Tropospheric Ozone: Seasonal Behavior, Trends, and Anthropogenic Influence

JENNIFER A. LOGAN

Center for Earth and Planetary Physics, Harvard University, Cambridge, Massachusetts

We present an analysis of data for tropospheric ozone with a focus on spatial and temporal variations. Surface ozone at mid-latitudes displays two modes of seasonal behavior: a broad summer maximum within a few hundred kilometers of populated and industrialized regions in Europe and the United States and a minimum in summer or autumn in sparsely populated regions remote from industrial activity—in Tasmania and Canada for example. The current data base for different regions, in combination with limited historical data, indicates that summertime concentrations of ozone near the surface in rural areas of Europe and the central and eastern United States may have increased by approximately 6–22 ppb (20%–100%) since the 1940s. The seasonal cycle of ozone in the middle troposphere over Europe, the United States, and northern Japan is very similar to that at the surface with a summer maximum, but it is quite different from that at 300 mbar, which is characterized by a maximum in spring. There is good evidence for an increase in ozone in the middle troposphere over Europe during the past 15 years and weaker evidence for a similar increase over North America and Japan. The increase in tropospheric ozone contributes significantly to the trend in the column of ozone and may compensate for 20%–30% of the decrease in ozone in the stratosphere over middle and high latitudes of the northern hemisphere. We argue that the summer maximum in ozone and the observed trends are due to photochemical production associated with anthropogenic emissions of NOx, hydrocarbons, and CO from combustion of fossil fuels. A strong seasonal variation in ozone observed at Natal, Brazil (6°S), may also result from emissions of NOx and hydrocarbons, in this case from agricultural burning. Maximum concentrations at Natal are similar to values found at mid-latitudes in summer. Tropical ozone exhibits strong spatial and temporal variability.

1. INTRODUCTION

Ozone plays an important role in controlling the chemical composition of the troposphere. Photolysis of ozone near 300 nm,

\[ O_3 + h\nu \rightarrow O(1D) + O_2 \] (1)

followed by reaction of the metastable \( O(1D) \) with water,

\[ O(1D) + H_2O \rightarrow OH + OH \] (2)

leads to production of OH. A variety of atmospheric species, including CO, CHx [Levy, 1971], NOx, and halocarbons are removed from the atmosphere by reaction with OH. Ozone by absorption of thermal radiation at 9.6 μm also plays an important role in the energy budget of the troposphere [Ramanathan and Dickinson, 1979; Fishman et al., 1979a].

Ozone enters the troposphere from the stratosphere and is destroyed by heterogeneous reactions at the earth’s surface [Regener, 1949; Junge, 1962; Junge and Czeplak, 1968; Pruchniewicz, 1973]. Ozone is also produced and destroyed within the troposphere by chemical reactions involving free radicals. It is formed during the oxidation of CO, CHx and hydrocarbons in the presence of nitrogen oxides and destroyed by reactions with NOx radicals [Chameides and Walker, 1973; Crutzen, 1973].

There is a growing body of evidence to suggest that concentrations of ozone in the nonurban troposphere are influenced by human activity. Concentrations of ozone are larger at mid-latitudes in the northern hemisphere than at corresponding southern latitudes [Pittock, 1977]. Fishman and Crutzen [1978] proposed that the observed excess of ozone in the north may reflect significant photochemical production associated with sources of NOx and CO from combustion of fossil fuels [see also Fishman and Seiler, 1983; Crutzen and Gidel, 1983]. Regional-scale pollution episodes, during which ozone concentrations may exceed 100 ppb for several days [e.g., Cox et al., 1975; Vekosich et al., 1977; Wolff et al., 1977; Guicherit and Van Dop, 1977; Wolff and Lievy, 1980], indicate an extensive anthropogenic influence on ozone near the surface in both Europe and the United States. Measurements from a rural site on the Baltic coast suggest that surface ozone has increased by ~60% since the 1950s [Warmbier, 1979]. Concentrations of ozone in the middle troposphere over Europe and North America appear to have increased at a rate of ~1% per year from 1969 to 1981 [Angell and Korshover, 1983]. These trends could be due to increasing emissions of ozone precursors such as NOx, hydrocarbons, and CO.

Increases in ozone are of concern, in part because of the important role ozone plays in controlling the chemical composition and climate of the troposphere and in part because of the deleterious effects of the gas on vegetation and human health. For example, changes in ozone could affect the concentration of OH, which in turn could influence concentrations of the many trace species removed from the atmosphere by reaction with OH. A doubling of tropospheric ozone could increase surface temperatures by 0.9°K, according to model results of Fishman et al. [1979a]. Ozone is thought to be responsible for most of the crop damage caused by air pollution in the United States. Recent field studies show that the yields of many crops decrease linearly, as ozone is increased, at a rate of 6%–8% per 10 ppb ozone [Heck et al., 1982]. It has been known since 1950 that certain species of trees are susceptible to damage by oxidants, and there is concern at present that ozone may be contributing to the observed decline of forests in Europe and the eastern U.S. [Skarby and Setliden, 1984].

This study presents a quantitative assessment of the impact of human activities on the distribution of tropospheric ozone. The assessment relies on systematic measurements of surface ozone in combination with sonde measurements of the vertical distribution. Previous analyses of the sonde data have focused primarily on ozone in the stratosphere [Dutsch, 1974, 1978;...]
London and Angell, 1982] or have considered the behavior of ozone at a single location [e.g., Dutsch and Ling, 1973; Mat- 
tana et al., 1973; DeMuer, 1976; Atmamspacher and Hartmans- 
gruber, 1976; Atmamspacher et al., 1984; Pittock, 1977; 
Bojkov, 1984]. The analysis presented here focuses attention 
on interesting features in the seasonal behavior of tropo- 
spheric ozone that were not apparent in earlier studies [e.g., 
Chatfield and Harrison, 1977a, b; Fabian and Pruehliewicz, 
1977; Fishman et al., 1979a]. Characterization of the seasonal 
behavior in different environments, in combination with long- 
term measurements available for only a few locations, permits 
useful estimates to be made for the change in ozone resulting 
from human activities.

Stratosphere-troposphere exchange is most effective during 
late winter and spring [Danielsen, 1968; Danielsen and 
Mohnen, 1977; Mahlman and Moxim, 1978], and the lifetime 
of ozone in the troposphere is only about 1 month. Thus one 
might expect concentrations of tropospheric ozone to be largest 
in spring in the absence of a significant photochemical influence 
on the distribution of the gas. Early measurements at a few 
sites did show a spring maximum in surface ozone, leading 
to the hypothesis that the stratosphere provides the 
dominant source of ozone to the troposphere [Rayner, 1949; 
Junge, 1962]. More recent data presented here and elsewhere 
[Olmiams, 1981; I. E. Galbally, private communication, 1984] 
confirm that surface concentrations of ozone at remote 
locations such as northern Canada, Tasmania, and the Pacific 
Islands are highest in winter or spring, reflecting the influence 
of the stratospheric source [cf. Levy et al., 1985]. By contrast, 
ozone concentrations remain high from spring into late 
summer at rural locations in Europe and the United States, 
regions where one might expect significant photochemical production of ozone associated with anthropogenic sources of 
NO, CO, and hydrocarbons. The broad summer maximum 
extends into the middle troposphere over these regions. 
Significant increases in ozone are found only in regions with a 
summer maximum. The data presented here provide evidence 
for a photochemical influence on large spatial scales.

We present a brief review of the chemistry of tropospheric 
ozone in section 2. The data analysis is described in section 3, 
and results are presented in section 4. Implications of these 
results are discussed in the concluding section.

2. CHEMISTRY OF OZONE IN THE TROPOSPHERE

Ozone is formed by

\[ O_3(3P) + O_3 + M \rightarrow O_3 + O_3 + M \]  

(3)

and is removed by photolysis

\[ hv + O_3 \rightarrow O_3(3P) + O_2 \]  

(1')

\[ hv + O_3 \rightarrow O_3(3P) + O_2 \]  

(1')

The metastable \( O_3(3P) \) is quenched by \( O_3 \) and \( N_2 \), though as 
shown above it can also react with \( H_2O \) (reaction (2)). Nitric 
oxide reacts with ozone to form \( NO_2 \)

\[ NO + O_3 \rightarrow NO_3 + O_2 \]  

(4)

with \( NO_2 \) removed by photolysis

\[ NO_2 + hv \rightarrow O_3 + NO \]  

(5)

Ozone removed by (4) is reconstituted by (5) followed by (3).

Because of the cyclic nature of the chemistry, it is convenient 
to define a family of species undergoing rapid reactions lead- 
ing to formation or removal of ozone. We identify this family-
odd oxygen—with \( O_3 \), \( O_3(3P) \), and \( NO_2 \).

Odd oxygen is conserved in reactions (1), (3), (4), and (5). It 
is formed by reactions of NO with \( HO_2 \), \( CH_2O \), and \( RO_2 \):

\[ HO_2 + NO \rightarrow OH + NO_2 \]  

(6)

\[ CH_2O + NO \rightarrow CH_2O + NO_2 \]  

(7)

\[ RO_2 + NO \rightarrow RO + NO_2 \]  

(8)

The species \( RO_2 \) represents a variety of complex organic peroxy radicals. These reactions occur during the photodissocia-
tion of CO, \( CH_4 \) and hydrocarbons, for example, by

\[ OH + CO + O_2 \rightarrow HO_2 + CO_2 \]

\[ HO_2 + NO \rightarrow NO_2 + OH \]

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

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

Net: \[ CO + 2O_2 \rightarrow CO_2 + O_3 \]

Odd oxygen is removed by reaction of \( O_3(D) \) with \( H_2O \), by 
reaction of \( O_3 \) with \( HO_2 \) and \( OH \),

\[ HO_2 + O_3 \rightarrow OH + 2O_2 \]  

(9)

\[ OH + O_3 \rightarrow HO_2 + O_2 \]  

(10)

by formation of nitrates from \( NO_2 \),

\[ OH + NO_2 + M \rightarrow HNO_3 + M \]  

(11)

and by heterogeneous reactions of \( O_3 \) and \( NO_2 \) at the earth’s 
surface.

Oxidation of \( CO \), \( CH_4 \), and hydrocarbons leads to net produc-
tion of odd oxygen in the presence of adequate \( NO_2 \). The rate 
for production of ozone is roughly proportional to the 
concentration of \( NO_2 \) while the rate for loss is almost indepen-
dent of \( NO_2 \) (NO + \( NO_2 \)) for concentrations below \( \sim \) 200 ppt 
[Fishman et al., 1979b]. Loss of odd oxygen, primarily by (2) 
and (9), is balanced by production in (6) and (7) for con-
centrations of \( NO_2 \) near 30 ppt [Fishman et al., 1979b; Logan 
et al., 1981]. Hence regions of the globe characterized by ex-
trremely low concentrations of \( NO_2 \) such as the remote Pacific, 
are likely to provide a net photochemical sink for odd oxygen 
[Liu et al., 1983], while the continental boundary layer at 
mid-latitudes, characterized by higher concentrations of \( NO_2 \), 
is likely to provide a net source. Model studies indicate that, 
averaged over the globe, chemical sources and sinks for odd 
oxigen are in approximate balance and are similar in magni-
tude to the source from the stratosphere and the sink at the 
ground [Fishman et al., 1979b; Logan et al., 1981; Chameides 
and Tan, 1981].

Production of ozone in the troposphere is limited ultimately 
by supply of \( CO \), \( CH_4 \), and hydrocarbons if \( NO_2 \) is available. 
One molecule of ozone may be formed for each molecule of 
\( CO \) as shown above, while the yield of ozone from oxidation 
of \( CH_4 \) could be as large as 3.5 [e.g., Logan et al., 1981]. The 
potential yield of ozone from higher hydrocarbons is larger 
still, 10-14 for butane and pentane [e.g., Singh et al., 1981].

3. DATA AND ANALYSIS

3.1. Surface Measurements of Ozone

Most of the data for near-surface ozone discussed here were 
obtained with instruments employing one of three techniques: 
a chemiluminescent analyzer sensitive to light emitted by the 
reaction of ozone with ethylene, an optical device measuring 
the absorption of ultraviolet light by ozone, and a variety of 
wl-chemical sensors in which detection of ozone is based on
## TABLE 1. Ozoneonde Data

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Longitude</th>
<th>Number</th>
<th>Sonde</th>
<th>Correction Factor</th>
<th>Dates</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Northern Hemisphere</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resolute*</td>
<td>75°</td>
<td>95°W</td>
<td>597</td>
<td>BM</td>
<td>1.21 ± 0.14 (2%)</td>
<td>January 1966 to November 1979</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ECC</td>
<td>1.03 ± 0.09 (2%)</td>
<td>November 1979 to December 1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ECC</td>
<td>—</td>
<td>July 1979 to June 1982</td>
</tr>
<tr>
<td>Poker Flat</td>
<td>65°</td>
<td>147°W</td>
<td>51</td>
<td>BM</td>
<td>1.27 ± 0.28 (17%)</td>
<td>October 1973 to August 1979</td>
</tr>
<tr>
<td>Churchill</td>
<td>59°</td>
<td>94°W</td>
<td>282</td>
<td>BM</td>
<td>1.24 ± 0.15</td>
<td>October 1973 to August 1979</td>
</tr>
<tr>
<td>Edmonton</td>
<td>53°</td>
<td>114°W</td>
<td>355</td>
<td>BM</td>
<td>1.04 ± 0.10 (1%)</td>
<td>September 1979 to December 1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ECC</td>
<td>1.25 ± 0.24 (8%)</td>
<td>October 1972 to August 1979</td>
</tr>
<tr>
<td>Goose Bay</td>
<td>53°</td>
<td>60°W</td>
<td>150</td>
<td>BM</td>
<td>1.05 ± 0.12 (3%)</td>
<td>August 1979 to December 1982</td>
</tr>
<tr>
<td>Berlin</td>
<td>52°</td>
<td>13°E</td>
<td>532</td>
<td>BM</td>
<td>1.29 ± 0.22 (8%)</td>
<td>June 1969 to August 1980</td>
</tr>
<tr>
<td>Lindenberg</td>
<td>52°</td>
<td>14°E</td>
<td>491</td>
<td>BM</td>
<td>1.26 ± 0.15 (0%)</td>
<td>August 1980 to December 1982</td>
</tr>
<tr>
<td>Uccle†</td>
<td>51°</td>
<td>4°E</td>
<td>358</td>
<td>BM</td>
<td>1.32 ± 0.27 (6%)</td>
<td>November 1966 to January 1973</td>
</tr>
<tr>
<td>Hohepenissenberge</td>
<td>48°</td>
<td>11°E</td>
<td>574</td>
<td>GDR</td>
<td>1.26 ± 0.29 (15%)</td>
<td>January 1975 to December 1982</td>
</tr>
<tr>
<td>Payenne</td>
<td>47°</td>
<td>7°E</td>
<td>483</td>
<td>GDR</td>
<td>1.21 ± 0.18 (0%)</td>
<td>January 1975 to December 1982</td>
</tr>
<tr>
<td>Biscarrosse</td>
<td>44°</td>
<td>1°W</td>
<td>357</td>
<td>BM</td>
<td>1.04 ± 0.09 (1%)</td>
<td>January 1969 to December 1980</td>
</tr>
<tr>
<td>Sassporo</td>
<td>43°</td>
<td>141°E</td>
<td>245</td>
<td>BM</td>
<td>1.27 ± 0.14 (0%)</td>
<td>January 1969 to December 1980</td>
</tr>
<tr>
<td>Bedford§</td>
<td>42°</td>
<td>73°W</td>
<td>595</td>
<td>BM</td>
<td>1.16 ± 0.17 (5%)</td>
<td>August 1963 to July 1966</td>
</tr>
<tr>
<td>Boulder§</td>
<td>40°</td>
<td>105°W</td>
<td>495</td>
<td>MB</td>
<td>1.24 ± 0.17 (5%)</td>
<td>July 1968 to August 1976</td>
</tr>
<tr>
<td>Cagliari</td>
<td>39°</td>
<td>9°E</td>
<td>219</td>
<td>MB</td>
<td>1.23 ± 0.14 (0%)</td>
<td>May 1970 to April 1982</td>
</tr>
<tr>
<td>Wollops Island</td>
<td>38°</td>
<td>76°W</td>
<td>457</td>
<td>ECC</td>
<td>1.00 ± 0.10 (1%)</td>
<td>December 1968 to December 1982</td>
</tr>
<tr>
<td>Taiano</td>
<td>36°</td>
<td>140°E</td>
<td>262</td>
<td>KC</td>
<td>1.03 ± 0.15 (4%)</td>
<td>December 1968 to December 1982</td>
</tr>
<tr>
<td>Palestine</td>
<td>32°</td>
<td>96°W</td>
<td>52</td>
<td>BM/ECC</td>
<td>—</td>
<td>October 1977 to June 1982</td>
</tr>
<tr>
<td>Kagoshima</td>
<td>32°</td>
<td>131°E</td>
<td>233</td>
<td>KC</td>
<td>0.99 ± 0.14 (1%)</td>
<td>December 1968 to December 1982</td>
</tr>
<tr>
<td>Kennedy, Florida*</td>
<td>29°</td>
<td>81°W</td>
<td>147</td>
<td>BM</td>
<td>—</td>
<td>February 1966 to February 1969</td>
</tr>
<tr>
<td>New Delhi</td>
<td>29°</td>
<td>77°E</td>
<td>99</td>
<td>I</td>
<td>1.42 ± 0.34 (28%)</td>
<td>January 1969 to December 1976</td>
</tr>
<tr>
<td>Grand Turk†</td>
<td>21°</td>
<td>71°W</td>
<td>80</td>
<td>BM</td>
<td>1.25 ± 0.30 (16%)</td>
<td>March 1966 to May 1969</td>
</tr>
<tr>
<td>Poons</td>
<td>19°</td>
<td>74°E</td>
<td>135</td>
<td>I</td>
<td>1.16 ± 0.17 (0%)</td>
<td>February 1966 to December 1975</td>
</tr>
<tr>
<td>Ft. Sherman§</td>
<td>9°</td>
<td>80°W</td>
<td>43</td>
<td>BM</td>
<td>—</td>
<td>June 1967 to May 1969</td>
</tr>
<tr>
<td>Trivandrum</td>
<td>8°</td>
<td>77°E</td>
<td>32</td>
<td>I</td>
<td>1.26 ± 0.26 (19%)</td>
<td>June 1969 to December 1976</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Longitude</th>
<th>Number</th>
<th>Sonde</th>
<th>Correction Factor</th>
<th>Dates</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Southern Hemisphere</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natal</td>
<td>6°</td>
<td>35°W</td>
<td>40</td>
<td>ECC</td>
<td>—</td>
<td>August 1979 to January 1982</td>
</tr>
<tr>
<td>Aspendale</td>
<td>38°</td>
<td>145°E</td>
<td>752</td>
<td>BM</td>
<td>1.23 ± 0.16 (2%)</td>
<td>June 1965 to April 1962</td>
</tr>
<tr>
<td>Christchurch</td>
<td>43°</td>
<td>173°E</td>
<td>25</td>
<td>BM</td>
<td>—</td>
<td>March 1965 to December 1965</td>
</tr>
<tr>
<td>Syowa</td>
<td>69°</td>
<td>39°E</td>
<td>135</td>
<td>KC</td>
<td>1.03 ± 0.14 (8%)</td>
<td>November 1969 to November 1980</td>
</tr>
</tbody>
</table>

All data were obtained on computer tape from the World Ozone Data Center, unless otherwise indicated. The first and second columns give the latitude and longitude of the station. The third column gives the total number of ozone soundings with data in the troposphere during the period given in the sixth column. The fourth column gives the type of ozoneonde used: BM, conventional Brewer-Mast; ECC, electrochemical concentration cell; GDR, Brewer, type GDR; KC, carbon-iodine, a version of the electrochemical concentration cell; MB, modified Brewer; I, Brewer, type India. The fifth column gives the average value and the standard deviation of the correction factor (C.F.) at that station and, in parentheses, the percentage of soundings with correction factors outside the range 0.9–1.6 (BM type) and 0.7–1.3 (ECC type). Where two values are given for a particular sonde type at one station, the second value is the average C.F. calculated by excluding all soundings with C.F. outside 0.9–1.6 for BM-type sondes and outside 0.7–1.3 for ECC-type sondes (see text). Measurement programs known to be continuing are indicated by a Y in the seventh column. A S marks stations where measurements are made irregularly in support of other programs. Note that the table does not include a few stations that started operation after 1979.

*An estimate of the correction factor is given in Ozone Data for the World for soundings during the winter months when a Dobson measurement of the ozone column cannot be made.

†Data taken from Bulletin Trimestral of the Royal Meteorological Institute of Belgium, provided by D. DeMuer.

‡Data taken from Chatfield and Harrison [1977].

†Data taken from Dutsch [1966].

its reaction with potassium iodide to form molecular iodine. The chemiluminescent and ultraviolet devices are not thought to suffer significantly from interference by other trace gases in nonurban air. The wet-chemical sensor is based on an oxidation reduction reaction that is not specific for ozone. Sulfur dioxide causes a negative interference of 1 mole of O₃ per mole of SO₂, while NO₂ gives a slight positive interference of a few percent [Katz, 1977; Schenkel and Broder, 1982]. Contamination by NO₂ should be unimportant at rural sites where concentrations of NO₂ are 0.2–10 ppb [Logan, 1983]. Modern instruments based on the KI reaction employ a filter or scrubber to remove SO₂ from the air being sampled. A field comparison of a chemiluminescent device, an optical device, and three wet-chemical sensors was carried out at Hohenpeissenberg Observatory for 6 months [Attmannspacher and Hartmansgruber, 1982]. Results from the three types of instru-
ments agreed within about 10% (C. M. Elsworth and I. E. Galbally, unpublished manuscript, 1984).

3.2. Ozoneonde Measurements

The two types of ozonesonde in common use, the Brewer Mast (BM) bubbler [Brewer and Milford, 1960] and the electrochemical concentration cell (ECC) [Kohmyr, 1969; Kohmyr and Harris, 1971], are based on the reaction of ozone with KI. The sondes differ in the design of the electrochemical cell. Measurements with Regener sondes have been shown to underestimate concentrations of ozone by 20%–60% below 10 km [Chatfield and Harrison, 1977a; Wilcox, 1978; Logan et al., 1981] and were not considered in this study. We discuss some of the difficulties associated with the electrochemical sondes and argue that the sondes data, with careful analysis, may provide useful information regarding spatial, seasonal, and temporal variations of ozone in the troposphere.

Sulfur dioxide is not removed from air sampled by ozonesondes. Sondes may tend to underestimate ozone in the boundary layer in polluted areas, particularly in winter, when ozone concentrations are lowest (~20–30 ppb) and SO$_2$ concentrations are highest. Concentrations of SO$_2$ at rural sites in the eastern United States, for example, are between 5 and 15 ppb in winter but below 5 ppb during other seasons [Mueller and Hidy, 1983]. Similar values are observed in southern Germany [Reiter and Kanter, 1982]. Concentrations of SO$_2$ above the boundary layer are generally below 1 ppb [Blumenthal et al., 1981; Georgii and Meixner, 1980].

The electrochemical technique does not provide an absolute measure of the ozone concentration. Preliminary studies using a standard ultraviolet photometer showed that concentrations of ozone were overestimated with ECC sondes by 3%–10%, while Brewer Mast sondes gave values too low by 4%–20%. The precision of the sondes in the troposphere was 5%–13% in field tests [Hilsenrath et al., 1984; Barnes et al., 1985]. Comparison of integrated ozone profiles recorded by Brewer Mast sondes with concurrent measurements of the ozone column recorded by a Dobson spectrophotometer indicates that the sondes results are too low by 10%–30% [e.g., Dutsch, 1966, see below]. Results from ECC sondes agree more closely with Dobson measurements, largely because the KI solution strength was originally adjusted to give this result [Kohmyr, 1969; Geraci and Luers, 1978; Torres and Bandy, 1978]. In practice, individual soundings are multiplied by a correction factor to ensure that the integrated ozone column is equal to the Dobson measurement of the ozone column. This procedure requires an estimate of the amount of ozone above the altitude reached by the sondes, ~30 km [Dutsch et al., 1970].

The scaling procedure introduces errors caused by uncertainty in the ozone amount above 30 km, errors associated with the Dobson technique, and probably bias resulting from variation of sondes efficiency with altitude. There is evidence to suggest that the response of the sondes to ozone is altitude dependent [Barnes et al., 1985]. Intercomparison flights have shown that ECC sondes give concentrations of tropospheric ozone higher than Brewer Mast sondes by 12%–20% after correction to the Dobson column. Systematic differences are less apparent in the stratosphere [Attmannspacher and Dutsch, 1970, 1981; Hilsenrath et al., 1984]. Uncertainties in the response of the sondes to ozone at tropospheric pressures and concentrations should be resolved by further laboratory and field studies. We believe that conclusions presented below are not seriously affected by current uncertainties in absolute concentrations. Our focus is on the seasonal behavior of tropospheric ozone and on temporal changes derived from internally consistent data sets.

---

Fig. 1. The influence of seasonal variations in the correction factor on the seasonal distribution derived for ozone. The solid line is an average of monthly mean values for ozone at 700 mbar at Goose Bay, Edmonton, and Churchill, obtained with Brewer-Mast sondes. The dashed line is obtained if results for each sounding are divided by the correction factor before forming monthly mean. Concentrations are about 20% lower, since the average correction factor for these stations is ~1.24, but the seasonal pattern is very similar.

Fig. 2. The ratio of the standard deviation of ozone to the monthly mean concentration of ozone (coefficient of variation) versus season. Results are shown for Hohenpeissenberg (H), Wallops Island (W.I), Goose Bay (G.B.), and Kagoshima (K) at the surface and at 700 mbar.

Fig. 3. The seasonal distribution of surface ozone at Hohenpeissenberg. The dashed line shows monthly averages of daily mean surface values, given in Ozone Data for the World (ODW). The dotted line shows monthly averages at 900 mbar (i.e., near surface) obtained from sondes measurements made at ~0800. The solid line shows the sonde data adjusted to daily mean values, using the diurnal behavior of surface ozone as a function of season at Hohenpeissenberg [Attmannspacher and Hartmannsgruber, 1980]. All results are averages of monthly means for 1976 to 1983. The vertical lines show the year-to-year standard deviation of the monthly mean. The diurnally averaged results estimated from the sondes data are in reasonable agreement with continuous measurements at the surface.
3.3. Analysis of Sonde Data

Ozonesondes data were obtained for the locations given in Table 1 from the Atmospheric Environment Service of Canada, which coordinates the World Ozone Data Center, and from published reports. These measurements provide the most coherent set of data for tropospheric ozone available at present. The majority of stations use conventional Brewer Mast sondes. The Canadian program changed from Brewer Mast to ECC sondes in ~1979; our analysis employs only BM data. Programs in India and the German Democratic Republic (GDR) use their own version of the Brewer Mast sonde; some difficulties were experienced with the operation of these devices at a recent field intercomparison [Attmanspacher and Dutsch, 1981]. The GDR sonde appears to overestimate tropospheric ozone by about 30%, based on comparison of results from Lindenberg and other European stations, as shown below in Figures 18–20. Wallops Island, U. S. A., and Natal, Brazil, employ identical ECC sondes, and their differential response to ozone (~15% compared to the Brewer Mast sonde) was discussed above. The program in Japan uses a version of the ECC sonde, which appeared in field tests to give results similar to the Brewer Mast sonde [Attmanspacher and Dutsch, 1981].

The mean correction factor for each station and its standard deviation are given in Table 1. These factors are about 1.2–1.3 (±0.1–0.3) for the Brewer Mast type of sonde and about 1.0 (±0.1–0.15) for the ECC type of sonde. The magnitude and variability of the correction factor provide a good indication of the quality of the measurements. A recent World Meteorological Organization (WMO) report recommends that profiles with factors outside the range 0.8–1.4 should be considered unacceptable for BM soundings [World Meteorological Association, 1982, hereinafter referred to as WMO 82]. This recommendation is based on results from Hohenpeissenberg where the correction factor is 1.09 (±0.09). The low correction factor at this station is attributed to careful preparation and conditioning of the sondes before use (WMO 82). We chose instead to omit from the analysis profiles with correction factors outside the range 0.9–1.6 for BM soundings.

![Fig. 4. Time series for ozone at 500 mbar. The seasonal cycle in ozone has been removed from the data as described in the text (see equation (12)); monthly residuals are shown as percent deviations from the monthly means. At Hohenpeissenberg the measurement frequency increased from weekly to three times a week in winter and two times a week in summer in 1978; at Aspendale the frequency decreased from weekly to biweekly in 1974; at Sapporo the frequency changed from weekly to, at most, biweekly in 1975; the influence of these changes on the variance of monthly mean values is evident. At Goose Bay, measurements were made with Brewer-Mast sondes until August 1980 and with ECC sondes thereafter; the latter give ~15% more ozone in the troposphere. At Wallops Island an instrument calibration program was instituted in 1978, and the variance in the data was reduced considerably.](image)

![Fig. 5. Comparison of annual mean values of ozone (mbar) at Hohenpeissenberg (solid) and Payner (dashed) at 900 mbar, 700 mbar, 500 mbar, 300 mbar, and 50 mbar. Measurements were made at ~1600 from 1969 to April 1977, at ~0930 from April 1977 to November 1980, at 1045 from November 1980 to December 1981, and at 1300 thereafter. Results for Hohenpeissenberg for 1967 to 1969 (dotted solid line) were given for 850 mbar rather than 900 mbar in ODW.](image)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>900 mbar</td>
<td>1.40 ± 0.14</td>
<td>0.96 ± 0.06</td>
<td>0.7</td>
</tr>
<tr>
<td>700 mbar</td>
<td>1.02 ± 0.04</td>
<td>0.91 ± 0.02</td>
<td>0.9</td>
</tr>
<tr>
<td>500 mbar</td>
<td>1.01 ± 0.04</td>
<td>0.90 ± 0.03</td>
<td>0.9</td>
</tr>
<tr>
<td>300 mbar</td>
<td>0.94 ± 0.08</td>
<td>0.99 ± 0.06</td>
<td>~1</td>
</tr>
</tbody>
</table>

At Hohenpeissenberg, ozone was measured at ~0800. At Payner, ozone was measured at ~1600 from 1970 to April 1977 and at ~0930 from April 1977 to 1980. The second and third columns give the average ratio (and standard deviation) of the annual mean value at Payner (P) to the annual mean value at Hohenpeissenberg (H) for 1970–1976 and 1977–1980, respectively. The fourth column gives the ratio of P/H for 1977–1980 to P/H for 1970–1976 and provides a measure of the systematic change in ozone concentrations caused by the change in the time of measurement at Payner.

**TABLE 2. Ratio of Ozone Concentrations at Payner and Hohenpeissenberg**
since the average correction factor for other stations using these sondes is 1.26. There is a small seasonal variation in the correction factor [Pittock, 1977], and use of the WMO criterion would have eliminated many more measurements in summer than in other seasons. We omitted profiles with factors outside the range 0.7-1.3 for ECC soundings. Revised correction factors, after application of these acceptance criteria, are given in Table 1.

We examined the influence of the seasonal variation in the correction factor on the seasonal distribution derived for ozone. Correction factors tend to be highest in late summer and lowest between January and May but are not exactly in phase at each station. The peak-to-peak amplitude of the monthly mean correction factor is <10% at eight stations, 10%-15% at seven stations, and 16%-24% at three stations (Churchill, New Delhi, and Tateno). The peak-to-peak amplitude of the monthly mean ozone concentration in the middle troposphere is 35%-50% of the annual mean value. Consequently, the seasonal variation in the correction factor has little influence on the seasonal distribution of ozone derived from the data, as shown for example in Figure 1.

Monthly mean values and standard deviations were calculated for each station at standard pressure levels (1000 or 900,
700, 500, 300, 200, and 150 mbar) for the entire period of observations, unless otherwise stated. The mean value in January, for example, is the arithmetic average of all values obtained in January of any year. Monthly mean values for stations in the North American Ozone Network [Hering and Borden, 1967] were taken from Chatfield and Harrison, [1977b], and results for Boulder are from Dutsch [1966]. The coefficient of variation is typically 0.15–0.35 at 500 mbar and 0.2–0.6 near the ground [Pittock, 1977; Chatfield and Harrison, 1977b], as shown in Figure 2. There does not appear to be a significant seasonal variation in the coefficient of variation in the middle troposphere, except at the Japanese stations.

In section 4 the seasonal variation in tropospheric ozone obtained from sonde measurements is compared with results from ground-based instruments. We demonstrate the comparability of the two techniques with data from Hohenpeissenberg. There is a significant diurnal variation in surface ozone [e.g., Decker et al., 1976; Evans et al., 1983] that must first be taken into account. The diurnal variation of surface ozone at Hohenpeissenberg obtained from continuous measurements [Attmannspacher and Hartmannspurger, 1980] was used to derive diurnal averages from sonde measurements made at 0700–0900. After adjustment to diurnal averages, the sonde data near the ground reproduced the long-term seasonal behavior of ozone derived from ground-based measurements, as shown in Figure 3. This comparison demonstrates that sonde instruments may provide reliable long-term average values for surface ozone and that results from the two techniques may be compared quantitatively with some confidence.

Data from sondes stations with records longer than 10 years were examined for trends. We caution that the quality of these data is rather uneven. The measurement frequency, procedure, time, and sondes type have changed at several stations. Figure 4 illustrates the influence of these changes on time series for ozone at 500 mbar. The seasonal cycle in ozone has been removed from the data by subtracting the average monthly mean value over the entire record from the given monthly mean \( z(\text{month}, \text{year}) = y(\text{month}, \text{year}) - y(\text{month}) \) (12)

Here, \( y(\text{month}) \) is the average of all the monthly means for the particular month: January, for example. Figure 4 shows time series of monthly residuals, \( z(\text{month}, \text{year}) \), expressed as percent deviations from the monthly means, \( y(\text{month}) \). The top three panels demonstrate qualitatively that the variance in monthly mean values decreases as the measurement frequency increases. A measurement frequency of three times weekly appears preferable to weekly or biweekly measurements. Almost no measurements were made for 2 years at the Japanese stations and few measurements after 1978; these data are far from ideal for trend detection. Measurements at Goose Bay were made with BM sondes until August 1980 and with ECC sondes thereafter; a discontinuity is evident in the data record. There are, however, similar discontinuities in the data for which there is no apparent rationalization and which could, of course, be real. The data from Wallops Island show the dramatic reduction in data variances that resulted from implementation of a sonde calibration program in 1978.

We found that a change in the time of measurement at Payerne and Hohenpeissenberg (see Figure 5 and Table 2). This need not imply a significant diurnal variation in ozone in the middle troposphere. The 10% difference could be an artifact introduced by the change in time of measurement, sonde preparation, etc.

Trends were calculated only for measurements made with a single instrument type, at the same time of day, to ensure that each data set is internally consistent. The seasonal cycle was removed from the time series by using equation (12), and the trend in the monthly residuals, \( z(\text{month}, \text{year}) \), was calculated by linear regression. Results are given in terms of percentage change in ozone per year, with 90% confidence intervals calculated by using the two-sided Students \( t \) test. Trends were calculated also for each season, using the series of residuals for the appropriate months, e.g., consecutive residuals for December, January, and February for winter. Sonde data have been scaled to the measured ozone column, and there is considerable variability in the correction factors, as shown in Table 1 and Figure 6. In order to remove any bias introduced by trends in either the ozone column or the correction factor, we repeated the analysis with the correction factor removed from each sounding. The trends in the correction factor and in the ozone column were calculated separately in the same manner as the trend in ozone.

4. Results

4.1. Ozone at Middle and High Latitudes

4.1.1. Ozone near the ground. The seasonal variation of surface ozone at mid-latitudes of the United States and Europe follows a common pattern. Maximum concentrations occur between March and August, as shown in Figure 7. Results from sondes stations in central Europe and the eastern United States (upper panel) are rather similar to those from rural locations in the United States (lower panel) [Mueller and Hidy, 1983; Shaw and Paur, 1983; Pratt et al., 1983]. Measurements from a network of rural sites in the United States are displayed in Figure 8, which includes a comparison with results from Germany. Average concentrations in spring and summer are between 30 and 50 ppb (upper panel), while daily maximum concentrations are between 45 and 65 ppb (lower panels). Sites within 100 km of major urban areas (St. Louis, MO and Munich, HP) exhibit the largest maximum concentrations and the most prolonged summer maxima. Maximum values at sites in less populated and less industrial environments (upper Wisconsin, WI, Vermont, VT, and coastal North Carolina (NC) are lower than values near St. Louis by 5–10 ppb in spring and summer, while maximum values at two remote mountain locations (Montana, MT) and Oregon (OR) are lower by 10–20 ppb.

The broad summer maximum extending through July or August is found over most of the U.S., from 35°N to 45°N (see Figures 7 and 8) [Singh et al., 1978; Viesee et al., 1982; Chatfield and Harrison, 1977b; Molten et al., 1977; Mueller and Hidy, 1983; Shaw and Paur, 1983; Pratt et al., 1983]. The same pattern is found in Ontario, Canada (42°–45°) [Mukamal, 1984]. In Europe the summer maximum extends to higher latitudes, from 39°N to 55°N [Fabian and Pruchnow, 1977; Attmannspacher and Hartmannspurger, 1980; Reiter and Kantor, 1982]. A different seasonal pattern is found at coastal locations near 30°N. Measurements from Florida [Chatfield and Harrison, 1977b] and Louisiana and preliminary data from Texas [Viesee et al., 1982] show a summer minimum with maxima in spring and late autumn. This pattern is also found in Japan near 30°N (Figure 9).
Fig. 10. The seasonal distribution of surface ozone at rural sites in Canada and Alaska. The upper panel shows Brown-Keene sonde results from Goose Bay (G.B.), Edmonton (ED) and Churchill (CH), while the lower panel shows results for Resolute. All sonde measurements were made near dawn. The lower panel also shows daily average surface data from Barrow, Alaska [Olomans, 1981]; the diurnal variation in ozone at this site is less than 1 ppb.

The seasonal cycle of ozone near the ground in Canada (53°-59°N) is rather different from that at mid-latitudes in the United States and Europe. Concentrations are highest in spring, while minimum values are found between August and October (Figure 10) [R. Angle, private communication, 1985]. Concentrations in summer are very similar at the three sonde stations located in western, central, and eastern Canada. A summer minimum is found also at higher latitudes, Resolute (75°N) and Barrow, Alaska (71°N) [Olomans, 1981], but maximum values occur in winter rather than in spring.

Surface ozone in Canada (53°-59°N) is compared with that in the United States and Europe in Figure 11. The results for the United States and Europe are daily average values, while those for Canada are values measured near dawn. We used recent observations of the diurnal variation of ozone at two rural sites in Alberta to estimate daily average concentrations from the Canadian sonde data, as shown by the hatched area in Figure 11. In summer, daily average values exceed dawn values by ~11 ppb at Ellerslie, near Edmonton, and by ~6 ppb at a more remote site, Bitemount, 57°N (R. Angle, private communication, 1985). We note that daily average values exceed dawn values by ~12 ppb in the eastern United States and by 5-8 ppb in the western United States [G. Evans, private communication, 1985]. The results in Figure 11 indicate that average concentrations of ozone in late spring and

Fig. 11. The seasonal distribution of surface ozone at northern and southern mid-latitudes. The line labeled E. U.S. is an average of results for the nine SURE sites, the three sites in Minnesota and North Dakota, and the four EPA sites in Vermont, North Carolina, Wisconsin, and Missouri (see Figures 7 and 8), with each of the three data sets given equal weighting. Also shown is the average of results for the rural site in Missouri and for Hohenpeissenberg, Germany, the two sites shown in Figure 8 with largest concentrations of ozone (U.S.-Europe, high). These distributions represent daily average values. The results for Canada (dashed line) are an average of measurements from Goose Bay, Edmonton, and Churchill at dawn (Figure 10). The cross-hatched area shows the daily average values estimated from this distribution, using the diurnal variation of ozone at Ellerslie, near Edmonton and Bitemount, Alberta (R. Angle, private communication, 1985). Results for Cape Grim (41°S) represent daily average values (E. E. Galtbally, private communications, 1984; C. M. Elsworth and E. E. Galtbally, unpublished manuscript, 1984); while results for Aspendale (38°S) are sonde measurements at 1000 mbar made in early afternoon. Measurements from the southern hemisphere are shown 6 months out of phase with respect to the northern hemisphere.

Fig. 12. Seasonal behavior of ozone at mountain locations in Europe. Monthly average values derived from daily maxima are shown for Arosa, Switzerland, 1860 m, for 1951-1953 [Junge, 1962] and for Garmisch-Partenkirchen, 740 m (G.P.), and nearby Wank Peak, 1780 m (W.P.), for 1977-1979 [Reiter and Kantor, 1982]. The data at 900 mbar for 1968-1976 are given for Payerne, near Arosa (P.A.Y.). These measurements were taken at ~1600 hours and should represent daily maxima. The seasonal variation of the correction factor was subtracted out of the Payerne data by dividing results for each sounding by the correction factor before forming monthly means and then multiplying the monthly means by the annual mean correction factor.

Fig. 13. The seasonal variation of ozone at Lansing, Michigan, in 1876-1880. These results were derived from daily measurements at 0700-1400 made with Schoubein's test paper (see text) and were taken from Linsell et al. [1980].
TABLE 3. Trend in Ozone Near the Ground

<table>
<thead>
<tr>
<th>Dates</th>
<th>Scaled to Column</th>
<th>Divided by Correction Factor</th>
<th>Trend in Correction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hoherneusenberg</td>
<td>January 1970 to December 1982</td>
<td>2.6 ± 0.7</td>
<td>3.2 ± 0.7</td>
</tr>
<tr>
<td>Sonde</td>
<td>January 1971–1983</td>
<td>2.8 ± 1.0</td>
<td>NS</td>
</tr>
<tr>
<td>Surface</td>
<td>January 1971–1983</td>
<td>1.5 ± 0.9</td>
<td>NS</td>
</tr>
<tr>
<td>Payerne</td>
<td>August 1968 to January 1977</td>
<td>(0.8 ± 1.4)</td>
<td>(0.6 ± 1.5)</td>
</tr>
<tr>
<td>Resolute</td>
<td>January 1965 to August 1979</td>
<td>(0.1 ± 1.0)</td>
<td>(0.0 ± 1.0)</td>
</tr>
<tr>
<td>Goose Bay</td>
<td>June 1969 to August 1980</td>
<td>(1.9 ± 1.1)</td>
<td>(1.1 ± 1.2)</td>
</tr>
<tr>
<td>Wallops Island</td>
<td>May 1970 to August 1981</td>
<td>(0.9 ± 1.2)</td>
<td>(0.9 ± 1.2)</td>
</tr>
<tr>
<td>Sapporo</td>
<td>January 1969 to December 1982</td>
<td>(1.5 ± 1.7)</td>
<td>(1.3 ± 1.7)</td>
</tr>
<tr>
<td>Tateno</td>
<td>January 1969 to December 1982</td>
<td>2.7 ± 1.0</td>
<td>2.3 ± 1.0</td>
</tr>
<tr>
<td>Kagoshima</td>
<td>January 1969 to December 1982</td>
<td>(0.5 ± 1.6)</td>
<td>(0.7 ± 1.5)</td>
</tr>
<tr>
<td>Aspendale</td>
<td>June 1965 to April 1967</td>
<td>(0.2 ± 0.8)</td>
<td>0.6 ± 0.2</td>
</tr>
</tbody>
</table>

Trend values in this table represent percentage change per year. All trends were calculated from monthly residuals (month, year) as described in section 3, unless otherwise indicated. Results are shown for 900 mbar for Payerne and Hoherneusenberg and for ~1000 mbar for the other stations. The third column gives the trend (and 90% confidence intervals) calculated from near-surface ozoneonde measurements that have been scaled to the Dobson measurement of the ozone column. The fourth column gives the trend obtained if results for each sounding are divided by the correction factor for that sounding before forming monthly means. This procedure should remove artifacts introduced by trends in either the correction factor or the ozone column. The fifth column gives the trend in the correction factor. NS indicates that the trend is not statistically significant. Results for Resolute and Goose Bay include only measurements made with Brewer-Mast sondes.

*Trend calculated from annual values for ozone at 900 mbar (sonde results).

†Trend calculated from annual values for ozone obtained with surface instruments. Data for 1971–1975 were taken from Atmannspacher and Hartmannsgruber [1980]. Data for 1976–1983 were taken from Ozone Data for the World.

‡Sapporo is a major city in northern Japan. Surface ozone concentrations given by the sonde measurements are lower than other mid-latitude stations, probably because of contamination by SO2. Trends in SO2 may therefore introduce an artifact in the trend estimated for ozone.

¶There is a 2-year gap in the data record for Kagoshima, and concentrations after 1978 appear to be systematically smaller than those before 1976.

Summer in the rural United States and Europe exceed those in remote regions of Canada by between 6 ppb and 22 ppb or by between 20% and 100%.

Figure 11 includes a comparison between surface ozone at mid-latitudes of the northern and southern hemispheres. Measurements from the clean air site at Cape Grim, Tasmania (41°S), show a summer minimum and winter maximum (I. Galbally, private communication, 1984) and little diurnal variation. Concentrations at Cape Grim in summer are about 20 ppb smaller than typical values in the United States and Europe. Ozone at Aspendale (38°S), 300 km north of Cape Grim, shows a late summer–autumn maximum and a winter minimum, with a much smaller seasonal amplitude than that found at northern mid-latitudes. It is known that ozone at Aspendale is influenced by proximity to the city of Melbourne [Gathally, 1971].

There appears to have been a significant change in the seasonal cycle of ozone in Europe over the past 30 years. Concentrations of ozone at Arosa, Switzerland (1700 m), were highest in May in the 1950s [Junge, 1962]. Recent measurements from nearby Payerne and from high-altitude stations in Germany [Reiter and Kanton, 1982] showed the characteristic summer maximum and mid-latitude ozone (see Figure 12). Concentrations of ozone in July and August are now similar to those in May, implying an increase in summertime values in excess of 10 ppb. Data from East Germany provide further evidence for a change in the seasonal cycle of ozone. Warnmb [1979] observed increases in both summer and winter values for ozone at Arkona (54°N) on the Baltic coast. Ozone concentrations in summer increased from 18 ppb in 1956–1960 to 31 ppb in 1973–1977, while winter values increased from 11 ppb to 16 ppb. There is no indication of a further increase in ozone since 1977 [Feister and Warnmb, 1984].

Measurements of ozone from the 19th century appear to indicate a similar change in the seasonal cycle of ozone in the United States. Ozone was measured on a daily basis in Michigan from 1871 to 1903, using Schoenbein's test paper. The paper, impregnated with starch, changes color in response to the reaction of O2 with potassium iodide. Limnill et al. [1980] calibrated the Schoenbein test results as a function of humidity by using a Dasibi ozone instrument and presented an analysis of the Michigan measurements from 1876 to 1880 in terms of parts per billion ozone (see Figure 13). The Schoenbein results are no doubt less reliable than data obtained with contemporary instrumentation, but the seasonal pattern may be reliable. It appears that ozone was significantly higher in spring than in summer in the 1870's in the midwestern United States, in contrast to results for the present day (compare Figures 7 and 8 with Figure 13).

We performed trend analyses on ozoneonde data near the ground, with results shown in Table 3. Sonde data suggest that ozone increased about 3% yr-1 from 1970 to 1982 at Hohenpeissenberg, Germany, while surface data suggest a smaller trend, ~1.5% yr-1. Unfortunately, the sonde data may be contaminated by SO4, as may surface results prior to 1976 when an SO4 filter was installed [Atmannspacher et al., 1984]. A negative trend in concentrations of SO4 could mimic a positive trend in O3. It appears that the sonde data may exaggerate the magnitude of the trend (Figure 14). Sonde data indicate that the trend is largest in summer, 1.1 ± 0.3 ppb yr-1 (Figure 15). Ozone did not change significantly from 1968 to 1977 at Payerne, Switzerland, on an annual basis, but summer values increased by 1.7 (± 1.3) ppb yr-1. The change in the time of measurement at Payerne in 1977 precludes accurate assessment of the trend over the entire record. Surface data from Wallops Island, U.S.A., suggest a slight increase in
ozone during the 1970s, but the trend is not statistically significant; neither is the decrease in ozone at Goose Bay, Canada, once the bias introduced by the trend in the correction factor is removed. It is noteworthy that increases in ozone are found only at stations that show a prolonged summer maximum in the seasonal distribution.

There is no significant trend in ozone at locations that exhibit a summer minimum: Resolute and Goose Bay in Canada (see Table 3); Barrow, Alaska; and the Pacific islands of Hawaii and Samoa [Oltmanns, 1981, 1984].

4.1.2. Ozone in the middle troposphere. The seasonal variation of tropospheric ozone at middle and high latitudes of the northern hemisphere is shown in Figure 16. Results for stations in Europe, the United States, and Japan at latitudes 38°–42° and 43°–48° are shown as composite profiles, as are results for Canada at 53°–59°. The variance of monthly mean values between stations in each group is similar to the variance in the monthly mean at an individual station.

A broad summer maximum is found at 700 mbar over Europe, the United States, and northern Japan, while a late spring maximum is found over Canada. The patterns are similar to those observed at ground level. The seasonal maximum extends from April to August at 48°–53° in Europe but occurs between March and June at 53° in Canada, indicating a longitudinal gradient in ozone at these latitudes. Ozone concentrations in summer over the United States and Europe appear to exceed those over Canada by 5–15 ppb, or between 10% and 40%. The difference in the seasonal cycle of ozone over the two regions is less pronounced at 500 mbar than at 700 mbar.

Data from Florida and the Bahamas [Chatfield and Harrison, 1977b] indicate that the summer maximum in ozone at 500 mbar extends as far south as 21°N in the western hemisphere. The summer maximum is not found at lower latitudes over Japan, as shown in Figure 17. Ozone decreases dramatically in early summer over Kagoshima (32°N), and results for Tateo at 36° also indicate the onset of a summer decrease. The decrease appears to be related to seasonal changes in circulation, as discussed below.

Maximum concentrations of ozone occur between March and May at 300 mbar, earlier than in the middle troposphere (Figure 16). The seasonal pattern in the upper stratosphere resembles that for ozone in the lower stratosphere. Ozone at 300 mbar shows a steep gradient with latitude which also resembles that for stratospheric ozone, with largest concentrations at high latitudes. This may reflect, in part, the frequency of sampling stratospheric air at 300 mbar, which increases at higher latitudes [Reiter, 1975].

The distribution of ozone with altitude in the middle troposphere is very different from that in the upper troposphere—
Fig. 17. The seasonal distribution of tropospheric ozone over Japan. Results are shown for Sapporo (43°), Tateno (36°), and Kagoshima (32°). Almost no measurements were made in July and August at Tateno.

lower stratosphere region. Largest concentrations are found at mid-latitudes in the northern hemisphere, between 30° and 50°, as shown in Figures 18–20. The mid-latitude maximum is present in all seasons at 700 mbar, but only in spring and summer at 500 mbar. Figures 18 and 19 give mean concentrations of ozone at sonde stations in January, April, July, and October at 700 mbar and 500 mbar, with supplementary results for August in Figure 20. The solid line indicates an 5°
moving average for 20°N to 60°N, while the dashed lines show snapshots of the latitudinal distribution obtained by aircraft sampling.

There is little evidence for a latitudinal gradient in ozone at middle and high latitudes of the southern hemisphere, except in summer (January), but the data are very sparse. Interhemispheric differences at mid-latitudes are shown more clearly in Figure 21. The amplitude of the seasonal cycle in the middle troposphere at 38°S (Aspendale) is much smaller than that at 38°-40°N, as noted previously by Pittock [1977] and by Fishman et al. [1979b], and concentrations are largest in spring in the south in contrast to the broad summer maximum in the north. There is a significant hemispheric asymmetry in the seasonal cycle of ozone at high latitudes also (see Figure 22). Ozone at 700 mbar and 500 mbar is largest in winter and smallest in summer at Syowa (69°S), in agreement with earlier results from Antarctica [Wiseman and Meierburg, 1969], while ozone is largest in late spring and early summer at Resolute (75°N). There is a summer minimum near the surface in both hemispheres.

Data from sonde stations indicate that tropospheric ozone may be increasing in the northern hemisphere. Angell and Korshover [1983] reported an average increase of ~12% from 1970 to 1981 at mid-latitudes; Bofkou and Reinsel [1984] reported similar results. We find that the evidence for an increase in ozone at 700–500 mbar is strongest for Europe (~2% yr⁻¹ over Hohenpeissenberg, with somewhat smaller increases over Payerne and Uccle) as shown in Table 4. The trends calculated for North America (Wallops Island and Goose Bay) are positive, once the bias introduced by the trend in the correction factor is removed, but are not statistically significant. The trend derived for Wallops Island is significant, 0.9 ± 0.6% per year, only if outliers are first removed from the data record (see Table 4). Angell and Korshover found a larger trend over North America than over Europe. Their analysis included measurements with Brewer Mast and ECC sondes at the Canadian stations and from two times of day at Payerne. These changes in measurement strategy may have introduced inconsistencies in the data they analyzed, as discussed earlier.

Measurements from Resolute indicate that ozone in the middle troposphere is increasing at high northern latitudes also, by ~1% yr⁻¹. The trend is much larger in spring and summer (~1 ppb yr⁻¹) than in other seasons, as shown in Figure 23. There is less seasonal variability in the magnitude of the trend at mid-latitudes, as shown by results for Hohenpeissenberg.

The altitude dependence of the trend in ozone is quite different at locations with a summer maximum in ozone compared to those with a summer minimum. Hohenpeissenberg

Fig. 18. The distribution of ozone with latitude at 700 mbar. The symbols show monthly mean concentrations for the stations listed in Table 1. The symbols are defined as follows: (solid squares) North America, BM sondes; (open squares) North American Ozonesonde Network, BM [Chatfield and Harrison, 1977]; (half-filled square) Americas, ECC; (solid circle) Europe; (open circle) Linden; (trian- gle) India; (diamond) Japan; (hexagon) Hawaii [Oltmans, 1981]; (plus) Australia and the Antarctic, including surface data from the South Pole from Oltmans [1981]. Seasonal values are shown for tropical locations (crosses) if they are somewhat different from midseason values because of the small number of tropical measurements. The plus at 2°S shows ECC measurements made at Canton Island (four profiles) in December [Kohler and Stickel, 1967]. The solid line is a 5° moving average of sonde results for 20°N to 60°N.
Fig. 19. The distribution of ozone with latitude at 500 mbar. Symbols are defined in Figure 18. The panel for April shows aircraft data from Roulhier et al. [1980] for the central Pacific south of 40°N and for North America north of 40°N for April and May (dashed lines). The panel for October shows aircraft data from Gregory et al. [1984] for a flight from Wallops Island to the west coast of South America. Southbound data are given by the dot-dashed line, northbound data by the dashed line.

(summer maximum) shows the largest increase at the surface and smaller increases at 700 mbar and 500 mbar. Resolute (summer minimum) shows no trend at the surface but a significant increase at 700 mbar and 500 mbar (see Figure 24). Both locations show a switch over from a positive trend in the middle troposphere to a negative trend in the lower stratosphere. This is a feature common to trend results for all the stations in the northern hemisphere (see appendix). At Aspendale, the only sondé station at southern mid-latitudes, there is no significant trend in the middle troposphere, but there is a decrease in ozone in the lower stratosphere (see appendix).

The trend in tropospheric ozone contributes significantly to the trend in the integrated column of ozone. The increase in the troposphere at Hohenpeissenberg appears to compensate for at least 30% of the decrease observed in the stratosphere over the same period and may be of comparable magnitude to the decrease in the stratosphere. The increase in tropospheric ozone at Resolute is about 20% of the decrease in the stratosphere (see appendix).

Fig. 20. The distribution of ozone with latitude at 500 mbar in August. Symbols are defined as in Figure 18, except that the sondé data in the southern hemisphere are shown as squares for clarity. The dashed line shows aircraft data of Roulhier et al. [1980] for the route described in Figure 19. The crosses show the aircraft measurements of Seller and Fishman [1981] taken over both coasts of North America and the west coast of South America. The cross-hatched area shows measurements over central Brazil [Delany et al., 1985; Cruzzen et al., 1984].

Fig. 21. Comparison of ozone at mid-latitudes of the northern and southern hemispheres. Results are shown for Aspendale, 38°S (solid), and for stations near 38°N (dashed; see Figure 16) for 300 mbar, 500 mbar, and 700 mbar. The vertical lines show the standard deviation of the monthly means.

4.2. Ozone in the Tropics

Recent measurements indicate that concentrations of ozone at Natal, Brazil, are much larger than at other tropical locations [Kirchhoff et al., 1983; Kirchhoff, 1984]. Figure 25 displays annually averaged concentrations of ozone in the tropics and subtropics (upper panel). The difference between concentrations at Natal (6°S) and Panama (9°N), ~60%, is much too large to be ascribed to the differential response of the ECC and Brewer-Mast sondes to tropospheric ozone, which could account for a difference of about 15%. There is a significant seasonal variation in ozone at Natal, with values in September and October about a factor of 2 higher than in February to April (Figure 25, lower panel). Ozone at Panama shows little seasonal variation [Chatfield and Harrison, 1977b]. Maximum concentrations in the middle troposphere at Natal are as large as those found at mid-latitudes in summer (compare Figures 16 and 25), while minimum concentrations correspond to those found all year at Panama. The results for Natal in Figure 25 suggest that ozone mixing ratios are almost constant above 600 mbar, but this picture is somewhat misleading. Inspection of individual vertical profiles reveals that high levels of ozone are found in layers above the trade wind inversion, ~800 mbar, as shown in Figure 26. A more detailed analysis of these data and more recent measurements from Natal will be presented elsewhere (V. W. J. H. Kirchhoff and J. A. Logan, unpublished manuscript, 1985). Surface data from Sa Da Bandeira, Angola (15°S), display the same seasonal behavior as ozone at Natal, with a September
Fig. 22. Comparison of ozone at high latitudes of the northern and southern hemispheres. Results are shown for Syowa (69°S, solid) and Resolute (75°N, dashed) for 500 mbar, 700 mbar, and ~1000 mbar. Surface measurements at the South Pole (90°S, dotted; Oltmans [1981]) are also included.

maximum [Fabian and Prachniewicz, 1977], while ozone at Samoa (14°S) is largest in July and August [Oltmans, 1981].

The sounds results suggest significant spatial and temporal inhomogeneities in ozone in the tropics. Recent aircraft measurements, shown in Figures 19 and 20, provide further evidence for inhomogeneities, particularly in the southern tropics. Roachier et al. [1980] found concentrations of about 20-30 ppb at 500 mbar over the Pacific Ocean in May and August, while Seller and Fishman [1981] reported similar values for the west coast of South America in August. These

<table>
<thead>
<tr>
<th>Dates</th>
<th>Scaled to Column</th>
<th>Divided by Correction Factor</th>
<th>Trend in Correction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>700 mbar, 500 mbar</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hohenpeissenberg</td>
<td>January 1969 to December 1982</td>
<td>1.9 ± 0.3</td>
<td>2.2 ± 0.3</td>
</tr>
<tr>
<td>Fayerne</td>
<td>August 1968 to January 1977</td>
<td>0.9 ± 0.7</td>
<td>(0.7 ± 0.8)</td>
</tr>
<tr>
<td>Ucle</td>
<td>January 1969 to December 1980</td>
<td>1.1 ± 0.7</td>
<td>NS</td>
</tr>
<tr>
<td>Resolute</td>
<td>January 1969 to March 1981</td>
<td>1.7 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>Goose Bay</td>
<td>June 1969 to August 1980</td>
<td>1.2 ± 0.5</td>
<td>1.1 ± 0.5</td>
</tr>
<tr>
<td>Wallops Island†</td>
<td>October 1970 to August 1981</td>
<td>(-0.2 ± 0.7)</td>
<td>(0.5 ± 0.7)</td>
</tr>
<tr>
<td>Sapporo</td>
<td>January 1969 to December 1982</td>
<td>0.4 ± 0.0</td>
<td>(0.4 ± 0.0)</td>
</tr>
<tr>
<td>Tatsui</td>
<td>January 1969 to December 1982</td>
<td>0.7 ± 0.5</td>
<td>(0.5 ± 0.5)</td>
</tr>
<tr>
<td>Kagoshima</td>
<td>January 1969 to December 1982</td>
<td>1.5 ± 1.0</td>
<td>1.5 ± 1.1</td>
</tr>
<tr>
<td>Aspendale</td>
<td>June 1965 to April 1982</td>
<td>(0.4 ± 0.5)</td>
<td>(-0.4 ± 0.4)</td>
</tr>
<tr>
<td><strong>300 mbar</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hohenpeissenberg</td>
<td>January 1969 to December 1982</td>
<td>0.8 ± 0.8</td>
<td>1.0 ± 0.8</td>
</tr>
<tr>
<td>Goose Bay</td>
<td>June 1969 to August 1980</td>
<td>-4.6 ± 1.7</td>
<td>-3.8 ± 1.7</td>
</tr>
<tr>
<td>Kagoshima</td>
<td>January 1969 to December 1982</td>
<td>(1.3 ± 1.3)</td>
<td>(1.4 ± 1.4)</td>
</tr>
</tbody>
</table>

Trends are given as the percentage change per year and are presented in the same format as Table 2. Trends were calculated from monthly residuals (month, year), as described in section 3. Concentrations at 700 mbar and 500 mbar were averaged before forming monthly means. Results are given for 300 mbar only if statistically significant.

†Trend derived from data provided in tabular form by D. DeMuer. Monthly mean values were calculated for soundings with correction factors between 0.8 and 1.4, omitting those flagged as being contaminated in the troposphere.

‡Trend derived from monthly mean values provided by J. London.

The calculated trend is 0.7 ± 0.6 (scaled to the ozone column) and 0.9 ± 0.6 (divided by C.F.) if ozone values more than 2 standard deviations from the monthly mean are removed from the data set prior to analysis.
Fig. 24. Vertical distribution of the trend in ozone (in percent per year) at Resolute and Hohenpeissenberg. The horizontal bars give the 90% confidence interval for the trend at each level. The shaded area shows the range of tropopause heights through the year.

concentrations are about a factor of 2 lower than results for Natal on the east coast of Brazil but are similar to results for Panama. Cruzen et al. [1985] reported values of 40–50 ppb over central Brazil in August. A recent expedition over the west coast of South America in October found concentrations of 35–55 ppb from 5°S to 20°S on the southbound flight, but concentrations were even higher, 55–80 ppb, on the northbound flight only a few days later [Gregory et al., 1984]. The high values are similar to results for Natal.

Sonde results from Natal (6°S) and Panama (9°N) in combination with the aircraft measurements indicate that ozone concentrations in the southern tropics are in some cases much greater than those of the northern tropics. The data in Figures 18–20 do not support the previously accepted view [e.g., Fishman et al., 1979b] that ozone is more abundant in the northern tropics. The analysis by Fishman et al. [1979b] may have been confounded by instrumental differences. They compared measurements made with Brewer-Mast sondes at Panama with results from Regener sondes at Canton Island (2°S) and La Paz (10°S).

5. DISCUSSION

Daily average concentrations of surface ozone in summer are between 30 ppb and 50 ppb in rural areas of the United States and Europe, while daily maximum concentrations are between 45 ppb and 65 ppb. We argue here that these concentrations are influenced significantly by photochemical production of ozone associated with emissions of NOx, hydrocarbons, and CO, and we present a quantitative assessment of the magnitude and extent of the anthropogenic influence. The persistence of high ozone concentrations from spring into summer occurs only at continental mid-latitudes of the northern hemisphere. Concentrations appear to be largest in the most densely populated and industrialized regions, the eastern United States and central Europe. The behavior of ozone is quite different in sparsely populated regions remote from industrial activity: for example, Cape Grim and much of

Fig. 25. Average vertical profiles for ozone in the tropics. The upper panel shows annual mean concentrations of ozone at Panama, 9°N (solid); Grand Turk, 21°N (dashes) [Chafin et al. and Harrison, 1977b]; Pohnpei, 19°N (dotes); and Natal, 6°S (dot-dash). Surface data are from Mauna Loa, 19°N (square), and Samoa, 14°S (circle) [Oltmans, 1981]. The lower panel shows average concentrations at Natal (solid) in September and October (11 profiles) and in February-April (10 profiles). Although few profiles are available for each month, the seasonal pattern is reproduced in 3 years of data. Horizontal bars shown one standard deviation based on individual profiles for Natal. Results are compared with the annual mean profile at Panama (dashes) and its standard deviation (based on monthly mean values).

Fig. 26. Vertical profiles of ozone at Natal (6°S). Results are shown for three consecutive days in October 1979. The figure includes the vertical distribution of water vapor, shown in terms of relative humidity, for October 9.

Fig. 27. Seasonal distribution of 013Sr at the surface. Data shown for Moosonee, Canada 52°N (solid), and for Sterling-NYC, 40°N (dashed) are from Staley [1982].
Fig. 28. Seasonal distribution of ozone at Hohenpeissenberg. The solid lines show sonde results for 700 mbar and 500 mbar. The dashed line shows daily mean values, and the dot-dashed line shows daily maximum values at the surface, derived from continuous surface measurements. Results are given for 1976 to 1983.

Canada, where ozone is largest in winter or spring and smallest in summer or autumn (15–25 ppb). The source of ozone from the stratosphere might be expected to give rise to a late winter or spring maximum in tropospheric ozone, since stratosphere-troposphere exchange is most effective during this period [Danielsen, 1968; Danielsen and Mohnen, 1977; Mahlman and Moxim, 1978].

The difference in seasonal behavior of surface ozone cannot be attributed simply to a latitudinal gradient or to differences between the hemispheres. We emphasize in this context first the summer maximum in surface ozone at 53°–59°N in Europe and the late summer-autumn minimum at similar latitudes in Canada. The Canadian sites experience surface air flow from the north in summer [Bryson and Hare, 1974] and therefore should represent some of the clearest continental air in the northern hemisphere. Second, we note that the seasonal cycles of 19S, a tracer of stratospheric air, are exactly in phase at 52° and 40° in North America (see Figure 27) [Staeb, 1982]. This suggests that the different seasonal cycles of ozone at these latitudes cannot be ascribed simply to variations in the source of ozone from the stratosphere. Ozone mixing ratios in rural areas are too large in any event to be supplied by downward transport. Daily maximum mixing ratios of ozone near the ground at Hohenpeissenberg, for example, exceed values at 700 mbar in spring and summer (Figure 28). A similar result was found by Reiter and Kanter [1982] at a nearby location. Maximum ozone concentrations at Garmisch (740 m) exceeded those on the neighboring Zugspitz peak (2940 m) by ~10 ppb on sunny summer days. Third, we note the summer-autumn maximum in near-surface ozone at Aspendale (38°S), in contrast to the summer minimum at Cape Grim (41°S). Aspendale is affected by urban air pollution [Galbally, 1971], while Cape Grim is usually under the influence of pristine marine air masses. Thus nearly all locations within a few hundred kilometers of anthropogenic sources of NOx and hydrocarbons exhibit a summer maximum in surface ozone, while very remote sites exhibit a summer or autumn minimum. The principal exceptions to this general behavior are southern coastal sites in the United States near 30°N and similarly situated Japanese stations. During summer, these locations experience tropical marine air flow [Bryson and Hare, 1974; Fukui, 1977] characterized by low concentrations of ozone (see Figures 18 and 19).

There is good evidence for a change in the seasonal distribution of surface ozone in Europe and the United States. This change implies substantial ozone increases in summer over regions of continental scale between 1950 and 1975. The available long-term measurements, from Arkona on the Baltic coast, show that ozone concentrations in summer increased by ~13 ppb (~70%) from 1958 to 1975, while winter values increased by ~5 ppb (~45%). Warmb et [1979] noted that ozone concentrations are highest during years with warm, dry, and sunny summers [see also Attmank et al., 1984; Reiter and Kanter, 1982]. The measurements from Arosa suggest that ozone has increased by at least 10 ppb (~35%) in summer over the same period, and they imply a larger increase in summer than in other seasons. Measurements from Hohenpeissenberg for 1970 to 1983 indicate an increase in ozone of perhaps 6 ppb (20%), also with evidence for a larger change in summer.

Maximum concentrations of ozone in Michigan occurred in April and May in the 1970s; the same months as they do today in Canada (53°–59°N). If we use as preindustrial values the present-day concentrations of ozone at the relatively remote sites in Canada (Figure 11), we estimate that daily average concentrations of ozone in summer have increased by as much as 6–12 ppb in the Midwest and possibly by as much as 10–22 ppb in highly impacted environments such as the Ohio River Valley. These changes correspond to increases of 20% to 100%. Alternatively, if we adopt ozone concentrations at Cape Grim, Tasmania (15–20 ppb), as representative of the preindustrial atmosphere, we estimate that average concentrations of ozone in summer in the United States and Europe have increased by 15–25 ppb (see Figure 11), consistent with results discussed above.

Increases in ozone of the magnitude discussed here appear to be consistent with current understanding of the photochemistry of rural air. Oxidation mechanisms for hydrocarbons (HC) in the presence of NOx indicate that several molecules of ozone may be formed for each molecule of NOx and HC that is released [e.g., Isaksen et al., 1978; Singh et al., 1981], and field observations of O3, NOx, and hydrocarbons in rural areas support this view [Fehsenfeld et al., 1983; Kelly et al., 1984; Parrish et al., 1985]. The average emission rate of NOx from combustion of fossil fuels is ~2 × 1014 molecules cm−2 s−1 in the eastern United States, about a factor of 10 larger than the flux from natural sources [Logan, 1983]. Even if only one molecule of ozone were formed for each molecule of NOx released, the production rate of ozone in the boundary layer in this region would exceed the average flux from the stratosphere ~5–8 × 1016 molecules cm−2 s−1 [Danielsen and Mohnen, 1977; Mahlman et al., 1980; Gidel and Shapiro, 1980]. Hence it does not seem unreasonable that ozone concentrations might have increased by as much as a factor of 2 as a result of photochemical production associated with emissions of NOx and hydrocarbons.

It is likely that much of the increase in ozone occurred between 1940 and the mid-1970’s, at least in the United States. Emissions of NOx from combustion increased by a factor of ~3 during this period, while emissions of hydrocarbons increased by a factor of ~2 [U.S. Environmental Protection Agency, 1982]. Emissions of NOx increased at a slower rate after 1970 and have decreased since 1979, while emissions of HC have decreased since 1970, in part as a result of pollution control measures, in part as a result of energy conservation.

It is more difficult to quantify the possible impact of anthropogenic emissions on concentrations of ozone above the boundary layer. The similarity between the seasonal cycle of ozone in the middle troposphere over Europe, the United States, and northern Japan and that at ground level and the
observed increases of ozone in the 1970's in the middle troposphere certainly argue in favor of a significant anthropogenic impact. It is extremely difficult to rationalize the persistence of high concentrations of ozone from April to August at 500 mbar without invoking a photochemical source, largely because of the short lifetime of ozone at mid-latitudes in summer, less than 1 month [Saksen et al., 1978]. Ozone or its precursors from the boundary layer are most likely to influence the distribution of ozone at higher altitudes in summer, when convective mixing is most effective.

Results from a recent study with a general circulation model also suggest that a photochemical source is required to explain the summer maximum [Levy et al., 1985]. The model allowed for downward transport of ozone from the stratosphere and removal at the surface but did not include photochemical production and loss; it reproduced the observed seasonal cycle at remote locations where ozone concentrations are highest in late winter or spring but failed to simulate the broad summer maximum at mid-latitudes.

The seasonal behavior of ozone and observed increases suggests that the anthropogenic influence extends from about 30°N to 75°N in the middle troposphere and that the latitudinal extent varies with circulation patterns. For example, the lack of a summer maximum in ozone over southern Japan (30°N) may be attributed to the onset of the summer monsoon when airflow from the Asian continent is replaced by air from the tropical Pacific [Fukui, 1977]. The increase in ozone over the Red Sea (75°N) at 500 mbar in spring and summer may result from long-range transport of ozone or its precursors from lower latitudes. Measurements of sulfate and particulates indicate that the Canadian Arctic is most likely to be influenced by air masses from mid-latitudes between December and May [Barrie et al., 1981; Rahn, 1981], and ozone data near the ground show scant evidence for an anthropogenic impact in summer. The lifetime of ozone in the middle troposphere is expected, however, to be longer than that of SO$_2$ and sulfate, which are removed from the atmosphere by precipitation scavenging, and hence transport of ozone or its precursors from mid-latitudes may influence high-latitude ozone at 500 mbar in summer.

The increases in tropospheric ozone implied by the sonde data are substantial, 1%-2% yr$^{-1}$ between 30°N and 75°N. It is unfortunate that there are no systematic observations from the period of most rapid growth in emissions of ozone precursors, 1940-1970. The trends in tropospheric ozone since 1967 contribute significantly to the trends in the integrated column of ozone and may compensate for 20%-30% of the decrease in ozone in the stratosphere over middle and high latitudes.

Studies of the influence of tropospheric ozone on climate have shown that surface temperature is most sensitive to changes in ozone near the tropopause [Wang et al., 1980], and the evidence for change in this region is rather weak. Measurements from only two locations, Hohenpeissenberg and Kagoshima, suggest an increase in ozone at 300 mbar, while results for Goose Bay suggest a decrease. However, the variance of ozone concentrations near the tropopause is much larger than in the middle troposphere, and derived trends are less reliable.

Recent observations from Brazil suggest that elevated ozone concentrations in the tropics may result from photochemical synthesis, with combustion of vegetation rather than fossil fuels providing the source of NO$_x$, HC, and CO [Crutzen et al., 1985]. Concentrations of ozone in the polluted boundary layer in a region of biomass burning in central Brazil, 60-65 ppb [Delany et al., 1985], and values over Natal in September and October, >60 ppb, are similar to concentrations at mid-latitudes of the northern hemisphere in summer. Biomass burning takes place during the dry season, which lasts from June to September in the southern and west of Natal [Ratisbona, 1976]. The prevailing winds in spring to the south of Natal are westerly above ~500 mbar, but from the ocean below [Sabal, 1979; Oort, 1983]. High levels of ozone are found above the trade wind inversion (~800 mbar) with much lower concentrations below. We speculate that the enhanced concentrations of ozone over Natal may be due to transport and photochemical degradation of emissions from biomass burning and possibly from biogenic emissions [Crutzen et al., 1985] in the interior of the continent. Stratospheric intrusions could contribute also to the ozone enhancements that occur in the southern spring.

The observations of ozone over Natal in combination with surface data from Samoa, 14°S [Oltmans, 1981], and Angola, 15°S [Fabian and Pruchniewicz, 1977], indicate a significant seasonal variation in tropical ozone, with highest concentrations in late austral winter or spring. Concentrations of ozone appear to vary significantly with longitude also (see Figures 19 and 20). The lifetime of ozone toward photochemical loss is about 2 weeks in the tropics [Liu et al., 1983; Logan et al., 1981], less than the transit time of air masses around the globe. It is, perhaps, not surprising therefore that the distribution of the gas in the tropics should be quite heterogeneous. The recent data do not support earlier conclusions [e.g., Fabian and Pruchniewicz, 1977; Fishman et al., 1979b] that ozone is more abundant in the northern tropics than in the south and more abundant at northern mid-latitudes than in the tropics. It is clear that latitudinal gradients in ozone vary significantly with season and with longitude.

Evidence presented here suggests that concentrations of ozone at middle and high latitudes of the northern hemisphere have been influenced significantly by photochemical production associated with emissions of NO$_x$, hydrocarbons, and CO from combustion of fossil fuels. Ozone over the tropical continents may also be influenced by emissions from combustion, in this case from agricultural burning. At present the seasonal behavior of tropospheric ozone is reasonably well characterized only over continental mid-latitudes of the northern hemisphere. Long-term measurements are sparse, even for Europe and North America. Data for ozone are particularly lacking for the tropics and subtropics. Given the central role of ozone in tropospheric chemistry, it is clear that a concerted effort should be made to determine the global climatology of ozone by establishing a network of suitably placed measurement stations. A serious commitment should also be made to measure ozone on a long-term basis with well-calibrated instruments at selected locations. Measurements of species that affect ozone, such as NO$_x$, hydrocarbons, and CO, are needed also in order to improve our understanding of the role of photochemistry in determining the distribution of ozone. It will be necessary, in addition, to develop more sophisticated models for chemistry and dynamics in order to test our concepts about the processes influencing ozone and to evaluate future effects on tropospheric ozone of combustion related emissions. Such models must allow for the transformation and transport of pollutants from urban source regions (or from regions of agricultural burning) to the middle troposphere and must adequately simulate intrusions of stratospheric air and removal of ozone at the surface over varied terrain.
The sondes data permit an evaluation of the contribution of the trend in tropospheric ozone to the trend in the ozone column at those locations where the trends are statistically significant throughout the troposphere and stratosphere. This condition is met most closely at Hohenpeissenberg and Resolute (see Figure A1). Trends in ozone integrated through the troposphere and stratosphere are given in Table A1 in terms of Dobson units. The trend in the ozone column derived from the sondes data is in excellent agreement with the trend derived from concurrent Dobson measurements, but this is not surprising, since the sondes concentrations are normalized to the Dobson data. The increase in the column of ozone in the troposphere is about 20% of the decrease in the column in the stratosphere at Resolute. The results for Hohenpeissenberg are more difficult to interpret. The increase in ozone in the troposphere is ~30% of the decrease in the stratosphere, based on sondes data that have been scaled to the Dobson measurement of the ozone column, but the increase and decrease are of equal magnitude if the conventional scaling procedure is not used. This discrepancy arises because there is a significant trend in the correction factor at Hohenpeissenberg, −0.4% yr\(^{-1}\), of comparable magnitude to the trend in stratospheric ozone (see Tables A1 and A2 and Figure A1). We note that the trend in the ozone column derived from Dobson data at Hohenpeissenberg, −0.28% yr\(^{-1}\), does not agree with the average trend in the ozone column over Europe for 1970–1981, 0.1 ± 0.27% in 12 years. The average trend was derived by Angell and Korshover (1982) from 13 Dobson stations. The sondes data that have not been scaled to the Dobson results give no change in the ozone column, in better agreement with the average result for Europe. If the unscaled data provided a better measure of the trend in ozone at Hohenpeissenberg, this could imply that the increase in tropospheric ozone is of similar magnitude to the decrease in stratospheric ozone over Europe.

The results in Table A1 and Figure A1 highlight one of the major difficulties with interpretation of long-term ozone sonde measurements. The procedure of normalizing sondes results to Dobson measurements may introduce a significant bias into

### TABLE A1. Trends in Ozone in the Stratosphere and Troposphere

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Trend</td>
<td>Scoured to Column Divided by Correction Factor</td>
<td>Scoured to Column Divided by Correction Factor</td>
<td>Scoured to Column Divided by Correction Factor</td>
</tr>
<tr>
<td>Sonde</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔO(_3), troposphere</td>
<td>+0.4</td>
<td>+0.5</td>
<td>+0.2</td>
</tr>
<tr>
<td>ΔO(_3), stratosphere</td>
<td>−1.5</td>
<td>−0.5</td>
<td>−0.7</td>
</tr>
<tr>
<td>ΔO(_3), total(^a)</td>
<td>−1.1</td>
<td>0.0</td>
<td>−0.9</td>
</tr>
<tr>
<td>Dobson</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔO(_3), column</td>
<td>−0.9 ± 0.5</td>
<td>−0.8 ± 0.5</td>
<td>0.6 ± 1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Dobson Units</th>
<th>Dobson Units</th>
<th>Dobson Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_3), troposphere</td>
<td>26</td>
<td>28</td>
<td>310</td>
</tr>
<tr>
<td>O(_3), stratosphere</td>
<td>284</td>
<td>281</td>
<td>305</td>
</tr>
<tr>
<td>O(_3), total(^a)</td>
<td>339</td>
<td>335</td>
<td>392</td>
</tr>
</tbody>
</table>

The upper portion of the table gives trends in ozone derived from ozonesonde measurements and from Dobson measurements made on the same day. Integrated trends in the stratosphere and troposphere were obtained from trend results for the standard pressure levels (see Figure A1) and are given in Dobson units per year (one D.U. = 2.69 x 10\(^{19}\) molecules cm\(^{-2}\)). The left-hand columns give results from sondes data that have been scaled to the Dobson measurements of the column, the right-hand columns give results from data that have not been scaled in this manner (see Table 3 footnotes). The lower portion of the table shows the integrated amount of ozone recorded by the sondes and by the Dobson instruments.

\(^{a}\)Column of ozone below 10 mbar.
TABLE A2. Trend in Stratospheric Ozone, 100-50 mbar

<table>
<thead>
<tr>
<th>Location</th>
<th>Scaled to Column</th>
<th>Divided by Correction Factor</th>
<th>Trend in Correction Factor</th>
<th>Trend in Column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hohenpeissenberg</td>
<td>-0.7 ± 0.3</td>
<td>-0.4 ± 0.3</td>
<td>-0.4 ± 0.2</td>
<td>-0.2 ± 0.15</td>
</tr>
<tr>
<td>Payenne (January 1969 to December 1981)</td>
<td>0.5 ± 0.3</td>
<td>-0.4 ± 0.4</td>
<td>NS</td>
<td>-0.23 ± 0.14</td>
</tr>
<tr>
<td>Ucle (January 1969 to March 1981)</td>
<td>-0.4 ± 0.4</td>
<td>a</td>
<td>NS</td>
<td>b -0.20 ± 0.18</td>
</tr>
<tr>
<td>Resolute</td>
<td>-0.7 ± 0.3</td>
<td>1.5 ± 0.5</td>
<td>0.5 ± 0.3</td>
<td>NS</td>
</tr>
<tr>
<td>Goose Bay (June 1969 to December 1982)</td>
<td>0.5 ± 0.3</td>
<td>a</td>
<td>b -0.20 ± 0.18</td>
<td>NS</td>
</tr>
<tr>
<td>Wallops Island (May 1970 to August 1981)</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Sapporo</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Tateni</td>
<td>-1.2 ± 0.5</td>
<td>1.5 ± 0.5</td>
<td>0.5 ± 0.3</td>
<td>NS</td>
</tr>
<tr>
<td>Kagoshima</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Aspendale (January 1969 to April 1982)</td>
<td>-0.5 ± 0.4</td>
<td>-1.1 ± 0.4</td>
<td>0.8 ± 0.3</td>
<td>NS</td>
</tr>
</tbody>
</table>

Trends are given as the percentage change per year for average concentrations at 100, 70, and 50 mbar. Trends were calculated as described in section 3 and are presented in the same format as Table 2. Results are given for January 1969 to December 1982, unless otherwise indicated. The trend in the ozone column was calculated from Dobson measurements made on the same days as the ozone soundings.

*The trend in the correction factor for January 1969 to January 1979 was 0.5(±0.3)% per year. The change from Brewer-Mast to ECC sondes in 1979 precludes meaningful interpretation of the trend in the C.F. thereafter.

*The trend in the C.F. for June 1969 to August 1980 was -0.7(±0.3)% per year. FCC sondes were used after August 1980.

**Acknowledgments.** This analysis would not have been possible without the dedicated efforts of the research groups who initiated and maintained the long-term measurement programs that formed the basis for this study. To them I extend my sincere appreciation. I am indebted to S. C. Wolfe for many enlightening discussions and would like to thank him and M. B. McElroy for their constructive comments on this paper. Special thanks are due to R. Yevich and C. S. Spivakovsky for their invaluable assistance with analysis of the ozone data. I would like to acknowledge useful discussions with H. Levy II and I. Galbally and to thank R. Angle, D. DeMooe, G. Evans, I. Galbally, V. Kirchoff, and V. Mohseni for kindly providing unpublished measurements of ozone. L. Morrison of Atmospheric Environment Service was most cooperative in supplying computer tapes of the sonde data. R. Bojkov brought to my attention the change in the time of measurements at Payenne. Finally, I would like to thank C. Demore for her expert editorial assistance and M. Burrell for her patience and skill in drafting the many figures. This work was supported by NSF grant ATM-81-17009, NASA grant NSC-2031 and CRC contract CAPA-22-83 to Harvard University.

**REFERENCES**


Cruzen, P. J., and L. T. Gidel, A two-dimensional photochemical model of the atmosphere, 2, The tropospheric budgets of the anthropogenic chlorocarbons, CO, CH₃, CH₂Cl, and the effect of...


J. A. Logan, Center for Earth and Planetary Physics, 108 Pierce Hall, 29 Oxford Street, Harvard University, Cambridge, MA 02138.

(Received February 25, 1985; revised May 17, 1985; accepted May 17, 1985.)