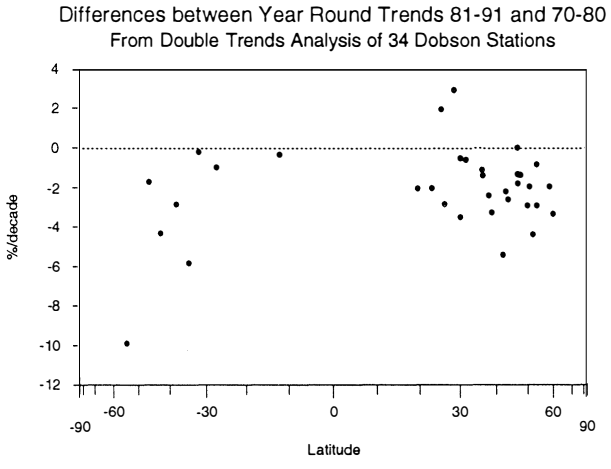

Figure 1-10. Differences between trends 1981-1991 and 1970-1980 at 34 Dobson stations from double trends analysis.

to-station variability as determined when TOMS is used as a transfer standard to look for short-term shifts. It is important that stations' records continue to be maintained and improved.

When the TOMS trends through May 1990 were evaluated (Stolarski *et al.*, 1991) the trend error was estimated to be 1.3% per decade (two sigma error). As a result of a recent evaluation it appears that the Nimbus 7 TOMS calibration has drifted by 1-2% since 1990. The changing seasonal cycle in the TOMS-Dobson and TOMS-SBUV differences appears to be caused by changing nonlinearity in the TOMS photomultiplier response. While the previous error estimate may be appropriate for equatorial and midlatitude summer data, the photomultiplier nonlinearity may be introducing as much as 2% per decade error into midlatitude winter trends.

The SBUV record has benefited greatly from the work done on the TOMS measurements (the same basic algorithm is used; the diffuser plate correction is the same). The drift in the calibration of total ozone by the SBUV instrument from January 1979 to June 1990 was 1% or less, and any seasonal differences relative to Dobson instruments in the Northern Hemisphere were less than 1%. The SBUV2 instrument has the on-board calibration lamps and has been compared with the Shuttle Solar Backscatter Ultraviolet (SSBUV) flights since 1989. There was good agreement during the 18 months that both SBUV and SBUV2 made measurements. The main problems with the combined SBUV/SBUV2 record are the possible aliasing of trends resulting from the changing orbit of the NOAA-11 satellite and the possibly linked seasonal difference of 1-2% (minimum to maximum) relative to the ground-based network in the Northern Hemisphere. The TOMS non-winter measurements agree well with those from SBUV and SBUV/2. Given these factors, and the extra year of data in the combined SBUV(/2) record, it is best at this time to focus on trends derived from the SBUV(/2) measurements.

The most obvious features of the total ozone trends have been commented upon in previous assessments. Statistically significant negative trends are seen at mid- and high latitudes in all seasons. The largest negative ozone trends at mid- and high latitudes in the northern Hemisphere are seen in winter (Dec-Feb) and spring (Mar-May); these trends are about -4 to -7%/decade. In the Southern Hemisphere, the annual variation in the trends at midlatitudes is smaller, though the average trend is similar to the Northern Hemisphere average.

The effect of including the 1992-1994 data in the trend calculations is less than one might expect, given the size of the 1992-1993 anomaly, although certainly on the average the updated trends are slightly more negative. The largest consistent effects are in the Jun-Jul-Aug period in the tropics (note the latest Jun-Jul-Aug data in this analysis are from 1993) seen in both SBUV and Dobson analyses; the effect is to make the trends about 1%/decade more negative. The Dobson data show about a 2%/decade effect in winter and spring in the mid- to high north latitudes, which is not so clear from SBUV except in the high north. In other seasons/latitudes, the effects are typically less than about 1%/decade.

Analysis of TOMS, SBUV(/2), Dobson, and ozonometer data through 5/91 reconfirms the results in the 1991 assessment (WMO, 1992), which were based on TOMS and Dobson analyses through 3/91. The SBUV(/2) trends tend to be slightly more negative than either TOMS or Dobson trends, particularly in the tropics, while as pointed out in the 1991 report, TOMS trends are also slightly more negative than Dobson. However, the differences between the instrument systems are within the 95% confidence limits.

SBUV(/2) trends in the tropics over the period 1/79 through 5/94 are estimated to be about -2%/decade in all seasons, with formal 95% confidence limits in the tropics of 1.5 to 2%/decade. This appears to be due to a combination of two effects: (1) SBUV/2 trends are about 1%/decade more negative than TOMS and Dobson in the tropics, raising suspicions of an instrumental drift; and (2) the inclusion of the low 1992-1994 data makes the trends an additional 1%/decade more negative in the tropics.

There was a statistically significant increase (about 2%/decade) at the Dobson stations north of 25°N in the average rate of ozone depletion in the period 1981-1991 compared to the period 1970-1980.

1.3 OZONE PROFILES

1.3.1 Ozone Profile Data Quality

Various techniques have been used to measure ozone profiles. However only a few of these have produced data sets that are long enough, and of sufficient quality, to be considered for trends. In this section we consider two ground-based methods that have been in use since the 1960s (Umkehr and ozonesondes) and two satellite instruments (SBUV and the Stratospheric Aerosol and Gas Experiment, SAGE).

1.3.1.1 Umkehr

The long-term records of Umkehr observations are made using Dobson spectrophotometers at high solar zenith angles using zenith sky observations (*e.g.,* Götz, 1931; Dobson, 1968). A new inversion algorithm has been developed (Mateer and DeLuisi, 1992), and all the Umkehr records submitted to the World Data Center have been recalculated. The new algorithm uses new temperature-dependent ozone absorption coefficients (Bass and Paur, 1985) and revised initial estimates of the ozone profiles. The correction for the presence of aerosols is still calculated after the ozone retrieval (DeLuisi *et al.*, 1989), and the aerosol corrections needed for the new and old retrievals are similar (Reinsel *et al.*, 1994b). Mateer and DeLuisi concluded that reliable ozone trends can only be found for Umkehr layers 4-8 (19-43 km). Lacoste *et al.* (1992) compared the lidar and Umkehr measurements made at Observatoire de Haute-Provence from 1985-1988. They found good agreement between these two measurements systems from layers 4-7 (the lidar was not sensitive below layer 4) and attributed the poor agreement in layer 8 to the low return signals in the lidar system from this high altitude at that time.

Some information is available below layer 4 because total ozone must be balanced within the complete profile. DeLuisi *et al.* (1994) have compared Umkehr observations (calculated using the old algorithms) with SBUV ozone profile data in the 30-50°N latitude band for 1979-1990 and showed that there is good agreement in layer 4 and above. The agreement in the SBUV and Umkehr profiles is not so good lower down, but useful trend information may be present, a situation that could improve when the new algorithm is used. For now, as in recent assessments, only the trends in layers 4 and above will be considered.

1.3.1.2 Ozonesondes

Ozonesondes are electrochemical cells sensitive to the presence of ozone that are carried on small balloons to altitudes above 30 km. Several versions have been used, and the important ones for ozone trend determination are the Brewer-Mast (BM), the electrochemical

concentration cell (ECC), and the OSE (used principally in Eastern Europe). The principle on which they work is that the current produced in the cell from the reaction of ozone with potassium iodide solution is proportional to the amount of ozone passing through the cell. This is not true if other sources of current exist. Two such cases are discussed here: the zero-ozone current output possibly caused by chemicals other than O_3; and the interfering gas, SO_2. Changes in operational procedures can also strongly influence the ozonesonde data quality. Two ways by which the quality of the ozonesondes can be assessed are also discussed: intercomparisons and correction factors.

The ozonesonde network is geographically uneven, with the large majority of stations in Europe and North America. The highest density of stations is in Europe, where they are all located between 44 and 52°N and between 5 and 21°E. The long-term records in Europe all involve BM sondes or OSE sondes. With the exception of Wallops Island, the North American stations do not have continuous records longer than 15 years, as Brewer Mast sondes were used at Canadian stations until about 1980, when there was a switch to ECC sondes. The frequency of launches at the Japanese stations has been quite low at times, which has the effect of increasing the uncertainties associated with the long-term trends. However, the most obvious shortage of data is in the Southern Hemisphere, where the only long-term, non-Antarctic records are at Natal (6°S) and Melbourne (38°S: Aspendale/Laverton). Unfortunately, the launch frequency at these sites has been irregular as well. Last, it should be noted that many stations have ongoing programs to assess and improve the quality of the measurements.

1.3.1.2a Background Current

The presence of a background (zero ozone) current has long been recognized in the ECC sonde and the standard operating procedures include a method for correction (Komhyr, 1969). For most ECC sondes that have been flown, a correction has been applied that assumes that the background current decreases with altitude (Komhyr and Harris, 1971). Measurements are sensitive to errors in the correction for the background current in regions where the ozone concentration is low, *i.e.,* at or near the tropopause. Such errors have the potential to be large as the background current can become similar in magnitude to the ozone-generated current, for example, in the tropical upper troposphere. In the stratosphere, where ozone concentrations are much higher, the errors associated with background current corrections are small.

The response time of the ECC sonde to ozone is about 20 seconds. Laboratory studies indicate that there is an additional component of the background current with a response time of 20-30 minutes (Hofmann, Smit, private communications). For this component there is a memory effect as the balloon rises and the background current would vary through the flight. Earlier studies (Thornton and Niazy, 1983; Barnes *et al.*, 1985) concluded that the background current remained constant in the troposphere. No correction is made for the zero current in BM sondes, although some stations measure it before launch. For BM sondes, the procedure is to reduce this zero current to a very low value by adjusting the sonde output, possibly at the expense of the sonde sensitivity. Any changes in the magnitude of the background current over the last 20-30 years will most strongly affect the trends calculated for the free troposphere. More work is needed to assess the size and impact of any changes in the background current in the different ozonesondes.

1.3.1.2b SO_2

The presence of SO_2 lowers the ozonesonde readings (one SO_2 molecule roughly offsets one O_3 molecule), an effect that can linger in the BM sonde because the SO_2 can accumulate in the bubbler (Schenkel and Broder, 1982). The SO_2 contamination is a problem at Uccle, where the measured SO_2 concentrations were high in the 1970s and have dropped by a factor of about 5 over the last 20 years. A procedure has been developed to correct for the SO_2 effect at Uccle, and the influence is found to be greatest in the lower troposphere (De Muer and De Backer, 1994). Logan (1994) argues that the Hohenpeissenberg, Tateno, and Sapporo ozonesonde measurements in the lower troposphere may have been affected by SO_2. This interference is worst in winter when the highest concentrations of SO_2 occur. Staehelin *et al.* (1994; personal communication) have found that SO_2 levels in Switzerland were too low to have a noticeable effect at Payerne. Other stations are also likely to have been less affected.

1.3.1.2c Operational Changes

Changes in operational procedures at an ozonesonde station can have dramatic effects on the ozone measurements, particularly in the troposphere. Two clear examples are: (a) the change from BM to ECC sondes at the Canadian stations that took place in the early 1980s, when there was an apparent jump in the amount of tropospheric ozone measured at most of these stations; and (b) the change in launch time at Payerne in 1982, which affected the measurements in the lowest layer of the troposphere (Staehelin and Schmid, 1991). Logan (1994) argues that there is a jump in lower and mid-tropospheric ozone values in the combined Berlin/ Lindenberg record, corresponding to the change in ozonesonde launch site from Berlin to Lindenberg and to the simultaneous change in sonde type from BM to OSE. Alterations in the manufacture of the sensors and in the pre-launch procedures can also have an effect.

Another possible cause of error is a change in the efficiency of the pump. The air flow through the ozone sensor is not measured, but is calculated from laboratory tests performed at a number of pressures (Görsdorf *et al.*, 1994; Komhyr *et al.*, 1994b, and references therein). It is possible that there have been some changes in the design of the pump that may have changed its efficiency over time and that primarily affect measurements made at altitudes above 25-28 km.

1.3.1.2d Intercomparisons

A series of campaigns have been mounted in which different ozonesondes have been compared to see whether the quality of any type of ozonesonde has changed over time and to find out what systematic differences exist between different types of sonde and between the sondes and other instruments (lidar, UV photometer). In each campaign good agreement was found between the various ECC sondes flown simultaneously. However in the most recent WMO campaign held at Vanscoy, Canada, in May 1991, the BM gave results 15% higher than the ECC in the troposphere, whereas in the previous campaigns (1970, 1978, 1984) the BM was reported as measuring 12% less tropospheric ozone than the ECC (Kerr *et al.*, 1994, and references therein). This result may indicate a change in the sensitivity of the BM to ozone. This conclusion is supported to some extent by the findings of a study at Observatoire de Haute Provence, where comparisons involving BM and ECC sondes, lidars, and UV photometers made in 1989 and 1991 showed a change in the BM sensitivity relative to ECC in the troposphere. However, operational practices maintained during campaigns can be different from those used at home, and it is hard to assess how representative the measurements made under campaign conditions are. The implications of such findings on trends in tropospheric ozone are discussed in Section 1.3.2.3. The measurements in the stratosphere show good agreement in all the comparisons.

Although one must be careful in the comparison of the regular Brewer-Mast sondes with the GDR sondes manufactured in the former East Germany, results of two intercomparison campaigns in Germany (Attmannspacher and Dütsch, 1970, 1981) showed similar differences between BM and OSE of 3 and 5 nbar, respectively, in the free troposphere (a difference of about 5% of the measured ozone concentration) and no differences in the stratosphere. This may be a good indication that OSE sonde quality remained the same, at least over the time period 1970-1978; and therefore differences between trend estimates obtained at various stations need not be strongly dependent on the type of sondes used, unless changes in sonde type occurred.

1.3.1.2e Correction Factors

Ozonesonde readings are normalized so that the integrated ozone of the sonde (corrected for the residual ozone at altitudes above the balloon burst level) agrees with the total ozone amount given by a nearby Dobson (or other ground-based) instrument. This is a good way to assess the overall sounding quality – an unusually high or low correction factor indicates that something might be wrong with a particular sounding. A correction factor of 1 is not a guarantee that the profile is correct.

However, care is needed in using correction factors, as new errors can be generated. First, the process relies on the quality of the local total ozone measurement. For instance, errors can be introduced either by a single, erroneous reading or through changes in the calibration of the ground-based instrument. It is important to ensure that the ozonesonde records are updated in line with the ground-based revisions. Second, errors in the pressure and ozone reading at the burst level will affect the value of the residual ozone, which in turn influences the rest of the profile through an inaccurate correction

factor. Third, any variation of the sonde sensitivity to ozone changes with altitude leads to an incorrectly shaped profile, which the use of a correction factor (based only on total column amounts) cannot adjust. ECC sondes are thought to have a more constant response with altitude than the BM sondes which tend to underestimate tropospheric ozone amounts.

No significant long-term trend in the correction factor has been seen at Hohenpeissenberg, Payerne, and Uccle, a fact which suggests that there has not been a change in sensitivity of the BM sonde, possibly indicating that the result of the intercomparisons arose from the different operational conditions used in the intercomparisons. Changes in correction factor over shorter times have occurred, *e.g.,* at Payerne in the early 1970s and since 1990 (Logan, 1994). Logan (1994) has compared the trends estimated using measurements calculated with and without correction factors and found only small changes in the ozone trends in all but 3 of the 15 ozonesonde records.

1.3.1.3 Satellite Measurements of the Ozone Profile

The SAGE I and SAGE II instruments were described in detail in the IOTP (WMO, 1990a). SAGE I operated from February 1979 to November 1981 and SAGE II from October 1984 to the present day. They are solar occultation instruments measuring ozone absorption at 600 nm. Correction is made for attenuation by molecular and aerosol scattering and NO_2 absorption along the line of sight by using the observations made at other wavelengths. Comparisons of SAGE II number density profiles with near-coincident balloon and rocket measurements have shown agreement on average to within ± 5-10% (Attmannspacher *et al.*, 1989; Chu *et al.*, 1989; Cunnold *et al.*, 1989; De Muer *et al.* 1990; Barnes *et al.*, 1991).

The SAGE I and SAGE II instruments are different in some respects, but, in principle, there are few reasons for calibration differences between the two instruments. One reason is the altitude measurements of the two instruments, which are now thought to be offset by 300 m. The effects of such an offset would be felt most at altitudes between 15 and 20 km, where the ozone concentrations vary rapidly with altitude. Two independent investigations have found a potential error in the altitude registration of the SAGE I data set. From a detailed intercomparison with sondes and lidars, Cunnold (private communication) has found that agreement between SAGE I and these other measurements can be significantly improved if the SAGE I profiles are shifted up in altitude by approximately 300 meters. The prelaunch calibration archives for SAGE I have been reexamined, and together these data show that the spectral location of the shortest wavelength channel may be in error by 3 nm (382 nm instead of 385 nm). Since this channel is used to correct the altitude registration via the slant path Rayleigh optical depth, a shift of 3 nm to shorter wavelengths would result in an upward altitude shift of about 300 ± 100 m. The full impact of this wavelength error is being studied and a preliminary version of the shifted SAGE I ozone data set is used in this assessment.

The presence of aerosols increases the errors associated with the measurement, as the aerosols are effective scatterers of light at 600 nm. Comparisons of SAGE II ozone measurements with those made by Microwave Limb Sounder (MLS) (which should be unaffected by aerosol) indicate that errors become appreciable when the aerosol extinction at 600 nm is larger than 0.003 km^{-1}, which corresponds to about 8 times the background aerosol at 18 km. Only measurements made with an aerosol extinction less than 0.001 km^{-1} are used in the trend analyses presented in the next section. Using the 0.001 per km extinction value as a screening criterion, the following general observations follow. The SAGE II ozone measurements were interrupted for a period of one year following the eruption of Mt. Pinatubo at 22 km near 40°N and 40°S. At the equator the gap in the series was two years at the same altitude. Extratropical measurements were uninterrupted at altitudes of 26 km and above (30 km and above at the equator). By early 1994, SAGE II was making measurements at all latitudes down to the tropopause.

SBUV operated from November 1978 to June 1990. The total ozone measurements are described in Section 1.2.1. Ozone profiles are found by measuring the backscatter from the atmosphere at wavelengths between 252 and 306 nm. The wavelengths most strongly absorbed by ozone give information about the higher altitudes. There is little sensitivity to the shape of the profile at or below the ozone maximum. As with the Umkehr measurements, some information is available below the ozone maximum because the complete profile must be balanced with the total ozone. Hood *et al.*

(1993) considered the partial column from the ground to 32 mbar (26 km) as the most useful quantity in this region.

Corrections have been made for the diffuser plate degradation using the pair justification method (Herman *et al.*, 1991; Taylor *et al.*, 1994), so the quality of the SBUV profile measurements has improved since the IOTP (WMO, 1990). The shorter wavelengths were corrected using a form of the Langley technique: near the summer pole, ozone measurements are made at each latitude with two solar zenith angles. If the zonal mean ozone values are constrained to be the same, the wavelength dependence of the correction to the diffuser plate degradation can be determined. The accuracy of any derived trend in the ozone profile is no better than 2-3% per decade. Above 25 km, the vertical resolution of SBUV is about 8 km, and this increases below 25 km to about 15 km. A limit on the independence of the SBUV ozone profile data in trend determination is that the retrieval algorithm requires further information on the shape of the ozone profile within these layers. It is thus possible that a trend in the shape of the profile within a given layer could induce a trend in the retrieved layer amount, even though the actual layer amount remains unchanged.

A problem with the synchronization of the chopper in the SBUV instrument occurred after February 1987. After corrections are made, there is no evidence of bias at the 1-2% level between the data collected before and after this date, although the latter data are somewhat noisier (Gleason *et al.*, 1993; Hood *et al.*, 1993).

McPeters *et al.* (1994) have compared the SAGE II and SBUV measurements from 1984 to 1990, the period when both instruments were in operation. Co-located data were sorted into 3 latitude bands (20°S-20°N, 30-50°N, and 30-50°S). Agreement is usually better than 5% (Figure 1-11, 20°S-20°N not shown). The main exceptions are near and below 20 km, where SBUV has reduced vertical resolution, and above 50 km, where the sampling of the diurnal variation of ozone is not accounted for in the comparison. A discrepancy between the SAGE sunrise and sunset data was found in the upper stratosphere near the equator. This may be related to the SAGE measurements made at sun angles, which causes the measurements to be of long duration so that the spacecraft motion during the event can be on the order of 10 great circle degrees.

The drift from 1984-1990 between the two measurements above 32 mb is less than 5% and is statistically insignificant (Figure 1-12). Below this, the drift is 10% per decade in the tropics and becomes smaller (4-6%) at midlatitudes. These are roughly consistent with the difference in the ozone trends from the two instruments. Some, or all, of this apparent drift may be caused by the requirement of information about the shape of the ozone profile in the SBUV retrievals (McPeters *et al.*, 1994). In contrast, the relative drift between SBUV and the Umkehr measurements (all between 30 and 50°N) is less than 2%. However, below the ozone maximum the average ozone amounts from SBUV and Umkehr differ by as much as 20% (DeLuisi *et al.*, 1994).

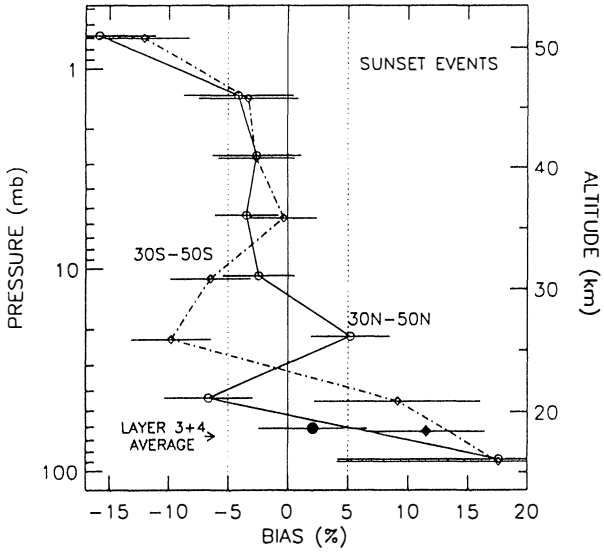

Figure 1-11. Ozone profile bias of SBUV relative to SAGE sunset data in northern midlatitudes (o) and southern midlatitudes (◊) for 1984-1990. The solid symbols are for layers 3+4 combined to represent the low SBUV resolution in the lower stratosphere. Standard deviations of the appropriate daily values used in calculating the average biases are also plotted. (McPeters *et al.*, 1994.)

1.3.2 Trends in the Ozone Profile

Ozone trends in three altitude ranges received special attention in the 1991 report. In the upper stratosphere (35 km and above) the ozone losses reported from two observational systems (Umkehr and SAGE) were

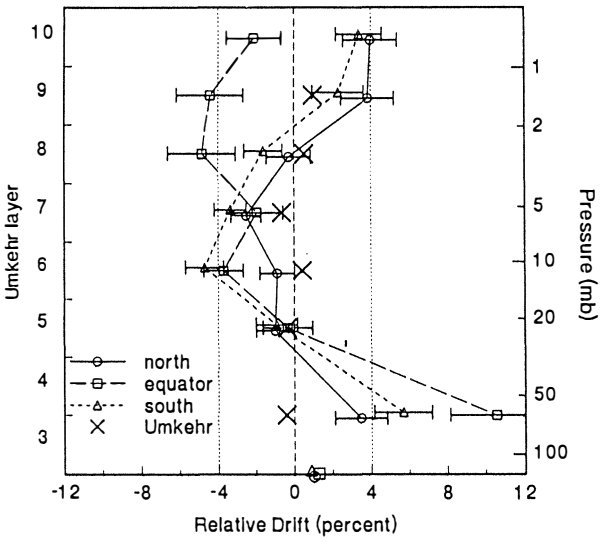

Figure 1-12. Linear drift of SBUV relative to SAGE II over the 1984-1990 time interval for layers 5-10 and for layer 3+4 combined, derived from a linear fit applied to percent difference data. (SBUV-SAGE)/SAGE in percent is plotted. Symbols on X axis give drift of layer 3-10 integrated ozone amounts. For comparison, drift relative to an average of five Umkehr stations (1984-1990) is also shown. The 1σ errors from the standard regression analysis are given. (McPeters *et al.*, 1994).

qualitatively similar but quantitatively different. These high altitude decreases have long been calculated in atmospheric models and are caused by gas phase chlorine-catalyzed ozone loss. Ozone losses were also reported below 25 km, though there were discrepancies between the values inferred from ozonesonde and SAGE measurements, especially below 20 km. In the free troposphere, long-term ozone increases were reported at three European ozonesondes sites. Ozone is an important radiative component of the free troposphere and a better understanding of ozone changes on a global scale is important. No significant ozone losses were reported around 30 km altitude or near the tropopause, where the lower stratospheric decrease switched to an upper tropospheric increase.

In this assessment the same altitude ranges are examined (starting in the upper stratosphere and working down) in the light of some new analyses of both the data quality (see Section 1.3.1) and of the data themselves. In addition, there is discussion of some ground-level measurements from which inferences can be drawn regarding changes in free tropospheric ozone.

McCormick *et al.* (1992) calculated trends using the combined SAGE I/II data set. The SAGE data used here are slightly different, as the altitude correction has been applied to the SAGE I data. Also, the base year used to calculate percentage changes is 1979 here (not 1988, used by McCormick *et al.*), so that the percentage changes in the lower stratosphere, where SAGE reports the largest decreases, are smaller. Hood *et al.* (1993) used the Nimbus 7 SBUV data from 1978 to 1990 to estimate trends. In this assessment we use the combined SBUV/SBUV2 data to extend the record, but the calculated trends are similar.

1.3.2.1 Trends in the Upper Stratosphere

In Section 1.3.1, we described an intercomparison of the various ozone data sets over a limited time interval. Upper stratospheric trends in ozone have been estimated from Umkehr, SAGE, and SBUV measurements using the full data sets. While the periods of time represented by each differ, they all represent, to first order, the changes observed from 1980 through 1990. Figure 1-13 shows the observed decadal trends as a function of altitude and latitude from the SBUV and SAGE I/II data sets. The two are now in reasonable agreement in the upper stratosphere. The altitude of the maximum percentage ozone loss is around 45 km and relatively independent of latitude. The magnitude of this peak decrease is smallest at the equator (about 5%/decade) and increases towards the poles in both hemispheres, reaching values in excess of 10% per decade poleward of 55 degrees latitude.

Figure 1-14 shows the ozone trend profile as a function of altitude in the latitude band from 30 to 50°N from SBUV and SAGE, along with the average Umkehr and ozonesonde trend profiles. SBUV, SAGE, and Umkehr all show a statistically significant loss of 5-10% per decade at 40-45 km, although there is some uncertainty as to its exact magnitude. Below 40 km the trends become smaller and are indistinguishable from zero near 25 km.

The seasonal dependence of the trends in the upper stratosphere has been investigated using the SBUV and Umkehr data (Hood *et al.*, 1993; DeLuisi *et al.*, 1994; Miller *et al.*, 1994). The Umkehr records between 19°N

and 54°N have been examined and their combined data do not show a significant seasonal variation in the trend. This is slightly at odds with the analysis of the SBUV measurements, which shows that the largest ozone decreases have occurred in winter at high latitudes in both hemispheres, though this difference may not be significant given the problems associated with measurements made at high solar zenith angles.

1.3.2.2 Trends in the Lower Stratosphere

As discussed in Section 1.3.1, we rely on SAGE and ozonesondes for information on ozone trends in the lower stratosphere, as the SBUV and Umkehr capabilities are limited at these altitudes. SAGE measures ozone from high altitudes to below 20 km. Ozonesondes operate from the ground up to about 30 km.

In the 1991 assessment, the SAGE I/II midlatitude trends below 20 km were reported as greater than 20% per decade, twice as large as were measured at two ozonesonde stations or than found from an average of five Umkehr records in the Northern Hemisphere. The size of the SAGE trends at these altitudes has provoked a great amount of discussion, partly because of the sensitivity of climate to changes in ozone in this region. As mentioned earlier, the SAGE I/II trends shown here differ in two respects from those reported previously. First, an altitude correction of 300 m has been applied to the SAGE I measurements. Second, the year used to calculate the percentage change is now 1979, not 1988. Below 20 km the effect of both these changes is to reduce the SAGE I/II trends because ozone changes rapidly with altitude and because the largest losses are observed at these altitudes so that the change in the base value is greatest. Two other factors complicate the SAGE measurement below 20 km: (i) ozone concentrations are smaller than at the maximum, so that the signal is lower; and (ii) the amount of aerosol is greater, which attenuates the signal and acts as an additional interference. These are well-recognized difficulties for which allowance is made in the calculation of the ozone amount and which contribute to the size of the uncertainties in SAGE ozone trends in the lower stratosphere.

Figures 1-13 and 1-14 show the lower stratospheric ozone trends in the 1980s from SBUV, SAGE, and the non-satellite systems. At altitudes between 25 and 30 km, there is reasonable agreement between SAGE I/II, SBUV, Umkehr, and ozonesondes that there was no significant ozone depletion at any latitude. The agreement continues down to about 20 km, where statistically significant reductions of 7 ± 4% per decade were observed between 30 and 50°N by both ozonesondes and SAGE I/II. In the equatorial region, the combined SAGE I/II record (1979-1991) shows decreases of more than 20% per decade in a region just above the tropopause between about 30°N and 30°S, although in absolute terms this loss in the tropics is quite small as there is not much ozone at these altitudes. The height of the peak decrease in ozone is about 16 km, and the region of decrease becomes broader away from the equator. At northern midlatitudes (Figure 1-14) the SAGE I/II trend at 16-17 km is -20 ± 8% per decade, compared with an average trend from the ozonesondes of -7 ± 3% per decade.

The SAGE I/II trends in the column above 15 km have been compared with the total ozone trends found from TOMS, SBUV(/2), and the ground-based network for 1979-1991. This comparison implicitly assumes little or no change in the ozone amount below 15 km. The SAGE I/II trends are larger than those found with the other data sets, peaking at -6% per decade in the northern midlatitudes, but the associated uncertainties are too large for firmer conclusions to be drawn. Hood *et al.* (1993) compared the tropical trend from SBUV for the partial column from the ground to 26 km with the SAGE I/II trends reported by McCormick *et al.* (1992). They decided that no conclusive comparison could be made, although they found trends of about +3 ± 4% per decade for SBUV for 1979-1990 (see Figure 1-13(a) for an updated version), while McCormick *et al.* found trends similar to the ones shown in Figure 1-13(b) for 1979-1991. While not shown here, comparisons of SBUV with SAGE II have recently been completed (McPeters *et al.*, 1994). Comparisons of the sum of ozone in Umkehr layers 3-10 (15 km-55 km) show that SBUV increased relative to SAGE (or SAGE decreased relative to SBUV) by 1.1% between 1984 and 1990.

Logan (1994), London and Liu (1992), and Miller *et al.* (1994) have reviewed the global long-term ozonesonde data records. Furrer *et al.* (1992, 1993) and Lityńska (private communication) have analyzed the records at Lindenberg, Germany, and Legionowo, Poland, respectively. These studies handled data quality issues differently and used different statistical models, but they gave broadly similar results in the lower stratosphere. The large natural variability of ozone concen-

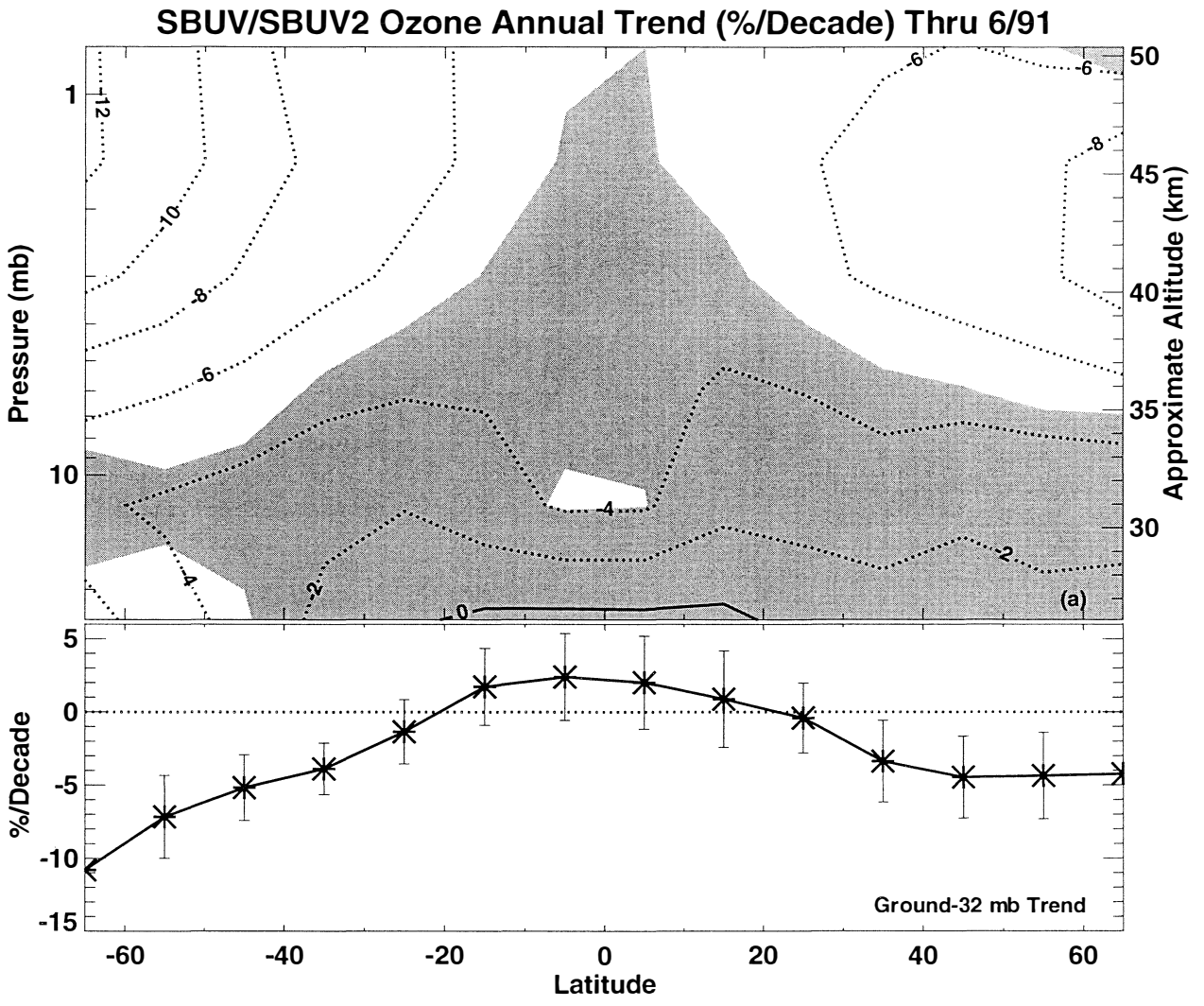

Figure 1-13. (a) Trends calculated for the combined SBUV/SBUV2 data set for 1/79 to 6/91. Hatched areas in the upper panel indicate that the trends are not significant (95% confidence limits). The lower panel shows the trends in the partial column between the ground and 32 mbar. Error bars in the lower panel represent 95% confidence levels.

trations is compounded at some stations by a low sampling frequency. It is hard to draw firm conclusions about seasonal effects. The following results are thus general and not true for all stations.

Figure 1-15 shows the ozone trends calculated from the ozonesonde records for the period 1970-1991. In the northern midlatitudes, a maximum trend of -8 to -12%/decade was found near 90 mbar from the early 1970s to 1991. Decreases extend from about 30 mbar down to near the troposphere. Significant ozone loss certainly appears to have occurred between 90 and 250 mbar. Few conclusions about the seasonal nature of the trends are statistically significant. A possible difference exists between the Canadian ozonesonde records where the summer trends are similar to, and possibly even greater than, the winter trends. At Wallops Island, U.S., and at the European stations, the winter loss is greater than the summer loss. These features are also seen in the total ozone record from 1978-1991 observed at these stations.

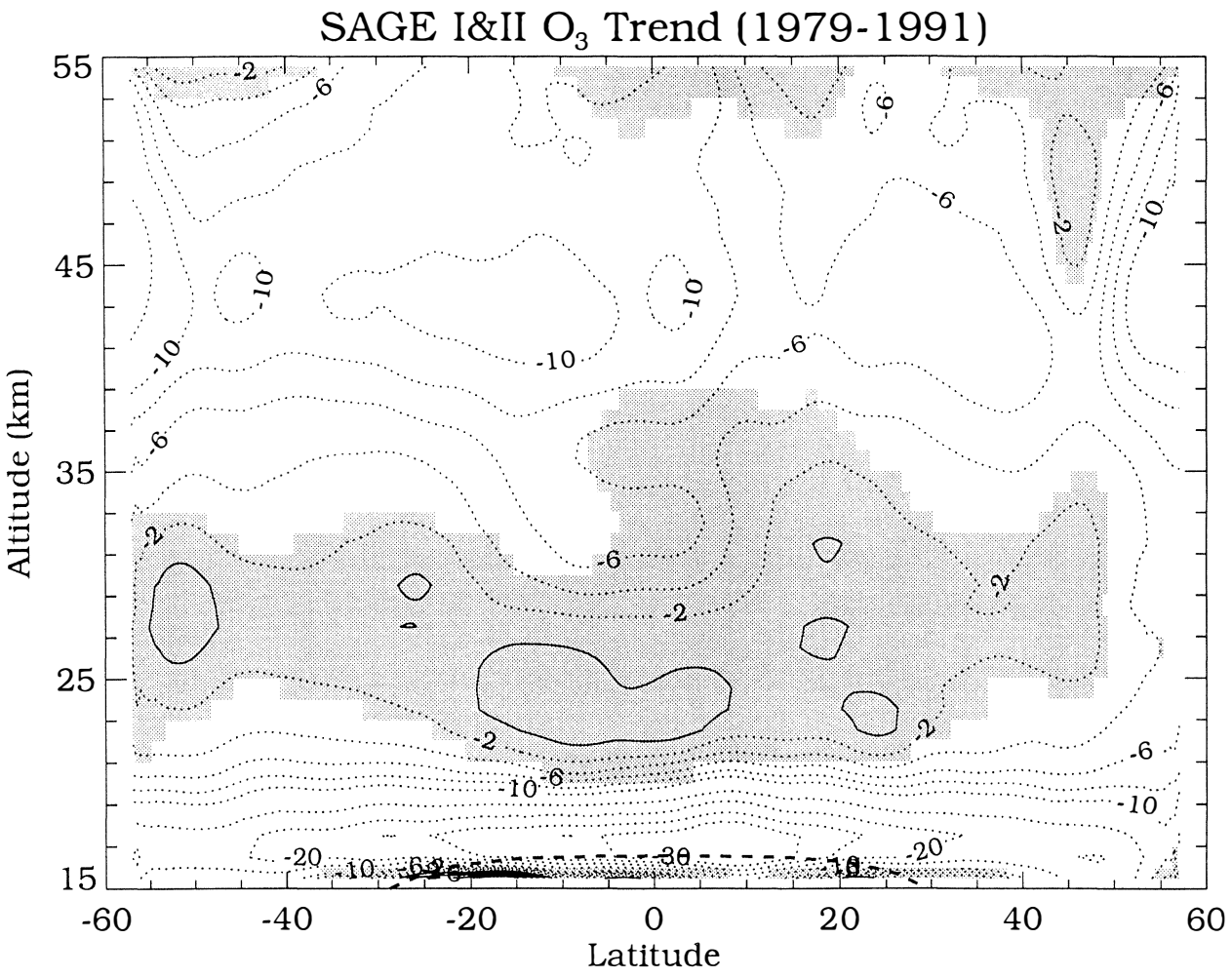

Figure 1-13. (b) Trends calculated for SAGE I/II for 1979-91. Hatched areas indicate trends calculated to be insignificant at the 95% confidence level. The dashed line indicates the tropopause. The altitudes of the SAGE I measurements have been adjusted by 300 meters.

In the tropics, only Natal (6°S) has an ozonesonde record longer than 10 years. The trend found by Logan at 70-90 mbar is -10 (± 15)%/decade. At Hilo, Hawaii (20°N), ozonesondes from 1982 to 1994 indicate insignificant trends of -12 ± 15% per decade near the tropopause (17-18 km) and -0.7 ± 6% per decade in the lower stratosphere at 20 km (Oltmans and Hofmann, 1994). Trends from both ozonesonde records are smaller than the calculated SAGE tropical trends, but the large uncertainties mean that the two trends are not inconsistent. In the Southern Hemisphere, the only long-running station outside Antarctica is at Melbourne, Australia, where a trend of about -10% per decade is observed in the lower stratosphere.

1.3.2.3 Trends in the Free Troposphere

Only ozonesonde data are available for ozone trend analyses in the free troposphere. As discussed in Section 1.3.1, the quality of the ozonesonde data in the troposphere is worse than in the stratosphere. The strong likelihood of regional differences in trends further confuses attempts to assess the consistency of a limited number of ozonesonde records. In the last report, ozone in the free troposphere at Payerne was shown to have

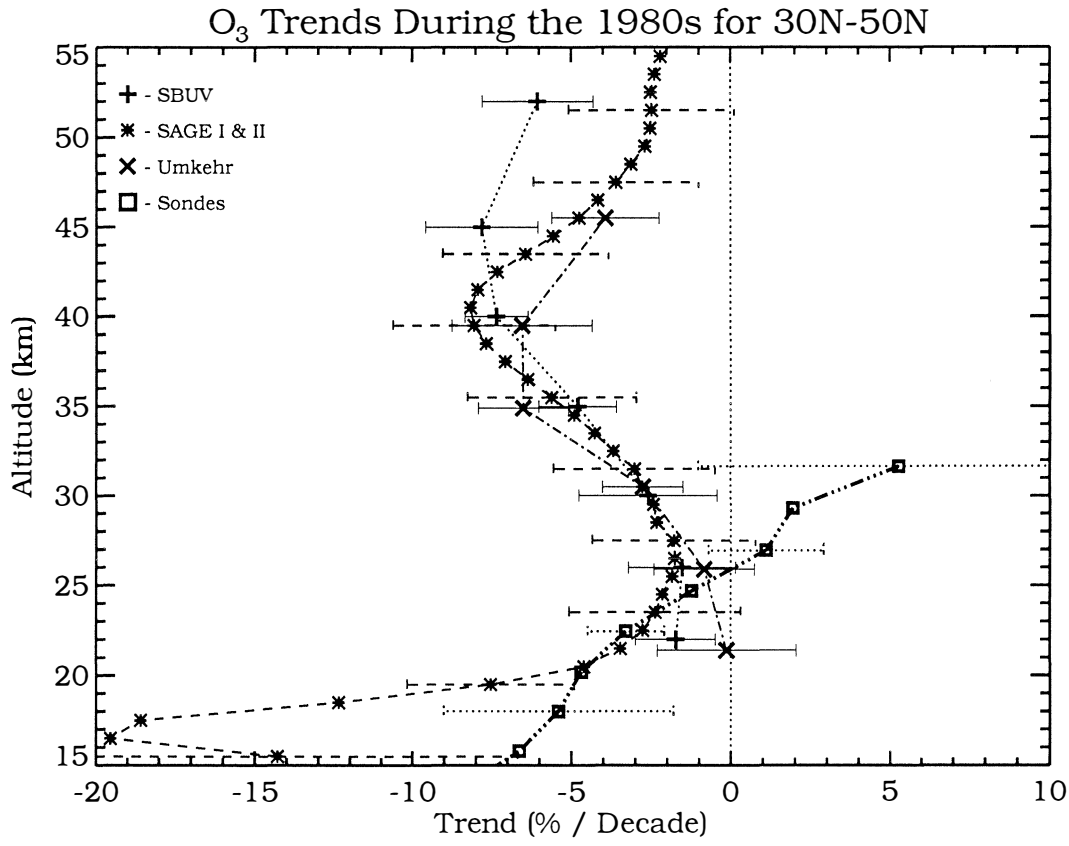

Figure 1-14. Comparison of trends in the vertical distribution of ozone during the 1980s. Ozonesonde and Umkehr trends are those from Miller *et al.* (1994). 95% confidence limits are shown.

increased by 30-50% since 1969. An assessment of data from several stations through 1986 was made (WMO, 1990b) that showed regional effects with increases at the European and Japanese stations. A tropospheric increase was also reported at Resolute (75°N), but decreases were found at the three midlatitude Canadian sites.

Since then, Logan (1994) and Miller *et al.* (1994) have analyzed the global ozonesonde record, paying particular attention to inhomogeneities in the data. A similar study by London and Liu (1992) did not account for instrumental changes at some sites. There is now evidence that the upward trend over Europe is smaller since about 1980 than before. The Hohenpeissenberg ozone measurements show no increase since the early to mid-1980s. The Payerne record shows a somewhat similar behavior until 1990. This conclusion is supported by the recent analyses of the Berlin/Lindenberg record (Furrer *et al.*, 1992, 1993) and of the Legionowo record (Lityńska and Kois, private communication). Furrer *et al.* found a large tropospheric trend from 1967-1988 of about +15%/decade, but this seems to have been at least partly caused by a jump in the measured ozone levels at the change of station in the early 1970s. Logan (1994) finds no significant trend at 500 mbar for 1980-1991 and points out that this trend is sensitive to changes in the correction factor over this period and could be negative. At Legionowo, an upper tropospheric trend of -10 (± 4.4)%/decade is reported for 1979-1993, a trend that is dominated by changes in spring.

Some of the trends, particularly those in Europe, might be influenced by changes in SO_2 levels. De Muer and De Backer (1994) have corrected the Uccle data set allowing for all known instrumental effects, including SO_2. The ozone trend in the upper troposphere was only slightly reduced (10-15%/decade, 1969-1991) and re-

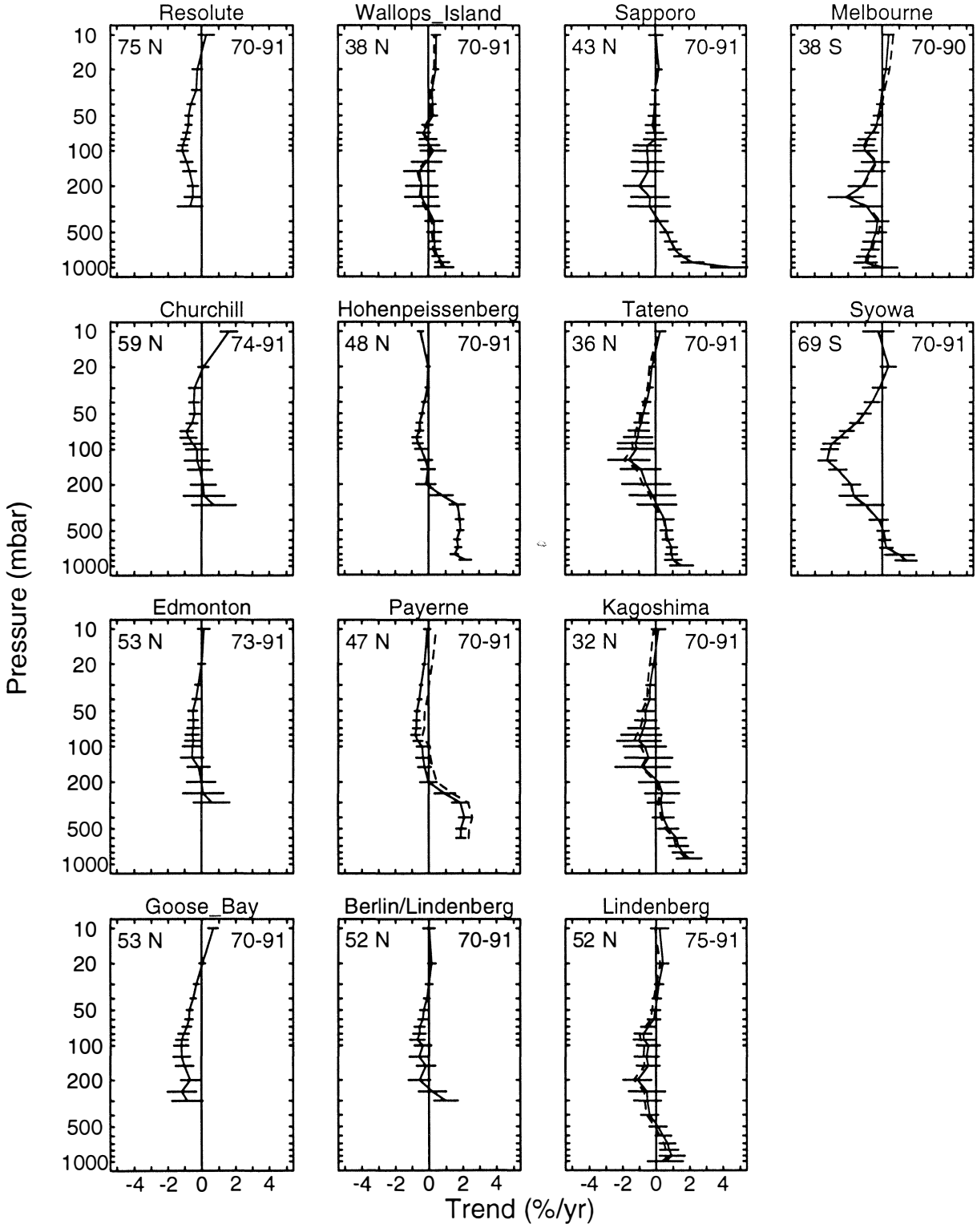

Figure 1-15. Trends for the periods shown in the ozonesonde measurements at different altitudes. 95% confidence limits are shown. (Adapted from Logan, 1994.)

mained statistically significant. However, below 5 km, the trend was reduced and became statistically insignificant, going from around +20%/decade to +10%/decade. Logan (1994) argues, using SO_2 emission figures and nearby surface measurements of ozone and SO_2, that measurements made at Hohenpeissenberg, Lindenberg, and possibly other European stations might be influenced by SO_2 and points out that any such effect would be largest in winter. In polluted areas, local titration of ozone by NO_x can also influence measurements of ozone at low altitude. However neither of these effects should have much influence except in the lower troposphere (<4 km).

Tropospheric ozone over Canada decreased between 1980 and 1993 at about -1 ± 0.5%/year (Tarasick *et al.*, 1994). The positive trend observed at Wallops Island has diminished and from 1980-1991 was close to zero (Logan, 1994). Prior to 1980 the situation is more confused. Wallops Island is the only station in North America with a homogeneous record from 1970 to 1991, and a trend of just under +10% per decade was observed (Figure 1-15). In two cases, the critical factor needed to deduce the long-term tropospheric ozone changes over North America is the ratio of the tropospheric ozone measured by BM and ECC sondes. First, the Canadian stations changed from BM to ECC sondes around 1980, and a conversion factor is needed if the two parts of the record are to be combined into one. Second, BM ozonesonde measurements were made at Boulder in 1963-1966 (Dütsch *et al.*, 1970), while ECC sondes have been used in the soundings made since 1985 (Oltmans *et al.*, 1989). Logan (1994) has compared the Boulder data by multiplying the BM data at 500 and 700 mbar by 1.15 and concluded that (a) no increase has occurred in the middle or upper troposphere, and (b) a 10-15% increase occurred in the lower troposphere caused by local pollution. The factor of 1.15 was based on a reanalysis of the intercomparisons in 1970, 1978, and 1984 (see Section 1.3.1.2d). Bojkov (1988; private communication) compared the concurrent measurements made by several hundred ECC sondes at Garmisch-Partenkirchen and BM sondes at Hohenpeissenberg, and concluded that the ratio should be between 1.04 and 1.12 depending on altitude. This approach would produce a larger change at Boulder in the lower troposphere and would indicate a small increase at 500 mbar. However, it is possible that the differences depend on the pre-launch procedures in use at the different sites, in which case no single factor can be used: this possibility is supported by the apparently different jumps seen at the changeovers at the four Canadian stations. Anyway, there is no sign that ozone concentrations over Boulder rose by the 50% observed at Hohenpeissenberg or Payerne since 1967; at most a 10-15% increase has occurred, similar to the increase observed at Wallops Island.

A reanalysis of the ozonesonde records from the three Japanese stations from 1969-1990 (Akimoto *et al.*, 1994) found annual trends of 25 ± 5%/decade and 12 ± 3%/decade for the 0-2 km and 2-5 km layers, respectively. Between 5-10 km the trend is 5 ± 6%/year. There is no evidence for a slowing of trends in the 1980s.

In the tropics, Logan (1994) reports that Natal shows an increase between 400 and 700 mbar, but which is only significant at 600 mbar. The Melbourne record shows a decrease in tropospheric ozone that is just significant between 600 and 800 mbar and is largest in summer.

1.3.2.4 Trends Inferred from Surface Observations

Some information about free tropospheric ozone is contained in measurements of ozone at the Earth's surface, although care has to be taken in the interpretation of these data as they are not directly representative of free tropospheric levels.

Ground-based measurements were made during the last century, mostly with the Schoenbein method (*e.g.* Anfossi *et al.*, 1991; Sandroni *et al.*, 1992; Marenco *et al.*, 1994), which is subject to interferences from wind speed (Fox, 1873) and humidity (Linvill *et al.*, 1980). Kley *et al.* (1988) concluded that these data are only semi-quantitative in nature and should not be used for trend estimates. Recent improvements in the analysis are still insufficient to allow simple interpretation of such data. A quantitative method was used continuously from 1876 until 1911 at the Observatoire de Montsouris, Paris (Albert-Levy, 1878; Bojkov, 1986; Volz and Kley, 1988). The average ozone concentration was around 10 ppbv, about a factor of 3-4 smaller than is found today in many areas of Europe and North America. However, the measurements at Montsouris were made close to the ground and, hence, are not representative of free tropospheric ozone concentrations during the last century.

Staehelin *et al.* (1994) reviewed occasional measurements by optical and chemical techniques at a num-

ber of European locations in the 1930s and measurements made at Arosa in the 1950s (Götz and Volz, 1951; Perl, 1965). Figure 1-16 shows a comparison of the ozone concentrations found in the 1930s and 1950s with measurements made at Arosa and other European locations in the late 1980s. On average, ozone concentrations in the troposphere over Europe (0-4 km) today seem to be a factor of two larger than in the earlier period. The Arosa data also suggest that the relative trends are largest in winter. The measurements in the 1950s were made by iodometry and are potentially biased low from SO_2 interferences caused by local sources, although Staehelin *et al.* (1994) argue that SO_2 at Arosa was probably less than a few ppbv.

Figure 1-16 also shows that, because of the variance between the different sites, little can be inferred about a possible increase in tropospheric ozone before 1950. In this context, it is interesting to note that the data from Montsouris (1876-1911; 40 m ASL) and those from Arosa (1950-1956; 1860 m ASL) do not show a single day with ozone concentrations above 40 ppb (Volz-Thomas, 1993; Staehelin *et al.*, 1994).

"Modern" ozone measurements, *e.g.,* using UV-absorption, were started in the 1970s at several remote coastal and high altitude sites (Scheel *et al.*, 1990, 1993; Kley *et al.*, 1994; Oltmans and Levy, 1994; Wege *et al.*, 1989). The records for Mauna Loa, Hawaii, and Zugspitze, Southern Germany, are shown in Figure 1-17. A summary of the trends observed at the remote sites is presented in Figure 1-18. All stations north of about 20°N exhibit a positive trend in ozone that is statistically significant. On the other hand, a statistically significant negative trend of about -7%/decade is observed at the South Pole. For the most part, the trends increase from -7%/decade at 90°S to +7%/decade at 70°N. Somewhat anomalous are the large positive trends observed at the high elevation sites in Southern Germany (10-20%/decade); these large trends presumably reflect a regional influence (Volz-Thomas, 1993). It must be noted, however, that the average positive trends observed at the high altitude sites of the Northern Hemisphere are largely due to the relatively rapid ozone increase that occurred in the seventies. If the measurements had started in the 1980s when the ozone concentrations tended to be at their peak (Figure 1-17), no significant ozone increase would have been found.

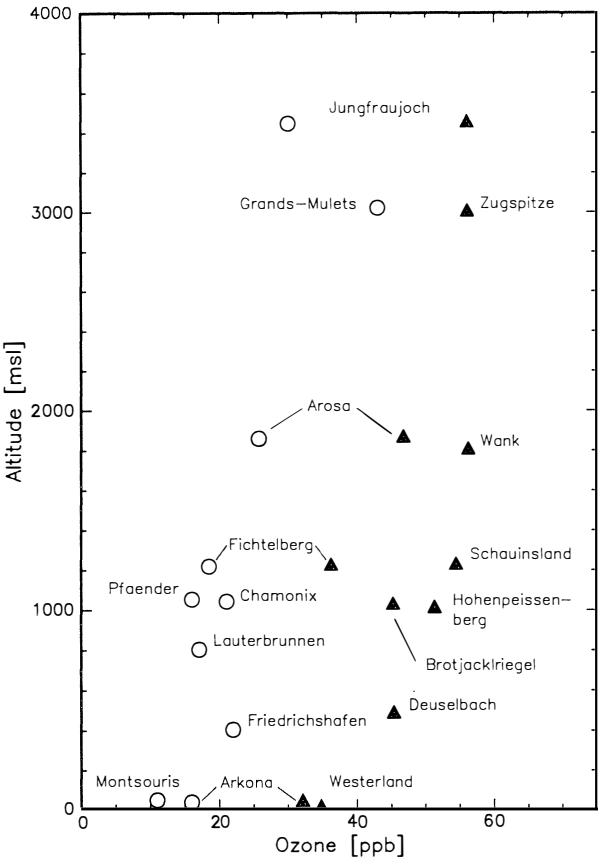

Figure 1-16. Measurements of surface ozone concentrations from different locations in Europe performed before the end of the 1950s (circles) and in recent years (1990-1991; triangles) during August and September, as function of altitude. (Reprinted from *Atmospheric Environment, 28,* Staehelin *et al.*, Trends in surface ozone concentrations at Arosa [Switzerland], 75-87, 1994, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.)

Unlike ozonesondes, and sites such as Mauna Loa and Zugspitze, where data are specifically identified as free tropospheric or otherwise (Oltmans and Levy, 1994; Sladkovic *et al.*, 1994), the ground-based instruments do not often sample free tropospheric air. However, the marine boundary layer sites like Samoa, Cape Point, and Barrow are representative of large geographical regions, and although the absolute concentrations may be different from those in the free troposphere, this fact should exhibit only a second-order influence on the trends.

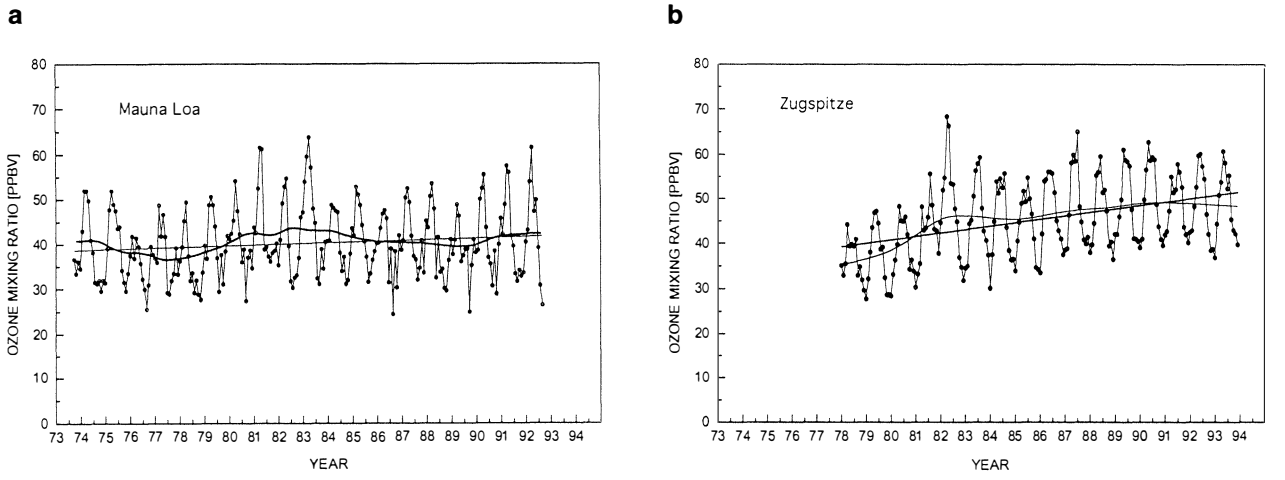

Figure 1-17. Surface ozone concentrations observed during the past two decades at Mauna Loa (Hawaii, 20°N, 3400m) (adapted from Oltmans and Levy, 1994) and Zugspitze (Germany, 47°N, 3000 m) (Sladkovic *et al.*, 1994).

Whether this is the case for Barrow is open to some question, as Jaffe (1991) has suggested it may be influenced by local ozone production associated with the nearby oil fields.

1.3.3 Discussion

The state of knowledge about the trends in the vertical distribution of ozone is not as good as that about the total ozone trends. The quality of the available data varies considerably with altitude.

The global decreases in total ozone are mainly due to decreases in the lower stratosphere, where the uncertainties in the available data sets are largest. SBUV and Umkehr measurements are most reliable around and above the ozone maximum. Information at lower altitudes is available from these techniques, but it is not clear at the present time whether much can be learned about trends in these regions. Ozonesondes make reliable measurements in the lower stratosphere, but the natural variability is such that the uncertainties associated with trends calculated for individual stations are large. Only in the northern midlatitudes do enough ozonesonde records exist for trends to be calculated with uncertainties smaller than 5%/decade. SAGE can measure ozone down to 15 km altitude. Two factors complicate the SAGE measurement below 20 km: (i) ozone concentrations are smaller than at the maximum,

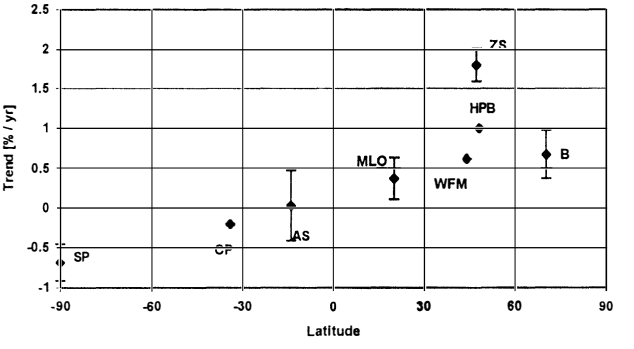

Figure 1-18. Trends in tropospheric ozone observed at different latitudes, including only coastal and high-altitude sites (after Volz-Thomas, 1993). CP: Cape Point, 34°S (Scheel *et al.*, 1990); SP: South Pole, 90°S, 2800m ASL; AS: American Samoa, 14°S; MLO: Mauna Loa, 20°N, 3400m; B: Barrow, 70°N (Oltmans and Levy, 1994); WFM: Whiteface Mountain, 43°N, 1600m (Kley *et al.*, 1994); ZS: Zugspitze, 47°N, 3000m; HPB: Hohenpeissenberg, 48°N, 1000m (Wege *et al.*, 1989).

so that the signal is lower; and (ii) the amount of aerosol is greater, so that there is an additional interference. These are well recognized difficulties for which allowance is made in the calculation of the ozone amount.

At altitudes of 35-45 km, there is reasonable agreement between SAGE I/II, SBUV(/2), and Umkehr

that, during 1979-1991, ozone declined 5-10% per decade at 30-50°N and slightly more at southern midlatitudes. In the tropics, SAGE I/II gives larger trends (ca. -10% per decade) than SBUV (ca. -5% per decade) at these altitudes.

At altitudes between 25 and 30 km, there is reasonable agreement between SAGE I/II, SBUV(/2), Umkehr, and ozonesondes that, during the 1979-1991 period, there was no significant ozone depletion at any latitude. The agreement continues down to about 20 km, where statistically significant reductions of 7 ± 4% per decade were observed between 30 and 50°N by both ozonesondes and SAGE I/II. Over the longer period from 1968 to 1991, the ozonesonde record indicates a trend of -4 ± 2% per decade at 20 km at northern midlatitudes.

There appear to have been sizeable ozone reductions during the 1979-1991 period in the 15-20 km region in midlatitudes. There is disagreement on the magnitude of the reduction, with SAGE indicating trends as large as -20 ± 8% per decade at 16-17 km and the ozonesondes indicating an average trend of -7 ± 3% per decade in the Northern Hemisphere. The trend in the integrated ozone column for SAGE is larger than those found from SBUV, TOMS, and the ground-based network, but the uncertainties are too large to evaluate the consistency between the data sets properly. Over the longer period from 1968 to 1991, the ozonesonde record indicates a trend of -7 ± 3% per decade at 16 km at northern midlatitudes.

In the tropics, trend determination at altitudes between 15 and 20 km is made difficult by the small ozone amounts. In addition, the large vertical ozone gradients make the trends very sensitive to small vertical displacements of the profile. The SAGE I/II record indicates large (-20 to -30% (±18%) per decade) trends in the 16-17 km region (-10% ±8% at 20 km). Limited tropical ozonesonde data sets at Natal, 6°S and Hilo, 20°N do not indicate significant trends between 16 and 17 km or at any other altitude for this time period. With currently available information it is difficult to evaluate the trends below 20 km in the tropics, as the related uncertainties are large. The effect on the trend in the total column from any changes at these altitudes would be small.

In the free troposphere, only limited data (all from ozonesondes) are available for trend determination. In the Northern Hemisphere, trends are highly variable between regions. Upward trends in the 1970s over Europe have declined significantly in the 1980s, have been small or non-existent over North America, and continue upward over Japan. The determination of the size of the change over North America requires a proper treatment of the relative tropospheric sensitivities for the type of sondes used during different time periods.

Surface measurements indicate that ozone levels at the surface in Europe have doubled since the 1950s. Over the last two decades there has been a downward trend at the South Pole and positive trends are observed at high altitude sites in the Northern Hemisphere. When considering the latter conclusion, the regional nature of trends in the Northern Hemisphere must be borne in mind.

1.4 OZONE AND AEROSOL SINCE 1991

Since the last report, record low ozone values have been observed. This section describes the ozone measurements in this period to allow the updated trends given in Section 1.2.2 to be put into perspective. There is also a brief discussion of a variety of possible causes, including the aftermath of the eruption of Mt. Pinatubo, aspects of which will be discussed at greater length in later chapters.

1.4.1 Total Ozone Anomalies

Figure 1-19(a) shows the daily global average (50°N-50°S) ozone amount during 1992-1994, together with the envelope of 1979-1990 observations. Persistent low ozone levels are observed beginning in late 1991 (not shown), with values completely below the 1979-1990 envelope from March 1992–January 1994. During 1993 total ozone was about 10-20 DU (3-6%) below the 1980s average. Total ozone in early 1994 recovered somewhat and was at the bottom end of the range observed in the 1980s.

Figure 1-19(b)-(d) shows similar plots for the latitude bands 30-50°S, 20°S-20°N, and 30-50°N. The largest and longest-lived anomalies are seen at the northern midlatitudes (15-50 DU lower in 1993), with 1980s values reached again in January 1994. Ground-based measurements made at sites with long records show that the anomalies in the northern midlatitudes were the largest since measurements began, and that values in early

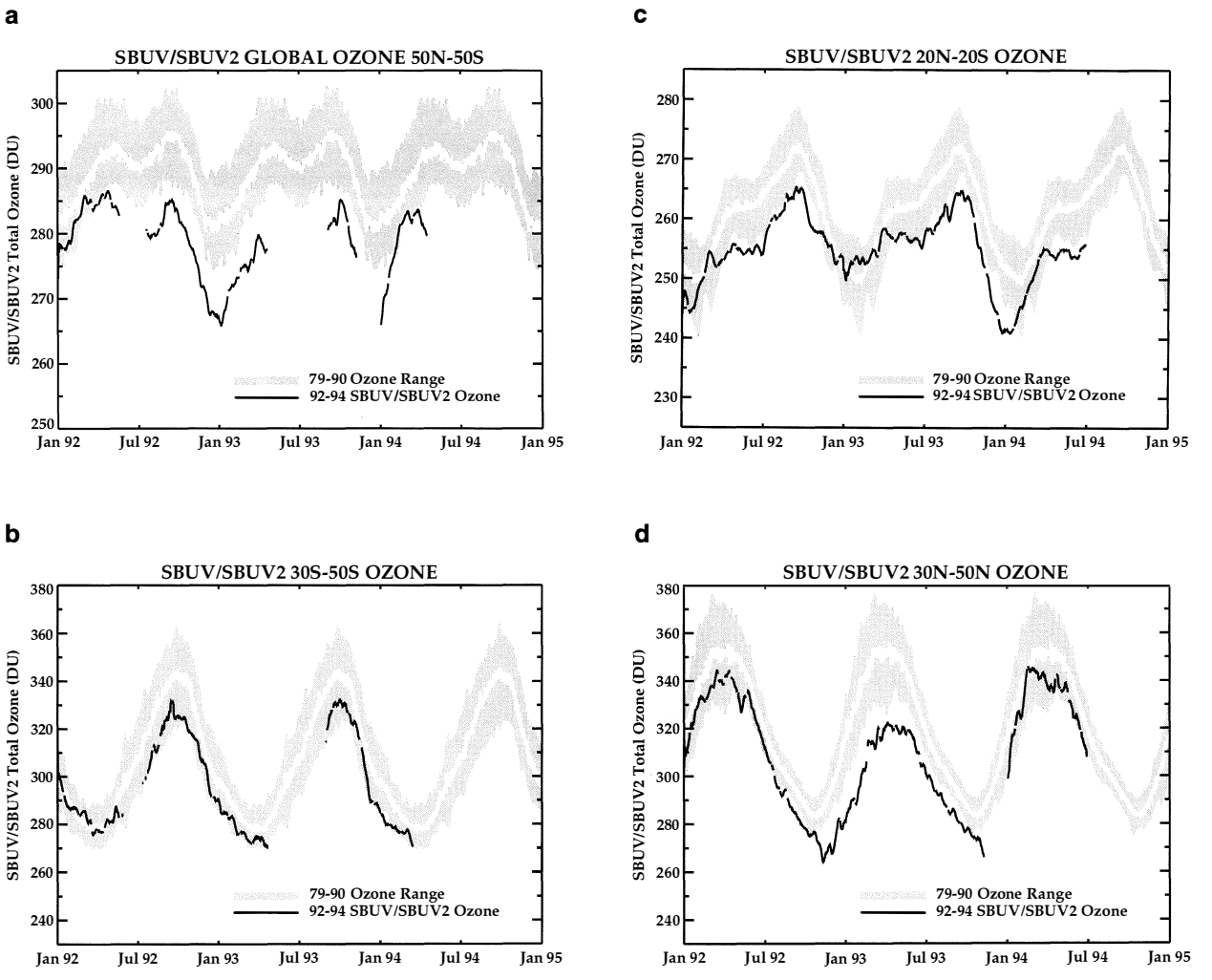

Figure 1-19. Total ozone measured by SBUV and SBUV(/2) since January 1992 compared with the 1980s range and average: (a) 50°N-50°S, Global ozone; (b) 30°-50°S; (c) 20°N-20°S; (d) 30°-50°N.

1993 were about 15% lower than the average values observed before 1970 (Bojkov *et al.*, 1993; Kerr *et al.*, 1993; Komhyr *et al.*, 1994a). The largest ozone losses occurred at higher latitudes in early 1993; deviations were in excess of 60 DU (15% lower than the 1980s mean). Total ozone values over North America in 1994 were in line with the long-term decline, but no longer below it (Hofmann, 1994).

In southern midlatitudes, total ozone values during 1993 were about 15-20 DU below the 1980s mean and were close to the low end of the 1980s range. In the tropics, the maximum negative anomaly was about 10 DU, and from late 1992 to early 1993 total ozone was slightly higher than the 1980s average. Locally, larger anomalies were seen, with negative ozone anomalies of about 15 DU (6%) occurring near the equator in September-November 1991 and in the southern tropics in mid-1992.

The solar cycle and the quasi-biennial oscillation (QBO) affect total ozone levels by a few percent and it is thus useful to remove these influences. Figure 1-20(a) shows the 60°S-60°N average total ozone from SBUV(/2) after these effects (and the annual cycle) have been removed by the statistical analysis described in Section 1.2.2. The most obvious remaining feature is the long-term decrease in total ozone, which has been fitted with a

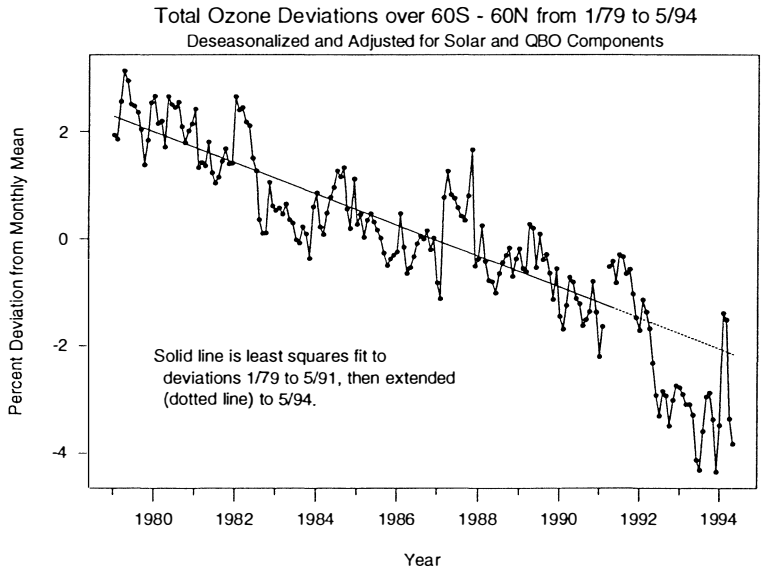

Figure 1-20. (a) Total ozone (60°N-60°S) from 1/79 to 5/94 measured by SBUV(/2). The annual cycle and the effects of the solar cycle and QBO have been removed. The solid line shown is a simple least squares fit to the data through 5/91. The dashed line is an extrapolation through 5/94.

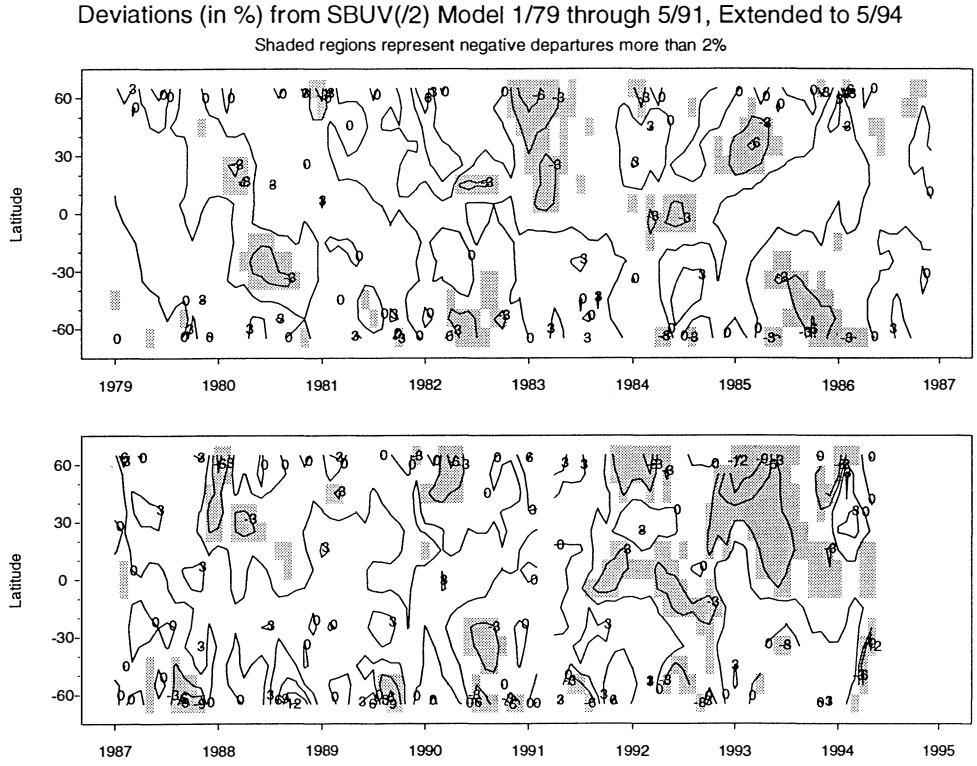

Figure 1-20. (b) Contour plots of total ozone residuals as a function of latitude and time from the statistical fit to the SBUV(/2) satellite data over the period 1/79 to 5/91. The fitted model was extrapolated through 5/94 to calculate the residuals over the extended period 1/79-5/94. The total ozone data have the seasonal, trend, solar, and QBO components removed, and the resulting deviations are expressed as percentages of the mean ozone level at the beginning of the series. Shown are contours of constant deviations at intervals of 3%, and the shaded areas indicate negative departures of at least 2%. The 1992-1993 low ozone values are prominent, as well as other periods of very low values in 1982-1983 and 1985.

linear trend (-2.9% per decade) from January 1979 to May 1991 (pre-Pinatubo). The recent (1992-1993) global anomaly is about 2% below the trend line and about 1% less than previous negative anomalies. The 1992-1993 anomaly also stands out as the most persistent, spanning nearly 2 years. The only other negative anomaly lasting more than one year followed the El Chichón eruption in 1982. Figure 1-20(b) shows the time evolution at all latitudes (60°S-60°N) of the total ozone deviations found after the removal of the trend found for 1/79 to 5/91 (extrapolated to 5/94), the annual cycle, and the effects of the solar cycle and the QBO. The strong regional nature of the deviations is again obvious, with the largest (6-10%) occurring in northern midlatitudes in January to April 1993. The Southern Hemisphere, by contrast, was hardly affected.

1.4.2 Vertical Profile Information

Figure 1-21(a) shows the ozonesonde measurements at Edmonton made in January-April in 1980/1982, 1988/1991, and 1993 (Kerr *et al.*, 1993). Similar results were found at Resolute, Goose Bay, and Churchill. These indicate that the decrease in early 1993 occurred in the same altitude region as the decline during the 1980s. The standard deviations are ±8 nbar (1980-1982 and 1988-1991 profiles) and ±9 nbar (1993 profiles) where the maximum ozone difference is found (100 mbar). The differences between the 1993 and 1980-1982 profiles are statistically significant (2 standard deviations) between 200 and 40 mbar. Ozone levels were depleted by about 25% over approximately 14-23 km (at and below the profile maximum), spatially coincident with the observed aerosol maximum, as shown in Figure 1-21(b) (Hofmann *et al.*, 1994a). Notably, there is substantial ozone increase above the profile maximum (above 25 km) at Boulder, of about 15% of background levels, which is also seen at Hilo, Hawaii (Hofmann *et al.*, 1993).

1.4.3 Stratospheric Aerosol after the Eruption of Mt. Pinatubo

The eruption in the Philippines of Mt. Pinatubo (15°N, 120°E) in June 1991 injected approximately 20 Tg of sulfur dioxide (SO_2) directly into the lower stratosphere at altitudes as high as 30 km. Within a month or so, this SO_2 was oxidized to sulfuric acid, which rapidly condensed as aerosol. In August 1991, Volcán Hudson (46°S, 73°W) erupted and deposited about 2 Tg of SO_2 into the lower stratosphere, mostly below 14 km. Several studies of the SO_2 and aerosol observations have been published (*e.g.,* Bluth *et al.*, 1992; Lambert *et al.*, 1993; Read *et al.*, 1993; Trepte *et al.*, 1993; Deshler *et al.*, 1993; Hofmann *et al.*, 1994b), which are now briefly discussed. The latitudinal variation of optical depth from 1991 to 1994 is shown in Figure 1-22 as measured by SAGE II and the Stratospheric Aerosol Measurement (SAM II) instrument.

The initial aerosol cloud from Mt. Pinatubo dispersed zonally but was confined mostly within the tropics below 30 km for the first several months. By September 1991 the Mt. Pinatubo aerosol had moved into the midlatitude Southern Hemisphere at altitudes between 15 and 30 km. It did not enter into the Antarctic vortex in 1991, unlike the aerosol from Volcán Hudson, which was observed at altitudes of 10-13 km over McMurdo station, 78°S (Deshler *et al.*, 1992). In the tropics the Mt. Pinatubo plume rose to altitudes of 30 km during December 1991-March 1992. Strong dispersal from the tropics into northern middle-high latitudes was observed during the 1991-1992 winter, and enhanced aerosol levels have been detected over 15-25 km in the Northern Hemisphere since that time.

The total mass of the stratospheric aerosol maximized several months after the eruption at about 30 Tg and thereafter remained fairly constant until mid-1992, since when it has been declining with an approximate e-folding time of one year. The total aerosol loading in January 1994 was about 5 Tg, still 5-10 times higher than the background levels observed before the Mt. Pinatubo eruption.

The size distribution of the aerosol particles evolved significantly over time, increasing in effective radius from approximately 0.2 μm just after the eruption to a peak of some 0.6-0.8 μm a year or so later, since when it has slowly decreased (Deshler *et al.*, 1993). At northern midlatitudes, the aerosol surface area peaked at about 40 $\mu m^2\ cm^{-3}$ (Figure 1-23). The altitude of the maximum surface area has episodically decreased since early 1992.

Negative total ozone anomalies of about 15 DU, 6%, occurred near the equator in September-November 1991 (Schoeberl *et al.*, 1993; Chandra, 1993), at the same time that the maximum temperature increase,

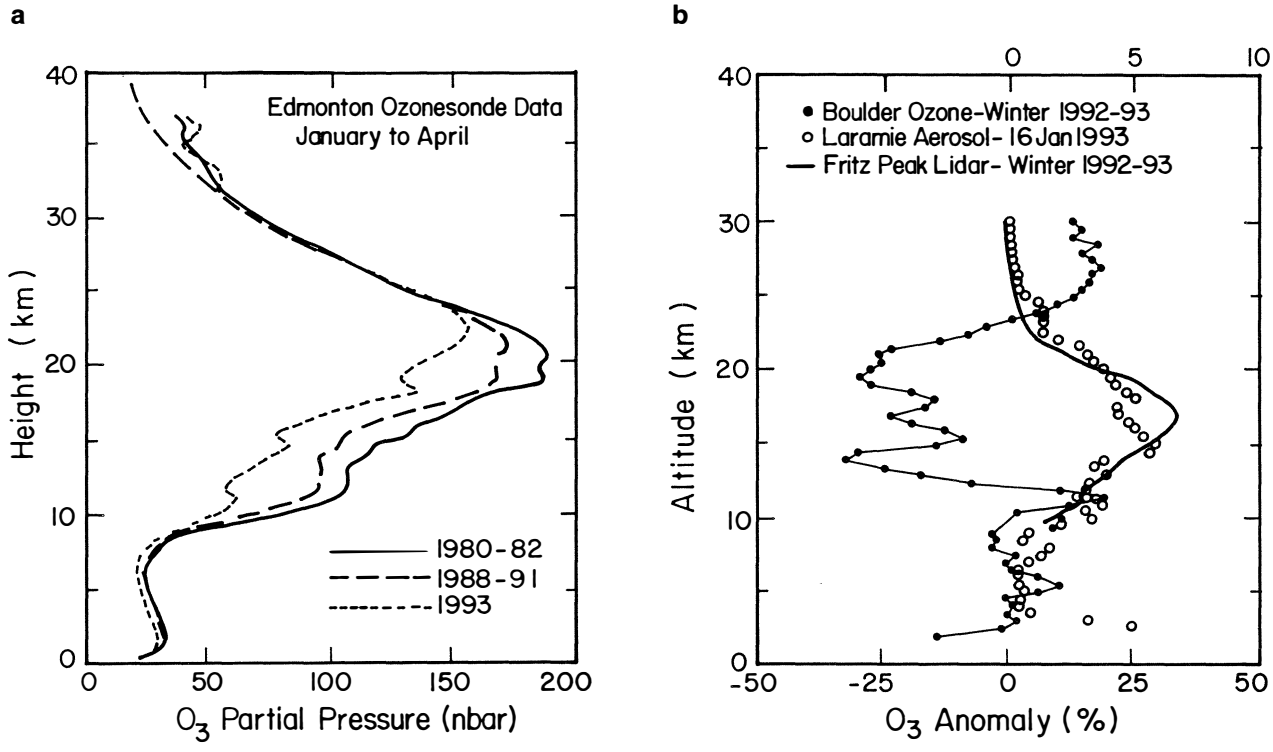

Figure 1-21. (a) Average ozone profiles found from ozonesonde measurements at Edmonton in spring (January to April) for 1980-1982 (46 sondes), 1988-1991 (42 sondes), and 1993 (13 sondes). Adapted from Kerr *et al.*, 1993. (b) Percentage differences (bottom axis) in the ozonesonde measurements at Boulder in 1992-1993 relative to 1985-1989. Also shown are the aerosol data from the Fritz Peak lidar (bottom axis: backscatter in 10^8 ST^{-1} m^{-1}) and the University of Wyoming particle counter (top axis: aerosol concentration in cm^{-3}) for winter 1992-1993. Adapted from Hofmann *et al.*, 1994a.

about 2-3K at 30-50 mbar, was observed (Labitske and McCormick, 1992). These early tropical ozone anomalies are probably related to enhanced vertical motions induced by the aerosol heating (Brasseur and Granier, 1992; Young *et al.*, 1994), but gas phase perturbations to the gas phase photochemistry by the initially high concentrations of SO_2 may also have played a part (Bekki *et al.*, 1993).

In addition to radiative and dynamical influences, the Mt. Pinatubo aerosol provides a surface on which chemical reactions can occur, possibly leading to chemical ozone loss, as discussed in Chapters 3 and 4. These reactions tend to proceed faster at lower temperatures and the ozone depletion process is more effective at low light levels. In this context it is worth noting that both the 1991/1992 and 1992/1993 northern winters were cold with later-than-average final warmings (*e.g.*, Naujokat *et al.*, 1993), and that the cold temperatures occurred both within and on the edge of the Arctic vortex, so that there was the opportunity for large areas to be affected.

For comparison, the maximum aerosol surface area and its peak altitude following the eruption of El Chichón in early 1982 are shown in Figure 1-23. The Mt. Pinatubo eruption provided twice the aerosol surface area as that from El Chichón. The total ozone anomalies in 1982/1983 (as compared with 1980, 1981, 1985, 1986 TOMS values) are now thought to have been smaller than the earlier initial estimates, about 3-4% in the 1982/1983 winter rather than 10% (Stolarski and Krueger, 1988).

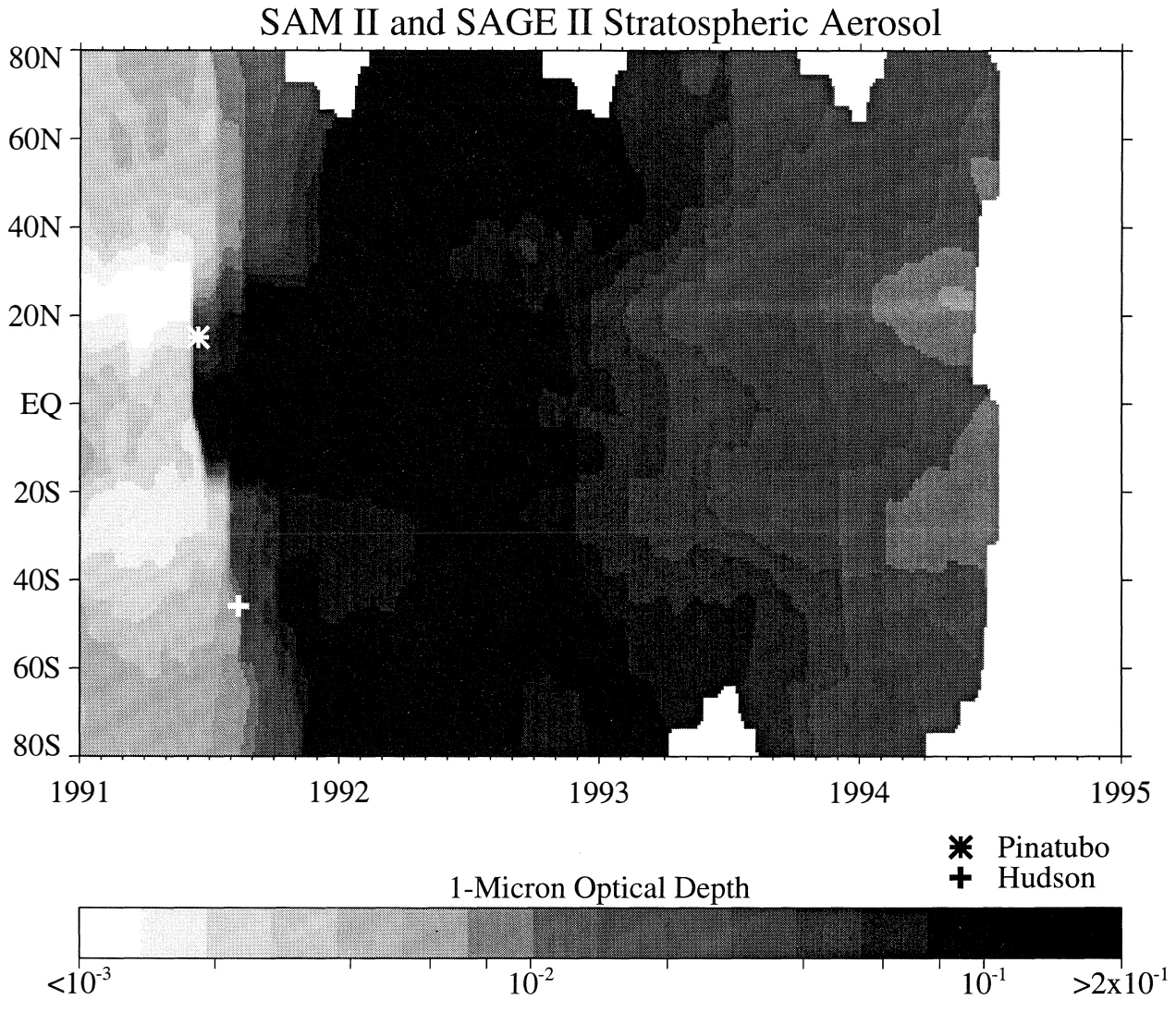

Figure 1-22. Aerosol optical depths from 1991-1994 measured by SAM II and SAGE II showing the effects of the Mt. Pinatubo (*) and Volcán Hudson (+) volcanic eruptions. (Updated by L. Thomason from data shown in Trepte *et al.*, 1993.)

1.4.4 Dynamical Influences

Natural variations in ozone are induced by meteorological phenomena such as the El Niño-Southern Oscillation (ENSO), in addition to the QBO (*e.g.*, Zerefos, 1983; Bojkov, 1987; Komhyr *et al.*, 1991; Zerefos *et al.*, 1992). Thus the observed ozone anomalies since 1991 will have been affected to some degree by the prolonged El Niño event that lasted throughout 1992/1993. The amplitude of the El Niño effect in total ozone is 2-6%, but such anomalies are highly localized. While ENSO effects for zonal or large-area means were about 1%, ozone in specific areas may have been reduced by an additional 2-3% in 1992-1993 (Zerefos *et al.*, 1992; Shiotani, 1992; Zerefos *et al.*, 1994; Randel and Cobb, 1994). Other dynamical influences can strongly affect total ozone on a regional basis; one clear example was the persistent blocking anti-cyclone in the northeast Atlantic from December 1991 to February 1992 (Farman *et al.*, 1994).

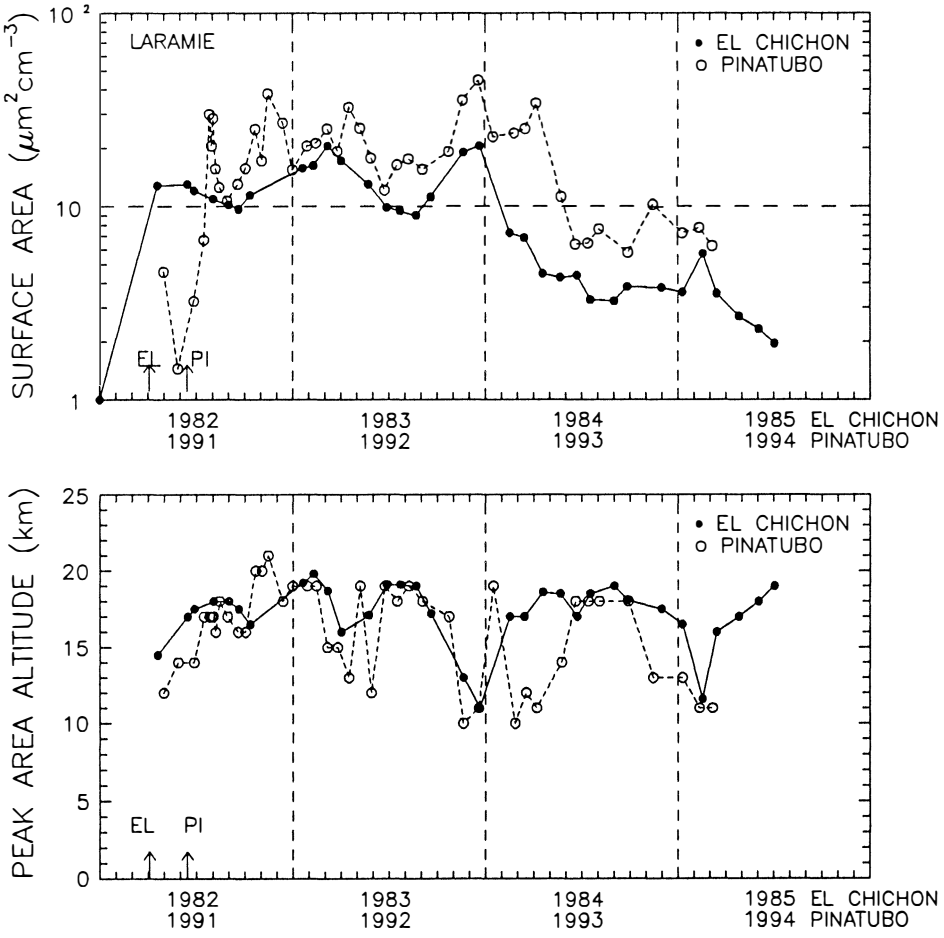

Figure 1-23. The maximum surface area and its altitude observed at Laramie, Wyoming, in the years following the El Chichón and Mt. Pinatubo eruptions (Deshler *et al.*, 1993).

1.5 ANTARCTIC OZONE DEPLETION

1.5.1 Introduction and Historical Data

Total ozone records obtained with Dobson spectrophotometers with a traceable calibration are available for Antarctica from 1957 at the British stations Halley (76°S, formerly Halley Bay) and Faraday (65°S, formerly Argentine Islands). They are available from the American station at the South Pole (Amundsen-Scott, 90°S) since 1962 and at the Japanese station Syowa (69°S) since 1966, although measurements had been obtained at Syowa in 1961. Figure 1-24 shows October monthly means for these four stations. In the case of the South Pole station, the average is for October 15-31 since inadequate sunlight precludes accurate total ozone measurements from the surface before about October 12.

Halley and Amundsen-Scott show similar long-term total ozone declines in October, presumably reflecting the fact that the region of most severe ozone depletion is generally shifted off the pole towards east Antarctica. The decline in ozone above these stations began in the late 1960s, accelerated around 1980, and after 1985 remained relatively constant at a total ozone value of about 160 DU. In 1993, record low values (about 116 DU) were recorded at Halley and Amundsen-Scott.

The decline in total ozone at Faraday and Syowa in October was more subtle, if existent at all, prior to 1980. The major decline occurred between 1980 and 1985, lev-

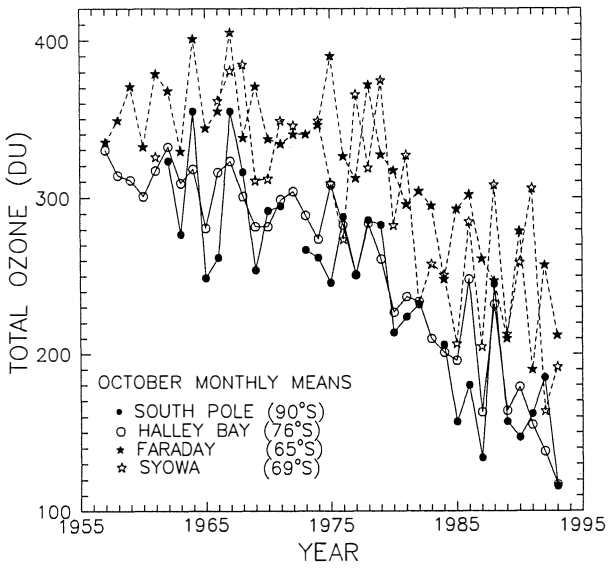

Figure 1-24. The historical springtime total ozone record for Antarctica as measured by Dobson spectrophotometers during October at Halley Bay, Syowa, and Faraday and from 15-31 October at South Pole. (Data courtesy J. Shanklin, T. Ito, and D. Hofmann.)

elling off with a value of total ozone of about 260 DU thereafter. An unusually low value of about 160 DU was observed at Syowa in 1992, a feature not seen at Faraday.

Although the earliest ozone vertical profiles showing the 1980 rapid ozone hole onset were obtained at Syowa in 1983 (Chubachi, 1984), the most extensive set of ozone profile data for trend studies has been obtained at the South Pole using ECC ozonesondes throughout (Oltmans *et al.*, 1994). This data set includes the approximately 500 year-round profiles measured between 1986 and 1993, and a series of about 85 profiles made between 1967 and 1971. Winter data for the earlier period do not extend to as high an altitude because rubber balloons were used. Figure 1-25 shows a comparison of smoothed monthly average ozone mixing ratio values at pressure levels 400 hPa (~6.5 km), 200 hPa (~10.5 km), 100 hPa (~14.5 km), 70 hPa (~16.5 km), 40 hPa (~19.5 km) and 25 hPa (~22.5 km) for these two periods. The major springtime ozone depletion has occurred in the 14-22 km region at the South Pole between the 1967-1971 and 1986-1991 periods, and it has worsened since 1992. The 1967-1971 data indicate a weak minimum in the spring in the 40-100 hPa (14-19 km) region. This feature might result from heterogeneous ozone loss related to considerably lower stratospheric chlorine levels, consistent with the weak downward trend in total ozone at South Pole for this period shown in Figure 1-24. In 1992 and 1993, ozone was almost completely destroyed in the 70-100 hPa range (14-17 km).

Summer (December to February) ozone levels in 1986-1991 are lower in the 70-200 hPa (10-17 km) region than they were in 1967-1971. The ozone that is transported to the South Pole following vortex breakdown at these altitudes now replenishes the ozone lost during the previous spring, rather than causing the marked late spring maximum which existed in 1967-1971. At all altitudes, ozone values from March to August are similar (to within about 10%) in the two periods.

Rigaud and Leroy (1990) reanalyzed measurements taken at Dumont d'Urville (67°S) in 1958 using a double monochromator with spectrographic plates (Fabry and Buisson, 1930; Chalonge and Vassey, 1934). They calculated some very low total ozone values (as low as 110 DU) that are only observed nowadays in the ozone hole. De Muer (1990) and Newman (1994) have examined the available 1958 meteorological and total ozone data. They find that the early Dumont d'Urville data are inconsistent with any other source of data from 1958: (a) the variability was greater throughout the year than that measured with any Dobson spectrophotometer in Antarctica that year (Figure 1-24); (b) Dumont d'Urville was not under the vortex that year (see also Alt *et al.*, 1959), but under the warm belt where ozone values are high; and (c) while the climatologies of measurements taken by Dobson instruments that year are fully consistent with those derived from TOMS measurements in the last decade, there is little or no consistency between the TOMS climatologies and that from Dumont d'Urville in 1958. Some doubts concerning a number of experimental aspects of the spectrographic plate instrument are also raised. These reported values thus appear to be a good example of being able to detect ozone without necessarily being able to measure it well.

1.5.2 Recent Observations

Figure 1-26 shows monthly average total column ozone measured at the South Pole by balloon-borne

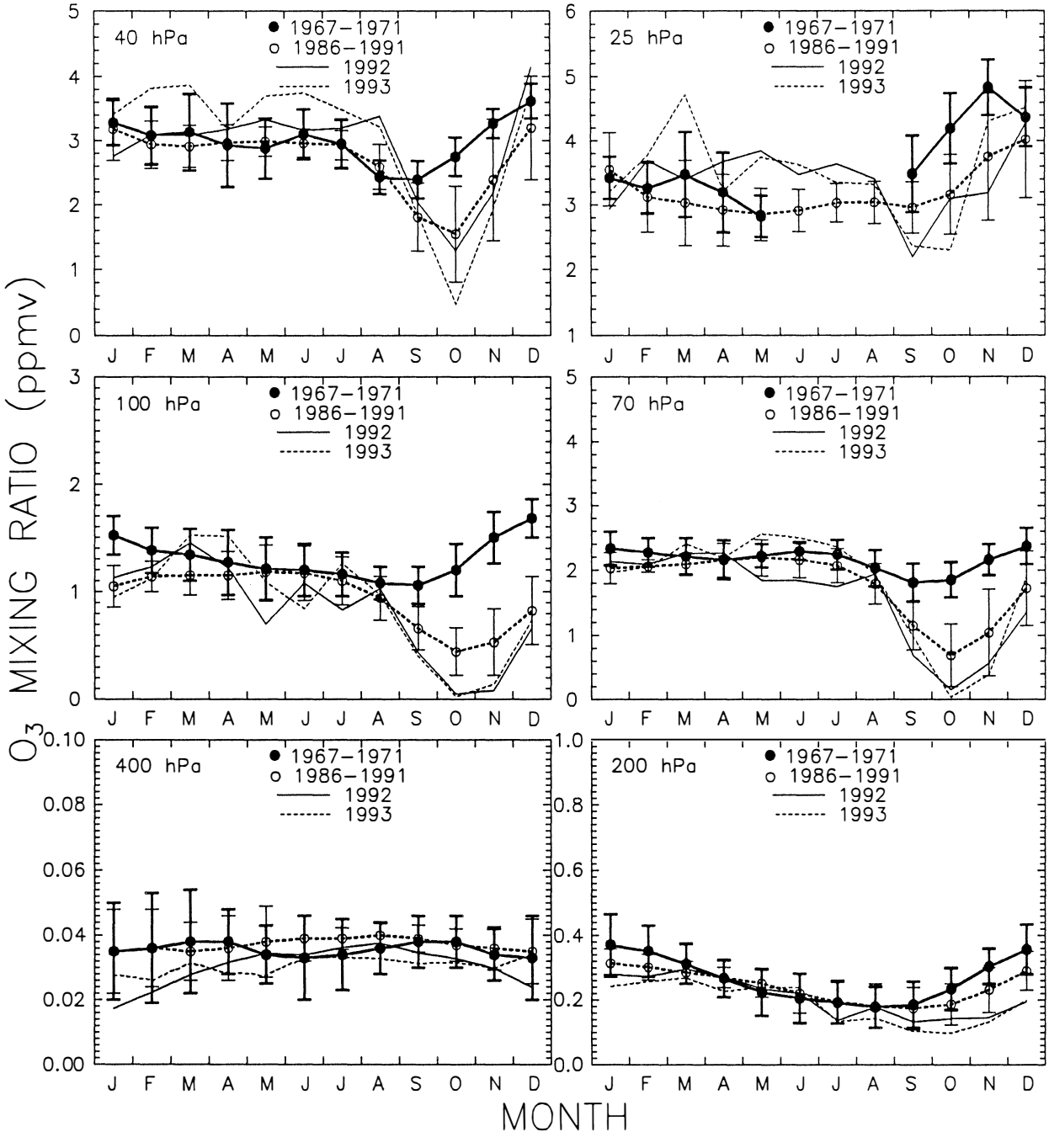

Figure 1-25. Comparison of smoothed monthly average ozone mixing ratios at 6 pressure levels for the 1967-1971 period (filled points and full lines), the 1986-1991 period (open points and dashed lines), and for 1992 and 1993 (straight and dashed lines, respectively). The error bars represent ±1 standard deviation. (Adapted from Oltmans *et al.*, 1994.)

ozonesondes since 1986 (Hofmann *et al.*, 1994b). (Total ozone is obtained by assuming that the ozone mixing ratio is constant above the highest altitude attained, a procedure that has an estimated uncertainty of about 2-3 DU.) These data are independent of the Dobson spectrophotometer data shown in Figure 1-24 and corroborate the fact that the major springtime depletion started between the 1967-1971 and 1986-1991 periods.

On 12 October 1993, total ozone at the South Pole fell to a new low of 91 DU, well below the previous low of 105 DU measured there in October 1992. Sub-100 DU readings were observed on 4 occasions and readings in the 90-105 DU range were measured on 8 consecutive soundings from 25 September to 18 October 1993.

Ozone levels in austral winter prior to the depletion period show no systematic variation, with values of 250 ± 30 DU. Similarly, coming out of the depletion period, January values show no systematic variation since 1986, but are lower than the 1967-1971 values.

At the South Pole, both Dobson spectrophotometer and Meteor TOMS measurements showed record low total ozone levels after the return of adequate sunlight in mid-October. Similarly, NOAA-11 SBUV2 measurements indicate new record lows for the 70°S-80°S region in 1993 (NOAA, 1993). Thus, since 1991, the September total ozone decline has continued/worsened.

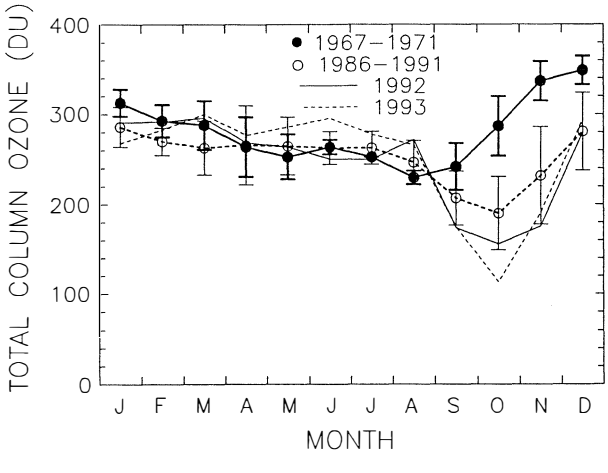

Figure 1-26. Monthly averaged total column ozone by month measured in balloon flights at South Pole for the 1967-1971 and 1986-1993 periods, and for 1992 and 1993 (straight and dashed lines, respectively). (Adapted from Oltmans *et al.*, 1994.)

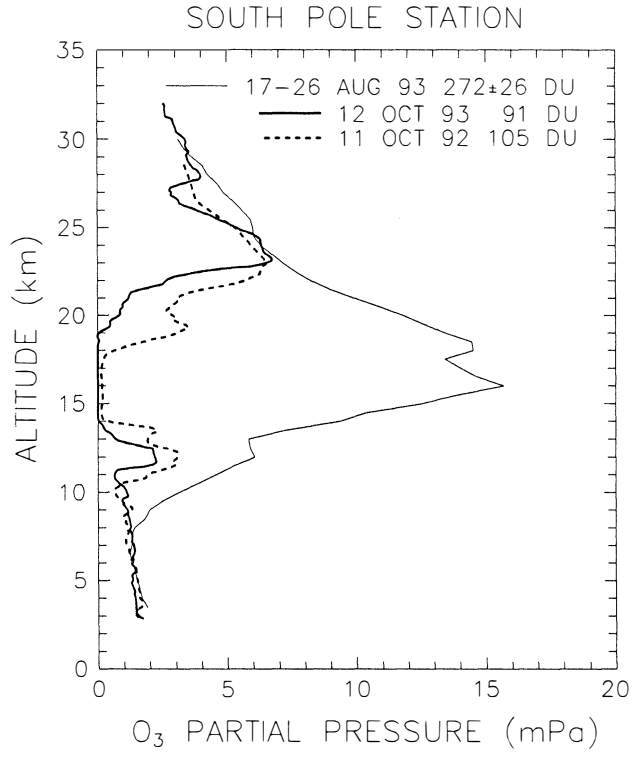

Figure 1-27. Comparison of the South Pole pre-depletion ozone profile in 1993 (average of 4 soundings) with the profile observed when total ozone reached a minimum in 1992 and 1993. (Adapted from Hofmann *et al.*, 1994b.)

In Figure 1-27 the average of four ozone profiles before depletion began in August 1993 is compared with the profiles at the time of minimum ozone in 1992 and 1993 (Hofmann *et al.*, 1994b). Total destruction (>99%) of ozone was observed from 14 to 19 km in 1993, a 1 km upward extension of the zero-ozone region from the previously most severe year, 1992. Unusually cold temperatures in the 20 km region are believed to be the main cause of lower-than-normal ozone in the 18-23 km range. These lower temperatures prolong the presence of polar stratospheric clouds (PSCs), in particular nitric acid trihydrate (NAT), thought to be the dominant component of PSCs. This tends to enhance the production and lifetime of reactive chlorine and concomitant ozone depletion at the upper boundary of the ozone hole, because chlorine in this region is not totally activated in years with normal temperatures. Temperatures at 20 km in September 1993 were similar to those of 1987 and

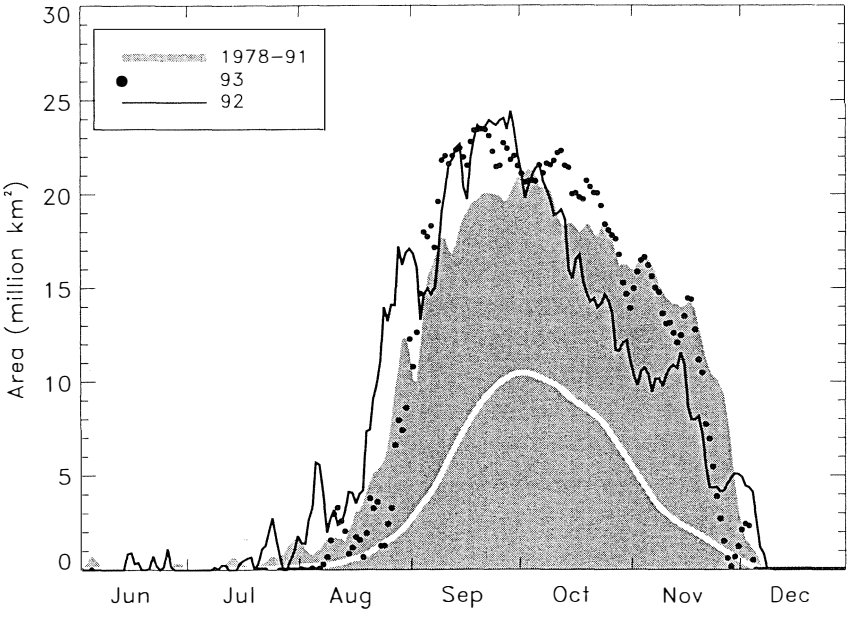

Figure 1-28. Area of the region enclosed by the 220 DU total ozone contour in the Southern Hemisphere. The white line represents the 1978-1991 average with the shaded area representing the extremes for this period. The 1992 and 1993 areas are represented by the continuous line and points, respectively. 12 million square kilometers is about 5% of the surface area of the Southern Hemisphere, so that the maximum extent of the region in 1992 or 1993 with total ozone less than 220 DU, if circular, was about 65°S. Data for 1978-1992 are from Nimbus 7 TOMS; data for 1993 are from Meteor TOMS. Only measurements made south of 40°S were considered, to avoid including any low tropical values recorded. (Courtesy of the Ozone Processing Team, NASA Goddard.)

1989, other very cold years at this altitude. Cold sulfate aerosol from Mt. Pinatubo, present at altitudes between 10 and 16 km, probably contributed to the low ozone through heterogeneous conversion of chlorine species (see Chapters 3 and 4).

Figure 1-28 shows the horizontal extent of the Antarctic ozone hole in terms of the area contained within the 220 DU total ozone contour from Nimbus TOMS (1978-1991 shaded region and 1992 curve) and from Meteor TOMS (1993 points). These data indicate that the 1992 and 1993 ozone hole areas were the largest on record and that the development of the depleted region began about 1-2 weeks earlier, a fact also apparent in the total ozone data in Figure 1-26.

Since 1991, springtime ozone depletion at the South Pole has worsened in the 12-16 km region, with total ozone destruction at 15-16 km in 1992 and 1993. Similar observations were made in 1992 at McMurdo, 78°S (Johnson *et al.*, 1994), Syowa, 69°S (T. Ito, private communication), and Georg Forster stations (71°S) (H. Gernandt, private communication), indicating that this depletion at lower altitudes was widespread. In addition, the 1993 springtime ozone loss was very severe in the 18-22 km region, effectively extending the ozone depletion region upward by about 1-2 km (Figure 1-27). This occurred in spite of ozone being considerably higher than normal during the preceding winter (Figure 1-26). Complete ozone destruction from 14 to 19 km was peculiar to 1993 and, combined with lower-than-normal ozone at 20-22 km, resulted in the record low total ozone recorded in early October 1993.

The decrease in summer ozone levels at 10-17 km since the late 1960s is not apparent in the 1986-1993 data, possibly because the record is too short.

REFERENCES

Akimoto, H., N. Nakane, and Y. Matsumoto, The chemistry of oxidant generation: Tropospheric ozone increase in Japan, in *The Chemistry of the Atmosphere: Its Impact on Global Change*, edited by J.G. Calvert, Blackwell Sci. Publ., Oxford, 261-273, 1994.

Albert-Levy, Analyse de l'air, *Annulaire de l'Obser. de Montsouris*, Gauthier-Villars, Paris, 495-505, 1878.

Alt, J., P. Astapenko, and N.J. Roper, Some aspects of the Antarctic atmospheric circulation in 1958, *IGY General Report Series, 4,* 1-28, 1959.

Anfossi, D., S. Sandroni, and S. Viarengo, Tropospheric ozone in the nineteenth century: The Montalieri series, *J. Geophys. Res., 96,* 17349-17352, 1991.

Attmannspacher, W., and H. Dütsch, International ozone sonde intercomparison at the Observatory of Hohenpeissenberg, *Berichte des Deutschen Wetterdienstes, 120,* 85 pp., 1970.

Attmannspacher, W., and H. Dütsch, 2nd International ozone sonde intercomparison at the Observatory of Hohenpeissenberg, *Berichte des Deutschen Wetterdienstes, 157,* 65 pp., 1981.

Attmannspacher, W., J. de la Noé, D. De Muer, J. Lenoble, G. Mégie, J. Pelon, P. Pruvost, and R. Reiter, European validation of SAGE II ozone profiles, *J. Geophys. Res., 94,* 8461-8466, 1989.

Barnes, R.A., A.R. Bandy, and A.L. Torres, Electrochemical concentration cell ozonesonde accuracy and precision, *J. Geophys. Res., 90,* 7881-7887, 1985.

Barnes, R.A., L.R. McMaster, W.P. Chu, M.P. McCormick, and M.E. Gelman, Stratospheric Aerosol and Gas Experiment II and ROCOZ-A ozone profiles at Natal, Brazil: A basis for comparison with other satellite instruments, *J. Geophys. Res., 96,* 7515-7530, 1991.

Bass, A.M., and R.J. Paur, The ultraviolet cross-sections of ozone: I. The measurements, in *Atmospheric Ozone*, edited by C.S. Zerefos and A.M. Ghazi, Reidel, Dordrecht, The Netherlands, 606-610, 1985.

Bekki, S., R. Toumi, and J.A. Pyle, Role of sulphur photochemistry in tropical ozone changes after the eruption of Mount Pinatubo, *Nature, 362,* 331-333, 1993.

Bhartia, P.K., J. Herman, R.D. McPeters, and O. Torres, Effect of Mt. Pinatubo aerosols on total ozone measurements from backscatter ultraviolet (BUV) experiments, *J. Geophys. Res., 98,* 18547-18554, 1993.

Bluth, G.J.S., S.D. Doiron, C.C. Schnetzler, A.J. Krueger, and L.S. Walter, Global tracking of the SO_2 clouds from the June 1991 Mount Pinatubo eruptions, *Geophys. Res. Lett., 19,* 151-154, 1992.

Bojkov, R.D., Surface ozone during the second half of the nineteenth century, *J. Clim. Appl. Meteorol., 25,* 343-352, 1986.

Bojkov, R.D., The 1983 and 1985 anomalies in ozone distribution in perspective, *Mon. Wea. Rev., 115,* 2187-2201, 1987.

Bojkov, R.D., Ozone changes at the surface and in the free troposphere, in *Tropospheric Ozone, Regional and Global Scale Interactions,* edited by I.S.A. Isaksen, NATO ASI Series C, 227, 83-96, Reidel, Dordrecht, The Netherlands, 1988.

Bojkov, R.D., L. Bishop, W.J. Hill, G.C. Reinsel, and G.C. Tiao, A statistical trend analysis of revised Dobson total ozone data over the Northern Hemisphere, *J. Geophys. Res., 95,* 9785-9807, 1990.

Bojkov, R.D., C.S. Zerefos, D.S. Balis, I.C. Ziomas, and A.F. Bais, Record low total ozone during northern winters of 1992 and 1993, *Geophys. Res. Lett., 20,* 1351-1354, 1993.

Bojkov, R.D., V.E. Fioletov, and A.M. Shalamjansky, Total ozone changes over Eurasia since 1973 based on reevaluated filter ozonometer data, *J. Geophys. Res., 99,* 22985-22999, 1994.

Brasseur, G., and C. Granier, Mount Pinatubo aerosols, chlorofluorocarbons and ozone depletion, *Science, 257,* 1239-1242, 1992.

Chalonge, D., and E. Vassy, Spectrographic astigmatique à prisme objectif, *Rev. Opt. Theor. Instrum., 13,* 113-126, 1934.

Chandra, S., Changes in stratospheric ozone and temperature due to the eruption of Mt. Pinatubo, *Geophys. Res. Lett., 20,* 33-36, 1993.

Chu, W.P., M.P. McCormick, J. Lenoble, C. Brogniez, and P. Pruvost, SAGE II inversion algorithm, *J. Geophys. Res., 94,* 8339-8351, 1989.

Chubachi, S., Preliminary result of ozone observations at Syowa Stations from February, 1982 to January 1983, *Mem. Natl. Inst. Polar. Res., Spec. Iss., 34,* 13-18, 1984.

Cunnold, D.M., W.P. Chu, R.A. Barnes, M.P. McCormick, and R.E. Veiga, Validation of SAGE II ozone measurements, *J. Geophys. Res., 94,* 8447-8460, 1989.

De Muer, D., Comment on "Presumptive Evidence for a Low Value of the Total Ozone Content above Antarctica in September, 1958" by P. Rigaud and B. Leroy, *Annales Geophysicae, 11,* 795-796, 1990.

De Muer, D., H. De Backer, R.E. Veiga, and J.M. Zawodny, Comparison of SAGE II ozone measurements and ozone soundings at Uccle (Belgium) during the period February 1985 to January 1986, *J. Geophys. Res., 95,* 11903-11911, 1990.

De Muer, D., and H. De Backer, Revision of 20 years of Dobson total ozone data at Uccle (Belgium): Fictitious Dobson total ozone trends induced by sulfur dioxide trends, *J. Geophys. Res., 97,* 5921-5937, 1992.

De Muer, D., and H. De Backer, Influence of sulphur dioxide trends on Dobson measurements and on electrochemical ozone soundings, in *Proceedings of the Society of Photo-Optical Instrumentation Engineers, 2047, 33,* 18-26, 1993.

De Muer, D., and H. De Backer, Trend analysis of 25 years of regular ozone soundings at Uccle (Belgium), Abstract, EUROTRAC meeting, Garmisch-Partenkirchen, April 1994.

Degórska, M., B. Rajewska-Wiech, and R.B. Rybka, Total ozone over Belsk: Updating of trends through 1991 and comparison of the Dobson data with those from TOMS in 1978-1991, *Publs. Inst. Geophys. Pol. Acad. Soc., 252,* 53-58, 1992.

DeLuisi, J.J., D.A. Londenecker, C.L. Mateer, and D.J. Wuebbles, An analysis of Northern middle latitude Umkehr measurements corrected for stratospheric aerosols for 1979-1986, *J. Geophys. Res., 94,* 9837-9846, 1989.

DeLuisi, J.J., C.L. Mateer, D. Theisen, P.K. Bhartia, D. Longenecker, and B. Chu, Northern middle-latitude ozone profile features and trends observed by SBUV and Umkehr, 1979-1990, *J. Geophys. Res., 99,* 18901-18908, 1994.

Deshler, T., A. Adriani, G.P. Gobbi, D.J. Hofmann, G. Di Donfrancesco, and B.J. Johnson, Volcanic aerosol and ozone depletion within the Antarctic polar vortex during the austral spring of 1991, *Geophys. Res. Lett., 19,* 1819-1822, 1992.

Deshler, T., B.J. Johnson, and W.R. Rozier, Balloonborne measurements of Pinatubo aerosol during 1991 and 1992 at 41°N: Vertical profiles, size distribution and volatility, *Geophys. Res. Lett., 20,* 1435-1438, 1993.

Dobson, G.M.B., Observers handbook for the ozone spectrophotometer, *Ann. IGY, 5,* 46-89, 1957.

Dobson, G.M.B., Forty years' research on atmospheric ozone at Oxford: A history, *Applied Optics, 7,* 401, 1968.

Dütsch, H.U., W. Zuliz, and C.C. Ling, Regular ozone observations at Thalwill, Switzerland and at Boulder, Colorado, *Rep. LAPETH 1*, Lab. Atmosphärenphys. Edigenöss., Tech. Hochsch., Zurich, 1970.

Fabry, C., and H. Buisson, L'absorption des radiations dans la haute atmosphere, *Memorial Sc. Phys., 11,* 1-64, 1930.

Farman, J.C., A. O'Neill, and R. Swinbank, The dynamics of the arctic polar vortex during the EASOE campaign, *Geophys. Res. Lett., 21,* 1195-1198, 1994.

Feister, U., and W. Warmbt, Long-term measurements of surface ozone in the German Democratic Republic, *J. Atmos. Chem., 5,* 1-21, 1987.

Fox, C.B., *Ozone and Antozone*, Churchill Publ., London, 1873.

Furrer, R., W. Döhler, H. Kirsch, P. Plessing, and U. Görsdorf, Evidence for vertical ozone redistribution since 1967, *J. Atmos. Terr. Phys., 11,* 1423-1445, 1992.

Furrer, R., W. Döhler, H. Kirsch, P. Plessing, and U. Görsdorf, Evidence for vertical ozone redistribution since 1967, *Surveys in Geophysics, 14,* 197-222, 1993.

Gleason, J.F., P.K. Bhartia, J.R. Herman, R. McPeters, P. Newman, R.S. Stolarski, L. Flynn, G. Labow, D. Larko, C. Seftor, C. Wellemeyer, W.D. Komhyr, A.J. Miller, and W. Planet, Record low global ozone in 1992, *Science, 260,* 523-526, 1993.

Görsdorf, U., H. Steinhagen, and H. Gernandt, Bestimmung der Forderleistung von Ozonsondenpumpen bei veränderlichen Messbedingungen, *Z. Meteoro.*, in press, 1994.

Götz, F.W.P., Zum Strahlungsklima des Spitzbergensommers. Strahlungs- und Ozonmessungen in der Königsbucht 1929, *Gerlands Beitr. Geophys., 31,* 119, 1931.

Götz, F.W.P., and F. Volz, Aroser Messungen des Ozonegehaltes in der unteren Troposphäre und sein Jahresgang, *Z. Naturforsch., 6a,* 634-639, 1951.

Grass, R.D., and W.D. Komhyr, Traveling standard lamp calibration checks of Dobson ozone spectrophotometers during 1985-1987, in *Ozone in the Atmosphere*, edited by R.D. Bojkov and P. Fabian, A. Deepak Publ., Hampton, Virginia, 144-146, 1989.

Henriksen, K., T. Svenøe, and S.H.H. Larsen, On the stability of the ozone layer at Tromsø, *J. Atmos. Terr. Phys., 54,* 1113-1117, 1992.

Henriksen, K., E.I. Terez, G.A. Terez, V. Roldugin, T. Svenøe, and S.H.H. Larsen, On the stationarity of the ozone layer in Norway and U.S.S.R., *J. Atmos. Terr. Phys., 55,* 145-154, 1993.

Herman, J.R., R.D. Hudson, R.D. McPeters, R.S. Stolarski, Z. Ahmad, X-Y. Gu, S.L. Taylor, and C.G. Wellemeyer, A new self-calibration method applied to TOMS and SBUV backscattered data to determine long-term global ozone change, *J. Geophys. Res., 96,* 7531-7545, 1991.

Herman, J.R., and D. Larko, Low ozone amounts during 1992-1993 from Nimbus 7 and Meteor 3 Total Ozone Mapping Spectrometers, *J. Geophys. Res., 99,* 3483-3496, 1994.

Hilsenrath, E., D.E. Williams, R.T. Caffrey, R.P. Cebula, and S.J. Hynes, Calibration and radiometric stability of the Shuttle Solar Backscattered Ultra-Violet (SSBUV) experiment, *Metrologia*, in press, 1994.

Hofmann, D.J., S.J. Oltmans, J.M. Harris, W.D. Komhyr, J.A. Lathrop, T. DeFoor, and D. Kuniyuki, Ozonesonde measurements at Hilo, Hawaii following the eruption of Pinatubo, *Geophys. Res. Lett., 20,* 1555-1558, 1993.

Hofmann, D.J., S.J. Oltmans, W.D. Komhyr, J.M. Harris, J.A. Lathrop, A.O. Langford, T. Deshler, B.J. Johnson, A. Torres, and W.A. Matthews, Ozone loss in the lower stratosphere over the United States in 1992-1993: Evidence for heterogeneous chemistry on the Pinatubo aerosol, *Geophys. Res. Lett., 21,* 65-68, 1994a.

Hofmann, D.J., S.J. Oltmans, J.A. Lathrop, J.M. Harris, and H. Voemel, Record low ozone at the South Pole in the spring of 1993, *Geophys. Res. Lett., 21,* 421-424, 1994b.

Hofmann, D.J., Recovery of stratospheric ozone over the U.S. in the winter of 1993-1994, *Geophys. Res. Lett., 21,* 1779-1782, 1994.

Hood, L.L., and J.P. McCormack, Components of interannual ozone change based on Nimbus 7 TOMS data, *Geophys. Res. Lett., 19,* 2309-2312, 1992.

Hood, L.L., R.D. McPeters, J.P. McCormack, L.E. Flynn, S.M. Hollandsworth, and J.F. Gleason, Altitude dependence of stratospheric ozone trends based on Nimbus 7 SBUV data, *Geophys. Res. Lett., 20,* 2667-2670, 1993.

Jaffe, D.A., Local sources of pollution in the Arctic: From Prudhoe Bay to the Taz Peninsula, *Pollution of the Arctic Atmosphere*, edited by W.T. Sturges, Elsevier, New York, 255-287, 1991.

Johnson, B.J., T. Deshler, and W.R. Rozier, Ozone profiles at McMurdo station, Antarctica during the austral spring of 1992, *Geophys. Res. Lett., 21,* 269-272, 1994.

Kerr, J.B., C.T. McElroy, D.I. Wardle, R.A. Olafson, and W.F.J. Evans, The automated Brewer spectrophotometer, in *Proceedings 1984 Quadrennial Ozone Symposium*, edited by C.S. Zerefos and A. Ghazi, Reidel Publ., Dodrecht, The Netherlands, 396, 1985.

Kerr, J.B., I.A. Asbridge, and W.F.J. Evans, Intercomparison of total ozone measured by the Brewer and Dobson spectrophotometers at Toronto, *J. Geophys. Res., 93,* 11129-11140, 1988.

Kerr, J.B., I.A. Asbridge, and W.F.J. Evans, Long-term intercomparison between the Brewer and Dobson spectrophotometers at Edmonton, in *Ozone in the Atmosphere*, edited by R.D. Bojkov and P. Fabian, A. Deepak Publ., Hampton, Virginia, 105, 1989.

Kerr, J.B., D.I. Wardle, and D.W. Tarasick, Record low ozone values over Canada in early 1993, *Geophys. Res. Lett., 20,* 1979-1982, 1993.

Kerr, J.B., H. Fast, C.T. McElroy, S.J. Oltmans, J.A. Lathrop, E. Kyro, A. Paukkunen, H. Claude, U. Köhler, C.R. Sreedharan, T. Takao, and Y. Tsukagoshi, The 1991 WMO international ozonesonde intercomparison at Vanscoy, Canada, *Atmosphere-Ocean*, in press, 1994.

Kley, D., A. Volz, and F. Mülhiems, Ozone measurements in historic perspective, in *Tropospheric Ozone, Regional and Global Scale Interactions,* edited by I.S.A. Isaksen, *NATO ASI Series C, 227,* 63-72, Reidel Publ., Dordrecht, The Netherlands, 1988.

Kley, D., H. Geiss, and V.A. Mohnen, Concentrations and trends of tropospheric ozone and precursor emissions in the USA and Europe, in *The Chemistry of the Atmosphere: Its Impact on Global Change*, edited by J.G. Calvert, Blackwell Sci. Publ., Oxford, 245-259, 1994.

Komhyr, W., and T.B. Harris, Note on flow rate measurements made on Brewer-Mast ozone sensor pumps, *Mon. Wea.. Rev., 93,* 267-268, 1965.

Komhyr, W.D., Electrochemical concentration cells for gas analysis, *Ann. Geophys., 25,* 203-210, 1969.

Komhyr, W.D., and T.B. Harris, Development of the ECC ozonesonde, *NOAA Technical Report* ERL 200-APCL 18, U.S. Department of Commerce, NOAA Environmental Research Laboratories, Boulder, Colorado, 54 pp., 1971.

Komhyr, W.D., S.J. Oltmans, R.D. Grass, and R.K. Leonard, Possible influence of long-term sea surface temperature anomalies in the tropical Pacific on global ozone, *Canadian. J. Phys., 65,* 1093-1102, 1991.

Komhyr, W.D., C.L. Mateer, and R.D. Hudson, Effective Bass-Paur 1985 ozone absorption coefficients for use with Dobson ozone spectrophotometers, *J. Geophys. Res., 98,* 451-465, 1993.

Komhyr, W.D., R.D. Grass, R.D. Evans, R.K. Leonard, D.M. Quincy, D.J. Hofmann, and G.L. Koenig, Unprecedented 1993 ozone decrease over the United States from Dobson spectrophotometer observations, *Geophys. Res. Lett., 21,* 210-214, 1994a.

Komhyr, W.D., J.A. Lathrop, D.P. Opperman, R.A. Barnes, and G.B. Brothers, ECC ozonesonde performance evaluation during STOIC 1989, *J. Geophys. Res.*, in press, 1994b.

Krzyścin, J.W., Interannual changes in the atmospheric ozone derived from ground-based measurements, *Papers in Met. and Geophys., 43,* 133-164, 1992.

Krzyścin, J.W., Total ozone changes in the Northern Hemisphere mid-latitudinal belt (30-60°N) derived from Dobson spectrophotometer measurements, 1964-1988, *J. Atmos. Terr. Phys., 56,* 1051-1056, 1994a.

Krzyścin, J.W., Long-term changes in the statistical distribution of Dobson total ozone in selected Northern Hemisphere geographical regions, in *Proceedings of the Quadrennial Ozone Symposium 1992*, Charlottesville, Virginia, NASA CP-3266, 207-210, 1994b.

Krzyścin,-J.W., Statistic analysis of annual total ozone extremes for the period 1964-1988, in *Proceedings of the Quadrennial Ozone Symposium 1992*, Charlottesville, Virginia, NASA CP-3266, 203-206, 1994c.

Kundu, N., and M. Jain, Total ozone trends over low latitude Indian stations, *Geophys. Res. Lett., 20,* 2881-2883, 1993.

Labitske, K., and M.P. McCormick, Stratospheric temperature increases due to Pinatubo aerosols, *Geophys. Res. Lett., 19,* 207-210, 1992.

Lacoste, A.M., S. Godin, and G. Mégie, Lidar measurements and Umkehr observations of the ozone vertical distribution at the Observatoire de Haute-Provence, *J. Atmos. Terr. Phys., 54,* 571-582, 1992.

Lambert, A., R.G. Grainger, J.J. Remedios, D.C. Rodgers, M. Corney, and F.W. Taylor, Measurements of the evolution of the Mt. Pinatubo aerosol clouds by ISAMS, *Geophys. Res. Lett., 20,* 1287-1290, 1993.

Lehmann, P., A statistical seasonal analysis of winter decreases in ozone at Macquarie Island, *Geophys. Res. Lett., 21,* 381-384, 1994.

Linvill, D.E., W.J. Hooken, and B. Olson, Ozone in Michigan's environment (1876-1880), *Mon. Wea. Rev., 108,* 1883-1891, 1980.

Logan, J.A., Trends in the vertical distribution of ozone: An analysis of ozonesonde data, *J. Geophys. Res.*, in press, 1994.

London, J., and S. Liu, Long-term tropospheric and lower stratospheric ozone variations from ozonesondes observations, *J. Atmos. Terr. Phys., 5,* 599-625, 1992.

Marenco, A., H. Gouget, P. Nédélec, J.-P. Pagés, and F. Karcher, Evidence of a long-term increase in tropospheric ozone from Pic du Midi data series —Consequences: Positive radiative forcing, *J. Geophys. Res., 99,* 16617-16632, 1994.

Marko, J.R., and D.B. Fissel, Empirical linkages between Arctic sea ice extents and Northern Hemisphere mid-latitude column ozone levels, *Geophys. Res. Lett., 20,* 37-40, 1993.

Mateer, C.L., and J.J. DeLuisi, A new Umkehr inversion algorithm, *J. Atmos. Terr. Phys., 54,* 537-556, 1992.

McCormick, M.P., R.E. Veiga, and W.P. Chu, Stratospheric ozone profile and total ozone trends derived from the SAGE I and SAGE II data, *Geophys. Res. Lett., 19,* 269-272, 1992.

McPeters, R.D., and W.D. Komhyr, Long-term changes in TOMS relative to World Primary Standard Dobson Spectrometer 83, *J. Geophys. Res., 96,* 2987-2993, 1991.

McPeters, R.D., T. Miles, L.E. Flynn, C.G. Wellemeyer, and J.M. Zawodny, Comparison of SBUV and SAGE II ozone profiles: Implications for ozone trends, *J. Geophys. Res., 99,* 20513-20524, 1994.

Miller, A.J., G.C. Tiao, G.C. Reinsel, D. Wuebbles, L. Bishop, J. Kerr, R.M. Nagatani, and J.J. DeLuisi, Comparisons of observed ozone trends in the stratosphere through examination of Umkehr and balloon ozonesonde data, in preparation, 1994.

Mylona, S., Trends of sulphur dioxide emissions, air concentrations and depositions of sulphur in Europe since 1880, in *European Monitoring and Evaluation Program/Meteorological Synthesis Center-West Report 2/93,* August 1993.

Naujokat, B., K. Petzoldt, K. Labitzke, R. Lenschow, B. Rajewski, M. Wiesner, and R-C. Wohlfart, The stratospheric winter 1992/1993: A cold winter with a minor warming and a late final warming, *Beilage zur Berliner Wetterkarte, SO 21/93,* 1993.

Newman, P.A., Antarctic ozone hole in 1958, *Science, 264,* 543-546, 1994.

NOAA (National Oceanic and Atmospheric Administration), Southern Hemisphere Winter Summary, Selected indicators of stratospheric climate, Climate Analysis Center, 1993.

Oltmans, S.J., W.D. Komhyr, P.R. Franchois, and W.A. Matthews, Tropospheric ozone: Variations from surface and ECC ozonesonde observations, in *Ozone in the Atmosphere,* edited by R.D. Bojkov and P. Fabian, A. Deepak Publ., Hampton, Virginia, 539-543, 1989.

Oltmans, S.J., D.J. Hofmann, W.D. Komhyr, and J.A. Lathrop, Ozone vertical profile changes over South Pole, in *Proceedings of the Quadrennial Ozone Symposium 1992,* Charlottesville, Virginia, 13 June 1992, NASA CP-3266, 578-581, 1994.

Oltmans, S.J., and H. Levy II, Surface ozone measurements from a global network, *Atmos. Environ., 28,* 9-24, 1994.

Oltmans, S.J., and D.J. Hofmann, Trends in the vertical profile of ozone at Hilo, Hawaii, from 1982 to 1994, in preparation, 1994.

Ozone Data for the World, Atmospheric Environment Service, Department of the Environment in cooperation with the World Meteorological Organization, Downsview, Ontario, Canada, *34,* 3, 1993.

Paur, R.J., and A.M. Bass, The ultraviolet cross-sections of ozone: II. Results and temperature dependence, in *Atmospheric Ozone,* edited by C.S. Zerefos and A.M. Ghazi, Reidel Publ., Dordrecht, The Netherlands, 611-616, 1985.

Perl, G., Das bodennahe Ozon in Arosa, seine regelmässigen und unregelmässigen Schwankungen, *Arch. Met. Geophys. Bioklimat., 14,* 449-458, 1965.

Placet, M., Emissions involved in acidic deposition processes, in *Acidic Deposition: State of Science and Technology*, Summary report of the U.S. National Acid Precipitation Assessment Program, edited by P.M. Irving, 1991.

Pommereau, J.-P., and F. Goutail, O_3 and NO_2 ground-based measurements by visible spectrometry during Arctic winter and spring 1988, *Geophys. Res. Lett., 15,* 891-895, 1988.

Randel, W.J., and J.B. Cobb, Coherent variations of monthly mean total ozone and lower stratospheric temperature, *J. Geophys. Res., 99,* 5433-5447, 1994.

Read, W.G., L. Froidevaux, and J.W. Waters, Microwave Limb Sounder measurement of stratospheric SO_2 from the Mt. Pinatubo volcano, *Geophys. Res. Lett., 20,* 1299-1302, 1993.

Reinsel, G.C., G.C. Tiao, A.J. Miller, D.J. Wuebbles, P.S. Connell, C.L. Mateer, and J. DeLuisi, Statistical analysis of total ozone and stratospheric Umkehr data for trends and solar cycle relationship, *J. Geophys. Res., 92,* 2201-2209, 1987.

Reinsel, G.C., G.C. Tiao, D.J. Wuebbles, J.B. Kerr, A.J. Miller, R.M. Nagatani, L. Bishop, and L.H. Ying, Seasonal trend analysis of published ground-based and TOMS total ozone data through 1991, *J. Geophys. Res., 99,* 5449-5464, 1994a.

Reinsel, G.C., W.-K. Tam, and L.H. Ying, Comparison of trend analyses for Umkehr data using new and previous inversion algorithms, *Geophys. Res. Lett., 21,* 1007-1010, 1994b.

Rigaud, P., and B. Leroy, Presumptive evidence for a low value of the total ozone content above Antarctica in September 1958, *Annales Geophysicae, 11,* 791-794, 1990.

Sandroni, D., D. Anfossi, and S. Viarengo, Surface ozone levels at the end of the nineteenth century in South America, *J. Geophys. Res., 97,* 2535-2540, 1992.

Scheel, H.E., E.G. Brunke, and W. Seiler, Trace gas measurements at the monitoring station Cape Point, South Africa, between 1978 and 1988, *J. Atm. Chem., 11,* 197-210, 1990.

Scheel, H.E., R. Sladovic, and W. Seiler, Ozone related species at the stations Wank and Zugspitze: Trends, short-term variations and correlations with other parameters, in *Photo-Oxidants: Precursors and Products*, Proc. EUROTRAC Symp. 1992, edited by P.M. Borell, P. Borell, T. Cvitas, and W. Seiler, Acad. Publ., The Hague, The Netherlands, 104-108, 1993.

Schenkel, A., and B. Broder, Interference of some trace gases with ozone measurements by the KI-method, *Atmos. Environ., 16,* 2187-2190, 1982.

Schoeberl, M.R., P.K. Bhartia, and E. Hilsenrath, Tropical ozone loss following the eruption of Mt. Pinatubo, *Geophys. Res. Lett., 20,* 29-32, 1993.

Shiotani, M., Annual, quasi-biennial and El Niño-Southern Oscillation (ENSO) time scale variations in equatorial total ozone, *J. Geophys. Res., 97,* 7625-7633, 1992.

Sladkovic, R., H.E. Scheel, and W. Seiler, Ozone climatology of the mountain sites, Wank and Zugspitze, in *Transport and Transformation of Pollutants in the Troposphere*, Proc. EUROTRAC Symp. April 1994, edited by P.M. Borrell, P. Borrell, P. Cvitas, and W. Seiler, in press, 1994.

Staehelin, J., and W. Schmid, Trend analysis of tropospheric ozone concentrations utilizing the 20-year data set of ozone balloon soundings over Payerne, *Atmos. Environ., 9,* 1739-1749, 1991.

Staehelin, J., J. Thudium, R. Bühler, A. Volz-Thomas, and W. Graber, Trends in surface ozone concentrations at Arosa (Switzerland), *Atmos. Environ., 28,* 75-87, 1994.

Stolarski, R.S., and A.J. Krueger, Variations of total ozone in the North Polar region as seen by TOMS, paper presented at the Polar Ozone Workshop, NASA/NOAA/NSF/CMA, Snowmass, Colorado, May 9-13, 1988.

Stolarski R.S., P. Bloomfield, R. McPeters, and J. Herman, Total ozone trends deduced from Nimbus 7 TOMS Data, *Geophys. Res. Lett., 18,* 1015-1018, 1991.

Stolarski, R., R. Bojkov, L. Bishop, C. Zerefos, J. Staehelin, and J. Zawodny, Measured trends in stratospheric ozone, *Science, 256,* 342-349, 1992.

Tarasick, D.W., D.I. Wardle, J.B. Kerr, J.J. Bellefleur, and J. Davies, Tropospheric ozone trends over Canada: 1980-1993, submitted to *Geophys. Res. Lett.*, 1994.

Taylor, S.L., R.D. McPeters, and P.K. Bhartia, Procedures to validate/correct calibration error in solar backscattered ultraviolet instruments, in *Proceedings of the Quadrennial Ozone Symposium 1992*, Charlottesville, Virginia, NASA CP-3266, 923-926, 1994.

Thornton, D., and N. Niazy, Effects of solution mass transport on the ECC ozonesonde background current, *Geophys. Res. Lett., 10,* 148-151, 1983.

Trepte, C.R., R.E. Veiga, and M.P. McCormick, The poleward dispersal of Mount Pinatubo volcanic aerosol, *J. Geophys. Res., 98,* 18563-18573, 1993.

Vigroux, E., Determination des coefficients moyen d'absorption de l'ozone, *Ann. Phys., 8,* 709-762, 1953.

Volz, A., and D. Kley, Evaluation of the Montsouris series of ozone measurements made in the nineteenth century, *Nature, 332,* 240-242, 1988.

Volz-Thomas, A., Trends in photo-oxidant concentrations, in *Photo-Oxidants: Precursors and Products, Proc. EUROTRAC Symp. 1992*, edited by P.M. Borrell, P. Borrell, T. Cvitas, and W. Seiler, Acad. Publ., The Hague, The Netherlands, 59-64, 1993.

Wege, K., H. Claude, and R. Hartmannsgruber, Several results from the 20 years of ozone observations at Hohenpeissenberg, in *Ozone in the Atmosphere*, edited by R.D. Bojkov and P. Fabian, A. Deepak Publ., Hampton, Virginia, 109-112, 1989.

Wellemeyer, C.G., S.L. Taylor, C.J. Seftor, and R.D. McPeters, TOMS profile shape errors estimates at high latitude, in *Proceedings of the Symposium on High Latitude Optics*, Tromsø, Norway, 1993.

WMO, *Report of the International Ozone Trends Panel: 1988*, World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 18, Geneva, 1990a.

WMO, *Scientific Assessment of Stratospheric Ozone: 1989*, World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 20, Geneva, 1990b.

WMO, *Scientific Assessment of Ozone Depletion: 1991*, World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 25, Geneva, 1992a.

WMO, *Handbook for Dobson Ozone Data Re-evaluation*, World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 29, Geneva, 1992b.

WMO, *Proceedings of the Fourth WMO/NOAA Workshop on Ozone Data Re-evaluation*, World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 36, Geneva, in preparation, 1994a.

WMO, *Proceedings of a Workshop on Homogenizing Total Ozone Records for Use in Ozone Assessments and Early Warning of Ozone Changes*, World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 35, Saloniki 1993, in preparation, 1994b.

Young, R.E., H. Houben, and O.B. Toon, Radiatively forced dispersion of the Mt. Pinatubo volcanic cloud and induced temperature perturbations in the stratosphere during the first few months following the eruption, *Geophys. Res. Lett., 21,* 369-372, 1994.

Zerefos, C.S., On the quasi-biennial oscillation in equatorial stratospheric temperatures and total ozone, *Adv. Space. Res., 2,* 177-181, 1983.

Zerefos, C.S., A.F. Bais, I.C. Ziomass, and R.D. Bojkov, On the relative importance of quasi-biennial oscillation and El Niño-Southern Oscillation in the revised Dobson total ozone records, *J. Geophys. Res., 97,* 10135-10144, 1992.

Zerefos, C., K. Tourpali, and A. Bais, Further studies on possible volcanic signal in total ozone, *J. Geophys. Res.*, in press, 1994.