TROPOSPHERIC OZONE: AN OVERVIEW

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ABSTRACT.   Although only about 10% of all atmospheric ozone
is located in the troposphere, it is the main driver of the
photochemical processes which lead to the recycling of most
of the gases that are emitted into the atmosphere by natural
processes and anthropogenic activities.
    Substantial changes are taking place in the troposphe-
ric ozone abundance. In this paper, an overview is given of
the chemical processes that lead to ozone formation and
destruction in the troposphere, emphasizing human impact on
the global scale. In the northern hemisphere, anthropogenic
emissions of NO_x clearly lead to high ozone concentrations
during photochemical pollution episodes. However, also in
the background free troposphere, pronounced ozone concentra-
tion increases have occurred, which are here confirmed by a
review of measurements that were made in the 1930's - 50's
in Europe.
    The potential for tropospheric ozone production from
carbon monoxide and hydrocarbon oxidation, with NO_x acting
as catalyst, is enormous. At this stage, only at most 10% of
this does actually occur, due to insufficient NO_x in the
background troposphere. Future human developments that lead
to increasing NO emissions may, therefore, lead to further
ozone increases, especially in the tropics.

1. INTRODUCTION

"Among the many interesting bodies which the researches of
modern chemists have brought to light, few are more remark-
able than the substance to which the name of ozone has been
given". With this sentence starts an article written in 1855
by Thomas Andrews, M.D. and Professor of Chemistry in
Queen's College, Belfast, one of the early pioneers of ozone
research. By that time the exact chemical composition of
ozone was yet not established. One proposal was that the gas

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was the teroxide of hydrogen HO_3, based on the fact it is
also formed when pure water is electrolyzed, a discovery
which was made in 1840 by the German chemist Schönbein,
working in Basel, Switzerland. Soret (1863, 1865) and
Andrews (1874) argued that ozone is a pure oxygen allotrope,
probably consisting of three oxygen atoms. The question
about the exact chemical composition of ozone seems firmly
to have been settled first by the beginning of this century.
A comprehensive overview of early ozone research is given by
Fonrobert (1916).

By the latter quarter of the 19th century, it had been
clearly demonstrated by Andrews and others that ozone was a
normal constituent of atmospheric air. This had already been
proposed in 1845 by Schönbein, who also introduced an
"ozonometer", consisting of iodized starch paper, which was
extensively used at many sites around the world. The
interest in ozone measurements was especially stimulated
since Schönbein discussed the possible role of ozone as a
disinfectant against epidemic disease and it is claimed by
Fonrobert (1916) that a million ozone measurements were made
with the Schönbein method. It is unfortunate that the many
data on tropospheric ozone that were taken with the
Schönbein test paper are only of limited value, because the
method is unspecific and even dependent on meteorological
factors such as wind speed and atmospheric humidity (Bojkov,
1986).

By 1874 some basic discoveries about surface ozone had
nevertheless already been made by some careful researchers.
We quote from Andrews (1874): "Ozone is rarely found in the
air of large towns, unless in a suburb when the air is
blowing from the country. ... It is, in fact, rapidly
destroyed by smoke and other impurities which are present in
the air of localities where large bodies of man have fixed
their habitations, and I have often observed this destruc-
tive action extending to a distance of one or two miles from
a manufacturing town, even in fine and bright weather. Ozone
is rarely, if ever, absent in fine weather from the air of
the country; and it is more abundant, on the whole, in the
air of the mountain than of the plain".

Unfortunately, we probably only have one long series
of measurements which may be taken representative for ground
level ozone concentrations during the past century, namely
those made by A. Levy and coworkers at the Montsouris
observatory in Paris between 1876 and 1907 (Levy, 1907). The
quality of those observations has recently been ascertained
by Volz and Kley (1987; also this volume). They indicate 3-4
times lower average concentrations of tropospheric ozone
than are presently measured at comparable sites. Because at
current levels ozone is phytotoxic (Prinz, this volume;
Skarby and Sellden, 1984), this is an extremely important
observation. Other measurements of tropospheric ozone which

are in agreement with these findings will be reviewed in
this paper.

Interest in the study of tropospheric ozone strongly
declined during the first decades of this century and one
may speculate whether this was not largely due to the low
quality of the measurements which precluded the discovery of
any temporal or spatial patterns in the observations. We
cite again from Andrews (1874): "The amount of ozone in the
air is greater, according to some observers, in winter than
in summer, in spring than in autumn; according to others, it
is greater in spring and summer than in autumn and winter.
As regards the influence of day and night, the observations
do not tell the same tale. Ozone has usually been found more
abundantly in the air at night than by day, but some careful
observers have found the reverse of this statement to be
true". Even after taking great care with the Schönbein
measurements, Friesenhof in 1904 could only summarize the
following results from a major observational program in
Austria: " ... and thus I have already noted that the
occurrence of thunderstorms in the vicinity are accompanied
by abnormally low ozone concentrations" and further: "The
second result was a diurnal period in ozone concentrations
with a maximum during the hours prior to midnight and a
minimum in the hours before noon" (transl. by author).

More serious research in tropospheric ozone had to
await the development of more reliable instrumentation, in
the first place optical techniques. With these Strutt (1918)
and Fabry and Buisson (1921) deduced that most ozone must be
located in the stratosphere with a total abundance of about
3mm STP. The ozone maximum was first thought to be located
near 50 km altitude (Cabannes et Dufay, 1927), but this was
later corrected to about 27 km (Götz et al, 1934). The
optical techniques were subsequently also applied to
tropospheric ozone measurements (e.g. Fabry and Buisson,
1931; Götz and Ladenburg, 1931). However, because the
spectrographic technique was too cumbersome to use for long
term observations, by the end of the 1930's improved
chemical techniques, mostly based on the conversion of
potassium iodide (KI) by ozone to iodine (I_2), were again
increasingly used (Cauer, 1935; Paneth and Edgar, 1938;
Regener, 1938). With this method many measurements were made
during and after worldwar II at several health and vacation
resorts in Germany and Switzerland. Most of these data are
probably of sufficient quality to reveal any substantial
differences between present tropospheric ozone concentra-
tions and those measured 30-50 years ago. Before giving a
brief review of past ozone measurements, we will, however,
first show why the study of tropospheric ozone is of
fundamental importance for an understanding of the photo
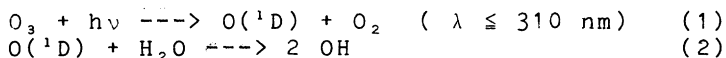chemistry of the atmosphere.

2. THE ROLE OF OZONE IN TROPOSPHERIC CHEMISTRY

After it became clear that most ozone is located in the
stratosphere, first by ground-based measurements (Strutt,
1918; Götz et al, 1934) and later by in-situ balloon-borne
observations (Regener and Regener, 1934; Regener, 1938), it
was for a long time generally believed that tropospheric
ozone originated from the stratosphere and that most of it
was destroyed at the earth's surface, although some loss
admittedly could also occur in the troposphere (e.g.
Regener, 1943). This idea was supported by the observed
strong correlations between total ozone and tropospheric me-
teorological patterns (Dobson et al, 1929). Furthermore,
since Chapman (1930), it had become clear that ozone was
produced by the photodissociation of O_2, which can only
occur at wavelengths shorter than 240 nm, precluding
production in the troposphere. From the mid-1940's, however,
it became obvious that ozone could also be produced in the
troposphere. After heavy injury to vegetable crops occurred
repeatedly in the Los Angeles area, it was shown by Haagen-
Smit (1952) that the plant damage could be reproduced by
ozone, which had been shown to be present in such high
concentrations in the Los-Angeles "photochemical smog" that
a stratospheric origin could be excluded (Haagen-Smit and
Fox, 1956). The overall reaction mechanism was identified
as:

$$NMHC + NO_X + h\nu \longrightarrow O_3 + \text{other pollutants}$$
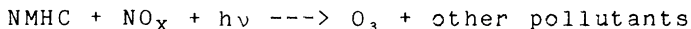
, where NMHC denotes various reactive non-methane-hydrocar-
bons, NO_X is $NO + NO_2$, and $h\nu$ is solar radiations of
wavelengths less than about 400 nm (Finlayson-Pitts and
Pitts, 1985). Ozone formation is possible, because solar
radiation between about 300 and 400 nm can reach
the earth's surface and dissociate NO_2 into NO and O. The
recombination of O with O_2 produces O_3. For about 20
years it was thought that ozone formation through this
mechanism could only take place in atmospheric environments
that were heavily polluted with automobile exhausts and
strongly illuminated with sunlight. It was only in the
1970's that photochemical smog was also discovered in Europe
(e.g. Guicherit and van Dop, 1977; Derwent and Stewart,
1973). At about the same time the first proposals were made
that significant in-situ photochemical production and
destruction could also take place on global scales (Crutzen,
1973, 1974; Chameides and Walker, 1973).
    Already in 1971 and 1972 Levy had proposed that ozone
photolysis at wavelengths shorter than about 310 nm leads to
the production of hydroxyl (OH)

$$O_3 + h\nu \; ---> \; O(^1D) + O_2 \quad (\lambda \leq 310 \text{ nm}) \quad (1)$$
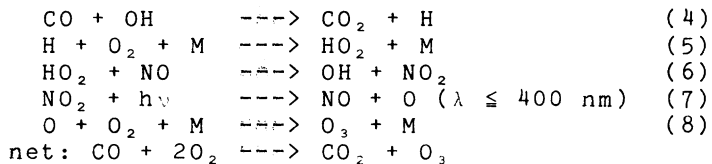$$O(^1D) + H_2O \; ---> \; 2 \; OH \quad\quad\quad\quad\quad\quad\quad (2)$$

and that hydroxyl plays an exceedingly important role in the
removal of many gases that are produced naturally or by
human activities. Levy (1971) also proposed that a chain
reaction leading to increased hydroxyl production could
occur via the formation of CH_2O in the methane oxidation
cycle. McConnell et al (1971) and Wofsy et al (1972) postu-
lated that reaction of hydroxyl with methane could be the
most important atmospheric source of carbon monoxide. In
earlier years it was either believed that the atmospheric CO
budget was totally dominated by natural processes or by
anthropogenic activities. McConnell et al (1971) and Wofsy
et al (1972) also proposed that the atmospheric CO distribu-
tion was mainly governed by the reactions

$$CH_4 + OH \; ---> \; ..... \; ---> \; CO \quad\quad\quad (3)$$
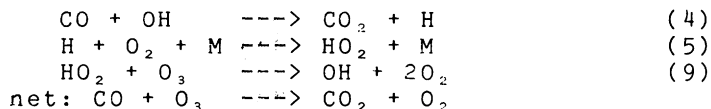$$CO + OH \; ---> \; H + CO_2 \quad\quad\quad\quad\quad (4)$$
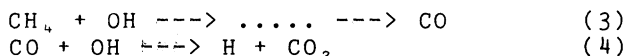
However, because carbon monoxide concentrations are much
more variable than those of methane, it is clear that a
variety of natural and anthropogenic processes must make
additional important contributions to the atmospheric CO
cycle, such as fossil fuel burning (Seiler, 1974), biomass
burning in the tropics (Crutzen et al, 1979; Crutzen et al,
1985) and oxidation of hydrocarbons emitted by forests.
    Crutzen (1973, 1974) pointed out that ozone could both
be produced and destroyed by the methane and carbon monoxide
oxidation cycles, depending on the concentrations of nitric
oxide (NO). For instance, the carbon monoxide oxidation
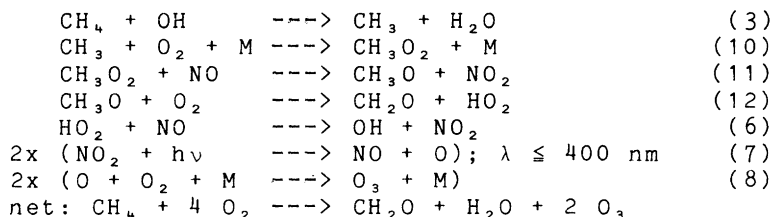cycles can either proceed via:

$$CO + OH \quad\quad ---> \; CO_2 + H \quad\quad\quad\quad\quad\quad (4)$$
$$H + O_2 + M \quad ---> \; HO_2 + M \quad\quad\quad\quad\quad\quad (5)$$
$$HO_2 + NO \quad\quad ---> \; OH + NO_2 \quad\quad\quad\quad\quad (6)$$
$$NO_2 + h\nu \quad\quad ---> \; NO + O \; (\lambda \leq 400 \text{ nm}) \quad (7)$$
$$O + O_2 + M \quad ---> \; O_3 + M \quad\quad\quad\quad\quad\quad (8)$$
$$\text{net: } CO + 2O_2 \; ---> \; CO_2 + O_3$$

or by

$$CO + OH \quad\quad ---> \; CO_2 + H \quad\quad\quad\quad\quad\quad (4)$$
$$H + O_2 + M \; ---> \; HO_2 + M \quad\quad\quad\quad\quad\quad (5)$$
$$HO_2 + O_3 \quad\quad ---> \; OH + 2O_2 \quad\quad\quad\quad\quad (9)$$
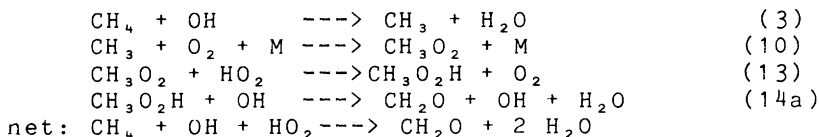$$\text{net: } CO + O_3 \; ---> \; CO_2 + O_2$$

    Because the rate coefficient for reaction (6) is about
4000 times faster than that for reaction (9), the ozone
producing carbon monoxide oxidation branch is more important
than the ozone destruction branch for NO to O_3 concentration

ratios exceeding 1:4000, i.e. for NO volume mixing ratios larger than about $5-10 \times 10^{-12}$ (5-10 pptv) in the lower troposphere.
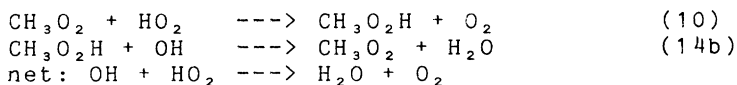
Similar, but more complex reaction cycles do also take place during the oxidation of hydrocarbon gases, with methane being the most important example in extensive portions of the atmosphere, especially in the remote marine environments. The oxidation of methane plays a large role in the tropospheric ozone and hydroxyl balance. Again the availability of NO plays a decisive role. For example, in NO-rich environments, the oxidation of CH_4 to CH_2O occurs mostly via the reaction steps
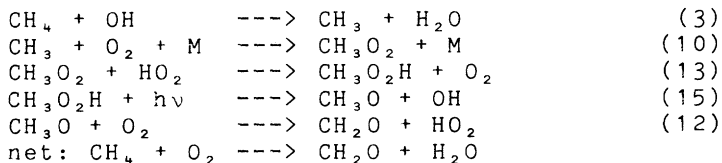
$$\begin{array}{lll}
CH_4 + OH & \longrightarrow CH_3 + H_2O & (3) \\
CH_3 + O_2 + M & \longrightarrow CH_3O_2 + M & (10) \\
CH_3O_2 + NO & \longrightarrow CH_3O + NO_2 & (11) \\
CH_3O + O_2 & \longrightarrow CH_2O + HO_2 & (12) \\
HO_2 + NO & \longrightarrow OH + NO_2 & (6) \\
2x \ (NO_2 + h\nu & \longrightarrow NO + O); \ \lambda \leq 400 \ nm & (7) \\
2x \ (O + O_2 + M & \longrightarrow O_3 + M) & (8) \\
net: CH_4 + 4 \ O_2 & \longrightarrow CH_2O + H_2O + 2 \ O_3 &
\end{array}$$

In NO-poor environments, other reaction paths, leading to loss of odd hydrogen ($OH + HO_2$) radicals are important:

$$\begin{array}{lll}
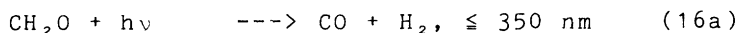CH_4 + OH & \longrightarrow CH_3 + H_2O & (3) \\
CH_3 + O_2 + M & \longrightarrow CH_3O_2 + M & (10) \\
CH_3O_2 + HO_2 & \longrightarrow CH_3O_2H + O_2 & (13) \\
CH_3O_2H + OH & \longrightarrow CH_2O + OH + H_2O & (14a) \\
net: CH_4 + OH + HO_2 & \longrightarrow CH_2O + 2 \ H_2O &
\end{array}$$

and a catalytic subcycle:

$$\begin{array}{lll}
CH_3O_2 + HO_2 & \longrightarrow CH_3O_2H + O_2 & (10) \\
CH_3O_2H + OH & \longrightarrow CH_3O_2 + H_2O & (14b) \\
net: OH + HO_2 & \longrightarrow H_2O + O_2 &
\end{array}$$

No net effect on either O_3 or odd hydrogen has the cycle:

$$\begin{array}{lll}
CH_4 + OH & \longrightarrow CH_3 + H_2O & (3) \\
CH_3 + O_2 + M & \longrightarrow CH_3O_2 + M & (10) \\
CH_3O_2 + HO_2 & \longrightarrow CH_3O_2H + O_2 & (13) \\
CH_3O_2H + h\nu & \longrightarrow CH_3O + OH & (15) \\
CH_3O + O_2 & \longrightarrow CH_2O + HO_2 & (12) \\
net: CH_4 + O_2 & \longrightarrow CH_2O + H_2O &
\end{array}$$

Finally, CH_2O is decomposed to CO either by the reaction

$$CH_2O + h\nu \longrightarrow CO + H_2, \leq 350 \ nm \quad (16a)$$

, or in NO-rich environments by

$$CH_2O + h\nu \quad ---> \quad CHO + H, \; \lambda \leq 350 \; nm \quad (16b)$$
$$CHO + O_2 \quad ---> \quad CO + HO_2 \quad (17)$$
$$H + O_2 + M \quad ---> \quad HO_2 + M \quad (5)$$
$$2x \; (HO_2 + NO \quad ---> \quad OH + NO_2) \quad (6)$$
$$2x \; (NO_2 + h\nu \quad ---> \quad NO + O) \quad (7)$$
$$2x \; (O + O_2 + M \quad ---> \quad O_3 + M) \quad (8)$$
$$net: \; CH_2O + 4O_2 \quad ---> \quad CO + 2 \; OH + 2 \; O_3$$

$$CH_2O + OH \quad ---> \quad CHO + H_2O \quad (18)$$
$$CHO + O_2 \quad ---> \quad CO + HO_2 \quad (17)$$
$$HO_2 + NO \quad ---> \quad OH + NO_2 \quad (6)$$
$$NO_2 + h\nu \quad ---> \quad NO + O \quad (7)$$
$$O + O_2 + M \quad ---> \quad O_3 + M \quad (8)$$
$$net: \; CH_2O + 2O_2 \quad ---> \quad CO + H_2O + O_3$$
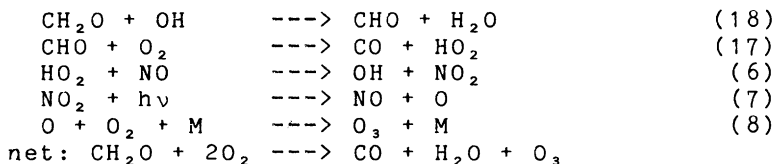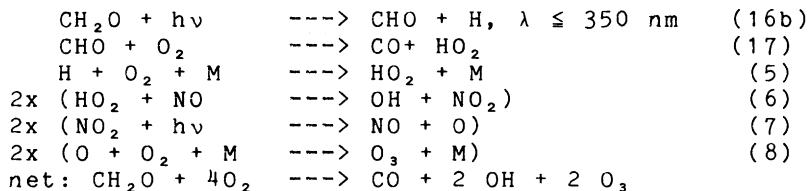
In NO-poor environments, the significant CH_2O reactions are:

$$CH_2O + h\nu \quad ---> \quad CHO + H \quad (16b)$$
$$CHO + O_2 \quad ---> \quad HO_2 + CO \quad (17)$$
$$H + O_2 + M \quad ---> \quad HO_2 + M \quad (5)$$
$$2x \; (HO_2 + O_3 \quad ---> \quad OH + 2 \; O_2) \quad (9)$$
$$net: \; CH_2O + 2 \; O_3 \quad ---> \quad CO + 2 \; O_2 + 2OH$$

$$CH_2O + OH \quad ---> \quad CHO + H_2O \quad (18)$$
$$CHO + O_2 \quad ---> \quad CO + HO_2 \quad (17)$$
$$HO_2 + O_3 \quad ---> \quad OH + 2 \; O_2 \quad (9)$$
$$net: \; CH_2O + O_3 \quad ---> \quad CO + H_2O + O_2$$
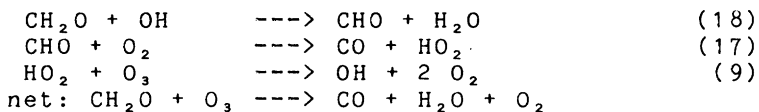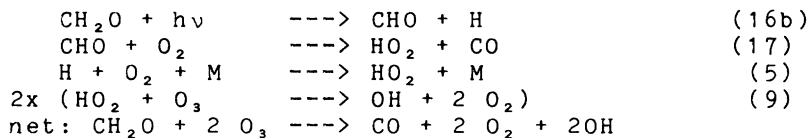
Altogether, the oxidation of one methane molecule to carbon monoxide and then to carbon dioxide may yield on the average the following, rather astonishing, net results (Crutzen, 1986):
(a) In NO-poor environments: a net loss of 3.5 odd hydrogen and 1.7 ozone molecules
(b) in NO-rich environments: a net gain of 0.5 odd hydrogen and 3.7 ozone molecules

Heterogeneous processes on aerosol particles and water droplets may modify these results through the removal of intermediate products, especially the peroxides CH_3O_2H and H_2O_2. Hydrogen peroxide is formed by

$$HO_2 + HO_2 \; ---> \; H_2O_2 + O_2 \quad (19)$$
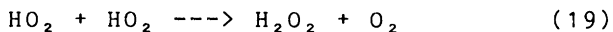
These results are very important for the photochemistry of the "background" troposphere, because CH_4 and CO are the main reaction partners of OH, and because CH_4 concentrations have been increasing by about 1% per year during the past decades (Rasmussen and Khalil, 1981, 1984; Blake et al, 1982; Blake and Rowland, 1986; Fraser et al, 1981;

Seiler, 1984; Rinsland et al, 1985). Analysis of spectra
taken on the Jungfraujoch in Switzerland at about 3.5 km
altitude (Rinsland and Levine, 1985) indicates that CO
mixing ratios may also have been increasing, on the average
by 0.5-4% per year between 1950 and 1977. However, Dianov-
Klokov and Yurganov (1981) infer by comparing their own
total vertical column CO observations in the 70's to those
by Shaw (1958) in the U.S. two decades earlier that CO
increased by about 2% per year only during winter time,
remaining unchanged during summer.

Natural sources of atmospheric NO_x include lightning,
about $3-8x10^{12}$g N/yr (Noxon, 1978; Chameides et al, 1987b)
and emanations from soils, about $5-15x10^{12}$g N/yr (Galbally
and Roy, 1980). More NO is, however, emitted to the atmo-
sphere by anthropogenic activities due to fossil fuel
burning at mid-latitudes in the northern hemisphere
($\approx 20x10^{12}$g N/yr) and biomass burning ($5-10x10^{12}$g N/yr)
during the dry season in the tropics (Ehhalt and Drummond,
1982 and this volume; Logan, 1983; Crutzen et al, 1979,
1985). However, because the average lifetimes of NO_x in the
atmosphere is of the order of a day, except for some
complications due to long-range transport of peroxy-acetyl
nitrate (Crutzen, 1979; Singh and Salas, 1983), it is clear
that the NO-rich atmospheric environments should mainly be
limited to the temperate zone of the northern hemisphere and
the boundary layer of the tropics during the dry season. The
NO-poor environments are mainly the marine areas, the free
troposphere of the tropics and most of the southern hemi-
sphere. Consequently, due to the photochemical reaction
chains presented before, we suspect that ozone and hydroxyl
concentrations are decreasing in clean atmospheric environ-
ments and increasing at mid-latitudes in the northern
hemisphere. This gradual shift in the oxidative power of the
atmosphere seems to be born out by ozone measurements at
some "background" stations (Oltmans, 1985), which show the
following average surface ozone concentration trends:
Barrow, Alaska (0.78 ± 0.52%/yr), Mauna Loa Observatory,
Hawaii (1.20 ± 0.52%/yr) and Samoa (- 0.70 ± 0.80%/yr).

Because the sources of atmospheric methane are mainly
influenced by anthropogenic activities (see Table I), these
trends in "background" ozone concentrations will likely
continue.

As a global average, hydroxyl concentrations are
estimated at about $5\pm2x10^5$/cm^3 (e.g. Crutzen and Gidel,
1983; Volz et al, 1981), with largest concentrations in the
tropics (Figure 1). As shown in Figures 2 and 3, this
implies that for several important gases, e.g. methane and
carbon monoxide, the largest atmospheric sources and sinks
are also likely located in the tropics (Crutzen and Gidel,
1983). It is interesting to note that during the dry season,
especially in the savanna regions, large ozone (and carbon

Methane

Sinks

   Tropospheric reactions with OH   290-350
   Stratospheric reactions with OH   25-35
   Uptake on aerobic soils   10-30

Annual growth ($\approx$1.1%/yr)   50-60

Total required sources   375-475
  (sum of above)

Sources
  Domestic animals   70-80
  Natural gas leaks $\leq$35
  Coal mining   35
  Landfills   30-70
  Biomass burning   30-100
  Wild ruminants   2-6
  Other fauna (e.g., insects)   <30
  Decay of animals wastes   ?
  Rice fields and natural wetlands   >44-228

Table I: Estimates of global sources and sinks of methane
     (units 10^{12}g per year), based on information in Seiler
     et al (1984), Keller et al (1983), Harriss et al
     (1982), Rasmussen and Khalil (1984), Khalil and
     Rasmussen (1986), Blake and Rowland (1986), Crutzen et
     al (1986), Crutzen (1986), Bingemer and Crutzen
     (1987), Crutzen et al (1985).

monoxide) concentrations do indeed build up, as expected
from photochemical reactions in the presence of oxides of
nitrogen resulting from biomass burning (Crutzen et al,
1985; Delany et al, 1985; Andreae et al, 1987). Elsewhere,
in clean environments, and during the wet season, ozone
concentrations are substantially lower (Logan and Kirchhoff,
1986).

3. TRENDS IN OZONE CONCENTRATIONS

Because we have reasons to expect that "background" ozone
concentrations have increased substantially in the mid-
latitude zone of the northern hemisphere, it is important to
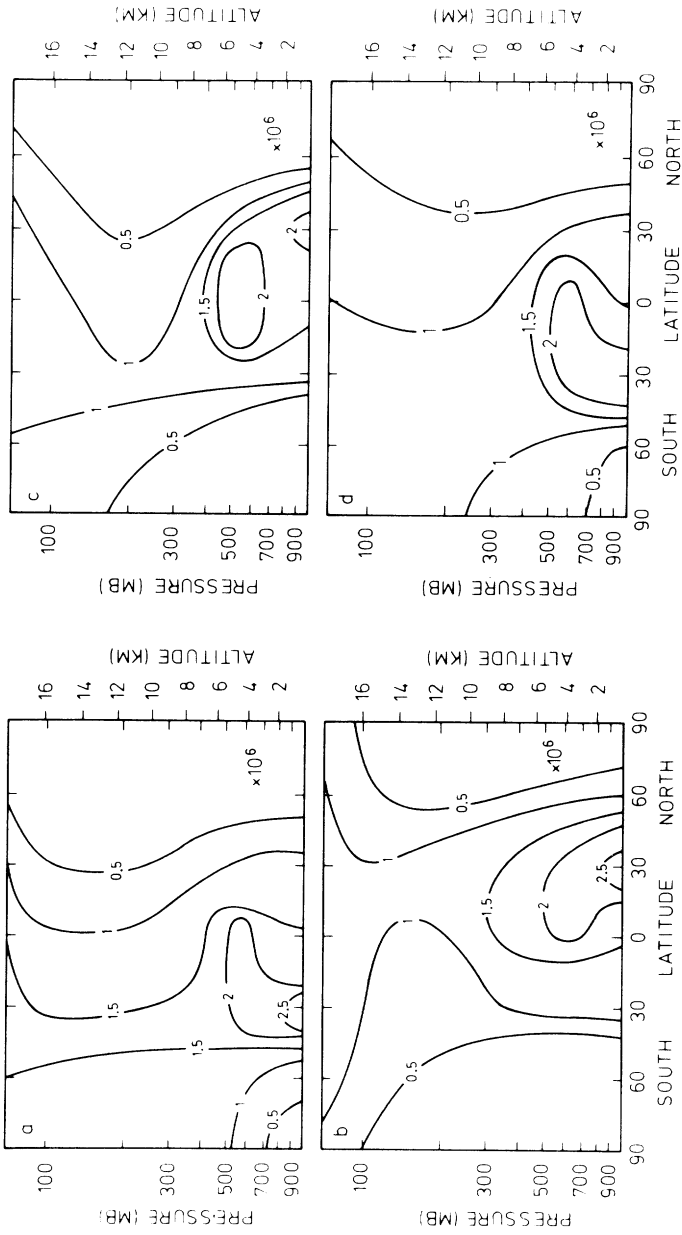look at long-term trends in tropospheric ozone concentra-

Figure 1: Calculated daytime average meridional distributions of OH (in units of 10^6 molecules cm^{-3}) for (a) January, (b) July, (c) April, and (d) October, (reprinted from Crutzen and Gidel, 1983).
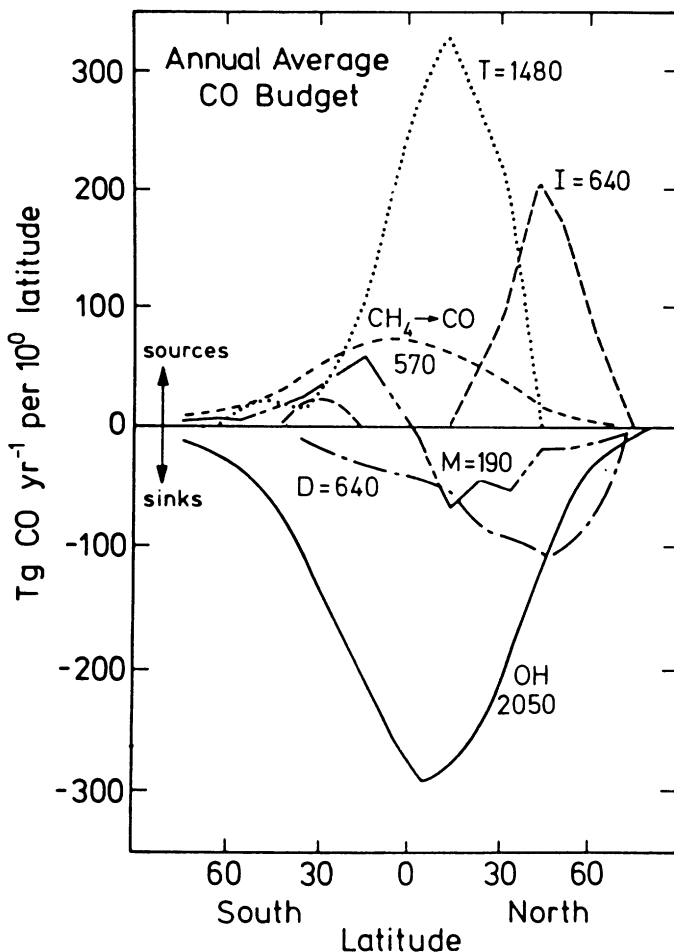
Figure 2: Annual CO budget estimated by Crutzen and Gidel
(1983) in units of 10^{12}g/yr; OH: destruction by
reaction with OH; D: destruction at the earth's
surface (Seiler, 1974); M: transport from northern to
southern hemisphere; CH_4: production by oxidation of
CH_4; I: fossil fuel burning (Seiler, 1974); T:
production by a variety of other sources, mainly
biomass burning and oxidation of hydrocarbons in the
tropics.
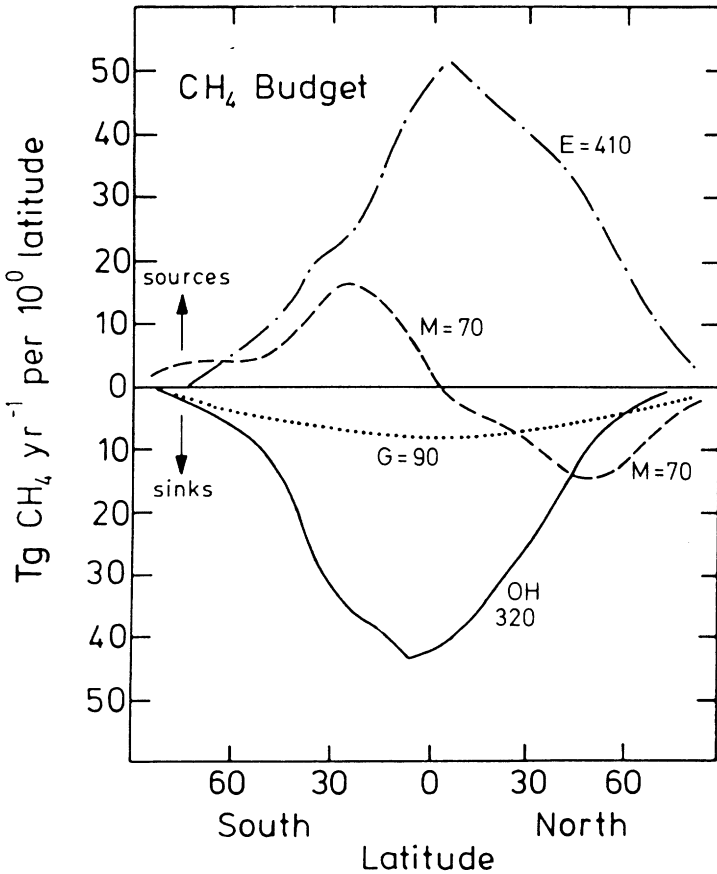
Figure 3: Annual CH₄ budget, according to Crutzen and Gidel
    (1983) in units of 10^{12} g/yr. OH: destruction by
    reaction with OH; M: transport from nothern to
    southern hemisphere; E. variety of sources (see Table
    1).

tions. A thorough analysis of this kind, mostly based on
measurements in the 60's and 70's by Logan (1985) indeed
established that ozone concentrations in rural areas at
mid-latitudes in the northern hemisphere have increased by
20-100%. Also in the free troposphere annual ozone concen-
tration increases by 1-2% between 30°N and 75°N were
observed. However, the rapid growth in NO_x and hydrocarbon
emissions started much earlier (see Figure 4). Consequently,
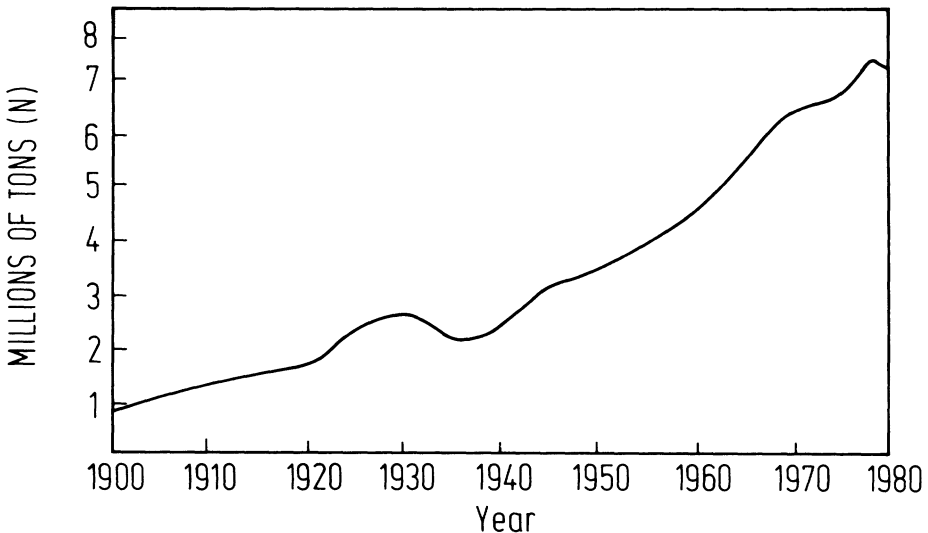it is important to look at even earlier ozone data. Most

Figure 4: Estimates of NO_x emissions in the U.S. in units of $10^{12}gN$ per year; adapted from NAPAP (1984).

reliable are those obtained by optical techniques especially
during the early 1930's. Unfortunately, only so few measure-
ments were made with this technique that they fit on
one-page (see Table II).
      It is interesting to note that all ozone observations
from low altitude ($<$ 1 km) stations are substantially lower
than currently measured with modern chemical techniques at
representative stations in similar areas, e.g. Hohenpeißen-
berg in Southern Germany (Attmannspacher et al, 1984).
However, because the exact measurement conditions were often
not reported, the comparisons should be supported by more
detailed analyses, provided the old field work reports are
still available. Most significant are the observations from
Arosa and especially those from the Jungfraujoch (alt.
3450 m) in Switzerland, which yield an average volume mixing
ratio of about 30 ppbv. In comparison, the summer time ozone
volume mixing ratios, that are currently measured above
Hohenpeißenberg at a similar altitude as the Jungfraujoch,
average about 60 ppbv (Attmannspacher et al, 1984), i.e.
about two times more than in 1933. This indicates a substan-
tial large scale increase in tropospheric ozone, confirming
the findings by Attmannspacher et al (1984) based on
measurements between 1968 and 1984.
      Chemical ozone observations, based on the $KI-O_3$
reactions, were improved considerably by Cauer (1935),
Paneth and Edgar (1938), Regener (1938), Ehmert and Ehmert

Table II: Compilation of ozone measurements made with
optical technique.

Location	Date	Height/m	Mixing ratio/ppbv	Authors
Arosa	03.09.32	1900	8-9	Götz and Maier-
	28.09.32		19-22	Leibnitz (1933)
Chur	29.09.32	600	18-21	
	01.10.32		19-21	
Arosa	28.03.33	1900	31-36	
	31.03.33		25-29	
Jungfrau-	21.08.33	3450	27	Challonge and Vassy
joch	24.08.33		35	(1934); Challonge
	25.08.33		25	et al (1934)
	26.08.33		33	
	27.08.33		24	
	28.08.33		35	
	29.08.33		33	
Lauter-	18.08.33	800	14	
brunnen	19.08.33		16	
	21.08.33		11	
	23.08.33		26	
	24.08.33		19	
	25.08.33		20	
	28.08.33		15	
	29.08.33		14	
	30.08.33		18	
	31.08.33		19	
Provence	Oct,1929	300	20-22	Fabry and Buisson
	March,1930		20-22	(1931)
Arosa	04.05.30	2300	22	Götz and Ladenburg (1931), corrected by Götz et al (1935)
Arosa	17.,19.,			Götz and Penndorf
	22.03.34	1900	29	(1941)
	22.04.34		25.4	
	24.04.34		27	
	25.04.34		24.5	
	26.04.34		24.7	
	27.04.34		27.7	
	28.04.34		24.3	
	01.05.34		26	
	02.05.34		32	
	22.03.34		32	Götz et al (1934)

(1941, 1949) and Ehmert (1949, 1951). With this technique a considerable amount of measurements were made in the 40's and 50's in Europe. The main drawback with the adopted chemical method is a negative interference by SO_2 (Schenkel and Broder, 1982). Observations were, however, taken at vacation and health resorts, while measurement techniques were intercompared, yielding satisfactory results (Regener, 1943). Consequently, it may be safely assumed that several of the stations may have given satisfactory observations. We next review some of the results of the chemical ozone mesurements made from the mid-1930's to the mid-50's.

The first surface ozone measurements by chemical techniques in the 30's were performed by Cauer (1936, 1937) during June - October between 1934 and 1936 in the Tatra mountains (now Poland) in various locations at altitudes between 400 and 1000 m. Only a limited amount ($\approx$ 400) of all measurements were reported. Except during periods of thunderstorm activity, measured daytime ozone volume mixing ratios, with few exceptions, were generally in the range of less than 10 to 25 ppbv. Cauer (1936) also reports some very early measurements on the Jungfraujoch (3450 m alt) in Switzerland made in September, 1932, which show below 10 ppbv of ozone, much less than those determined by optical methods (see Table II). It is clear that these very early measurements with the KI-technique must have been incorrect.

Regener (1938) in August 1938 made 12 measurements at the Jungfraujoch (3600 m altitude). The range of observed ozone volume mixing ratio was 24-43 ppbv with an average of 30 ppbv in very good agreement with the earlier optical observations, discussed above. The average of six ozone measurements near Friedrichshafen at Lake Constance (400 m asl) during daytime gave an average volume mixing ratio of 21 ppbv. An extensive series of measurements near the same site by Auer (1939) between September and December, 1938, from 10 a.m. until 16 p.m. generally gave ozone volume mixing ratios of 10-25 ppbv. During night, ozone concentrations were much lower due to ozone destruction at the ground.

Using the Cauer method, Tichy (1939) in February - April, 1937 and 1938 made a total of 252 ozone measurements during fair weather conditions in Schreiberhau (Silezia, now Poland) at 700 m altitude. The well known diurnal cycle with maximum ozone values in the early afternoon hours, which is caused by turbulent downward transport of ozone from the free troposphere (Regener, 1938), is quite apparent, although Tichy seemed to imply that this is correlated with the measured intensity of ultraviolet radiation. Altogether, early afternoon ozone concentrations are generally in the range 10-15 ppbv, i.e. about 2-3.5 times lower then at Hohenpeißenberg in 1982, but about equal to the measured values at this station in 1968

(Attmannspacher et al, 1982).

Extremely interesting are the observations that were made during the period Sept., 15-24, 1940 by Ehmert and Ehmert (1941, 1949) in Friedrichshafen at Lake Constance and on the Pfänder mountain at an altitude of 1064 m on the east side of the same lake. Most ozone volume mixing ratios are between 10 and 15 ppbv and no values are reported that are higher than 20 ppbv. The low altitude Friedrichshafen station clearly shows the well known diurnal behavior of surface ozone concentrations.

Paneth and Edgar (1938) measured ground level ozone mixing ratios between 5 and 23 ppbv in the London area in the spring of 1938. In a late series of measurements during windy conditions in December, 1940, Paneth and Glückauf (1941) near Durham in England measured ozone volume mixing ratios ranging between 15 and 25 ppbv, which values may have been representative for free tropospheric air.

After the second world war, Effenberger (1949) on the island Westerland/Sylt on the German Northsea coast made extensive ozone measurements during May - August, 1947. Earlier, Effenberger (1948) had intercompared the Cauer and Regener chemical ozone measurement devices and had come to satisfactory conclusions. The summer of 1947 must have been particularly bad in West Europe with much windy and rainy weather. Nevertheless, for more than half of the measurement period ozone volume mixing ratios remained below 20 ppbv. Maximum ozone valus (≈ 60 ppbv) were reported in connection with thunderstorm activity. The measurements by Fabian and Pruchniewicz (1977), using automatic sampling systems, at the German stations of Norderney and Westerland during 1971 and 1972 also showed ozone volume mixing ratios of only about 20 ppbv, but generally substantially higher concentrations in 1973 and 1974 (≈ 40 ppbv). Unfortunately, these Northsea island stations, which are located at a distance of only about 150 km from each other, often show large differences in monthly averaged ozone trends, so that the quality of some of the data may be doubtful.

An extensive series of ozone measurement were conducted in Arosa, Switzerland from April, 29, 1954 to October, 18, 1958 (Perl, 1965). Average ozone concentrations show an annual cycle with a minimum of about 12 ppbv in December and a maximum of 30 ppbv in May - June. Maximum measured ozone concentrations are about 20-30% larger than the average. Interestingly, fair weather ozone concentrations are generally somewhat higher than average, indicating the possibility that some ozone buildup by photochemical reactions may already have begun by the latter half of the 1950's. Earlier tropospheric ozone measurements at Arosa by Götz and Volz (1951) from April, 1950 to March, 1951 agree quite well with those by Perl (1965). The measurements made from the middle of March to early May of 1934 by the optical tech-

nique (Götz and Penndorf, 1941) gave ozone volume mixing
ratio values ranging from 26 ppbv to 35 ppbv, with an
average of 32 ppbv. This is about 20% larger than the values
measured by Perl (1965) and Götz and Volz (1951), giving
credence to the observational methods and the measured ozone
concentrations.

A long series of ground based ozone measurements at
Arkona on the Baltic coast in the German Democratic Republic
have shown a large annual upward trend by 2.8% between 1956
and 1971, followed by a downward trend of -0.74% between
1972 and 1984 (Warmbt, 1979; Feister and Warmbt, 1987). The
trend analysis may, however, have been compounded by the in-
troduction of an SO_2 scrubber in 1972.

Altogether, the historical ozone data, which have been
reviewed in this chapter, indicate that surface ozone
concentrations in the first half of this century were mostly
in the range 10-20 ppbv at European clean air stations,
somewhat higher than the early measurements by Levy (1907).
It is interesting to note that background surface ozone
volume mixing ratios in the 10-20 ppbv range are also
typical for mid-latitudes in the southern hemisphere. In New
Zealand, Farkas (1979) measured ozone volume mixing ratios
in the 10-20 ppbv range with some tendency for the higher
values to occur during winter and spring, indicating either
enhanced downward transport from the stratosphere during
winter and spring or photochemical destruction over the
oceans during summer. Ozone surface measurements are also
made at the baseline station Cape Grim in Tasmania. Volume
mixing ratios during 1982-1985 generally ranged from about
15 ppbv in January to 30 ppbv in July (Douglas et al, 1986).
Finally, measurements by Winkler (1980) on ship cruises over
the Atlantic gave ozone volume mixing ratios between 10 and
15 ppbv in the southern hemisphere, compared to about
30 ppbv at mid-latitudes in the northern hemisphere.

Because ozone is much more efficiently destroyed on
land surfaces than on the ocean, the fact that there is now
so much more ozone in the northern hemisphere than in the
southern hemisphere (Routhier et al, 1980; Fishman, 1985;
Logan, 1985; Seiler and Fishman, 1981) is indicative of
substantial ozone production in the northern hemisphere
(Fishman and Crutzen, 1978; Fishman et al, 1979). The
appearance of simultaneous O_3 and CO bands in the northern
hemisphere is evidence of this (Fishman et al, 1980, 1987).

According to Becker et al (1985), present day average
annual ozone volume mixing ratios at low altitude stations
in West Germany are typically in the range 25-35 ppbv, with
average summer time (April - September) values of
35-45 ppbv. At more elevated observational sites (alt:
800-1300 m) summer time ozone values are about 5-10 ppbv
higher. Maximum volume mixing ratios nowadays frequently
exceed 100 ppbv (Becker et al, 1985; Derwent et al, 1987),

values which were never reported in the old data sets.
Clearly, there have been an enormous increases in background
ozone concentrations over the past 30 years, especially in
heavily motorized industrial areas. However, also at other
more remote background stations substantial ozone increases
have taken place.

It is extremely interesting to do a much more thorough
analysis of "ancient" ozone data than was possible for this
study, e.g. by rebuilding the instruments used, checking
them against modern techniques and recalibration (e.g. Volz
and Kley, 1987). It may also be so that there is a consider-
able amount of data that was never published and still
stored away in old archives. Finally, it would be very
interesting to compare certified old data with modern data
taken at the same sites as where the "ancient" data were
taken.

4. THE GLOBAL POTENTIAL FOR OZONE FORMATION

As shown before, the oxidation of carbon monoxide and
hydrocarbons leads to the production of ozone, provided
sufficient concentrations of NO are present in the atmo-
sphere. From knowledge of the mean global distributions of
CH_4, CO and hydroxyl, the latter calculated (Crutzen and
Gidel, 1983), the atmospheric sinks of CH_4 and CO can be
estimated. These are presented in Figures 2 and 3. Alto-
gether about $1.5x10^{15}g$ CO and $4.1x10^{14}g$ of CH_4 are emitted
in the atmosphere from a variety of sources. In comparison,
other alkane emissions are substantially smaller. For
instance, the global production of ethane (C_2H_6) is equal to
about $10-16x10^{12}g$ per year (Blake and Rowland, 1986). If
enough NO were present to produce ozone by the reaction
cycles shown before, one ozone for each carbon monoxide and
2.7 ozone molecules for each methane molecule that is
oxidized, the maximum global production potential of ozone
would be equal to $6x10^{15}g$ O_3 annually (or $5x10^{11}$ molecules
$cm^{-2}s^{-1}$), about ten times larger than the estimated downward
flux of ozone from the stratosphere to the troposphere, and
the ozone destruction flux at the earth's surface. To this,
the potential ozone production should be added which results
from the oxidation of reactive non-methane-hydrocarbons
(NMHC) coming from forest emissions. For the U.S., this
contribution was previously estimated by Zimmerman et al
(1978) to be equal to about $7x10^{13}g$ C/year, which was
extrapolated to a global production of $8.3x10^{14}g$ C/year. A
recent study by Lamb et al (1987) gives an estimated annual
emission rate of $3.1x10^{13}g$ NMHC in the U.S. Contrary to
Zimmerman et al (1978), isoprene emissions contributed only
about 15% of the total. If we extrapolate this new informa-
tion by the same method as Zimmerman et al (1978) an annual

global NMHC emission flux of about 3.7×10^{14}g is estimated.
If we assume that for each C atom in any of these organic
molecules, there are produced two ozone molecules under
NO-rich conditions (Liu et al, 1987), then an additional
potential, global production of about 2×10^{15}g ozone
($\approx 1.5 \times 10^{11}$ molecules $cm^{-2}s^{-1}$) emerges.

Altogether, the total potential for global ozone
production may, therefore, add up to about 7×10^{11} molecules
$cm^{-2}s^{-1}$, which is more than a factor of ten larger than all
other sources and sinks of ozone. Clearly, most hydrocarbon
and carbon monoxide are oxidized in the atmosphere without
producing ozone, because the necessary concentrations of NO
are not present in natural atmospheric environments. Our
analysis shows, however, that any future human developments,
that lead to NO emissions in the vicinity of forested
regions will probably lead to growing ozone concentrations.
For the U.S. this has been shown convincingly by Trainer et
al (1987).

Compared to the total annual, natural NMHC source
of 3.1×10^{13}g in the U.S., the volatilization from various
anthropogenic sources of about 2×10^{13}g is not much different
(Liu et al, 1987; Derwent et al, 1987). Because much
of the latter category of hydrocarbons is emitted together
with anthropogenic NO_X, it is likely that a substantial
fraction of these contribute to ozone formation.

In a very interesting study, Liu et al (1987) estimated
that at least one molecule of ozone is produced for each
NMHC that is oxidized. For summer time conditions they
estimate an average ozone production rate for the U.S. of
about 10^{12} molecules $cm^{-2}s^{-1}$. They relate the O_3 production
rates with those of NO_X, such that during summer daily ten
ozone molecules are produced for each NO_X molecule. Also for
other seasons, they claim a similar ozone production
efficiency, because a longer NO_X lifetime compensates for a
less efficient daily ozone production rate. Their analysis
did, however, neglect reactions of NO_3 and N_2O_5 on wet
surfaces during nighttime, so that the latter hypothesis is
probably not valid. Extrapolation of this information to
other industrialized nations implies that probably of the
order of $4-7 \times 10^{14}$g O_3 ($\approx 5-10 \times 10^{10}$ molecules $cm^{-2}s^{-1}$) may
annually be produced through the oxidation of anthropogenic
non-methane hydrocarbons in the northern hemisphere. In
fact, this may be a lower limit, because the anthropogenic
NMHC emissions may be significantly underestimated (Westberg
and Lamb, 1985).

The oxidation of anthropogenic NMHC is clearly an
important contribution to the ozone budget of the northern
hemisphere. Much of this ozone is produced in the atmo-
spheric boundary layer over limited continental areas,
leading to high ozone concentrations. However, a fraction of
the hydrocarbons can escape to the free troposphere by

convection, especially in the tropics and during summer at
mid-latitudes (Gidel, 1983; Chatfield and Crutzen, 1984;
Ehhalt et al, 1985). If this happens in industrialized
areas, then together with the hydrocarbons also NO_x pollu-
tants will be transported upward, setting up favorable
conditions for ozone formation in the upper troposphere with
more efficient ozone formation per NMHC molecule emitted
(Liu et al, 1987). The convective activity will also be ac-
companied by NO_x formation through lightning (Chameides et
al, 1987 a, b). Because convection is particularly important
above tropical forests, a substantial fraction of the large
amounts of hydrocarbons that are produced in this ecosystem
(Zimmerman et al, 1978; Crutzen et al, 1985; Greenberg and
Zimmerman, 1984) will be rapidly transferred to the upper
troposphere, where their oxidation may produce significant
amounts of ozone.

From tropospheric ozone budget considerations it is
quite clear that most CO and organics that are emitted into
the atmosphere are oxidized in NO poor atmospheric environ-
ments. This is possible because the average atmospheric
lifetime of NO_x is only about one day. Effective ozone
production does, therefore, probably still only occur in the
temperate latitudes in the northern hemisphere and maybe in
the upper troposphere of the tropics. Extremely low back-
ground NO concentrations ($\leq$ 1 pptv) are indeed observed in
clean environments, such as in the lower atmosphere over the
Pacific between Hawaii and California (Davis et al, 1987;
McFarland et al, 1979; Ridley et al, 1987).

The overall budget of tropospheric ozone remains
uncertain (Fishman, 1985). The annual average downward flux
of ozone from the stratosphere is in the range $4-8 \times 10^{10}$ and
$3-5 \times 10^{10}$ molecules $cm^{-2} s^{-1}$ in the northern and southern
hemisphere, respectively (Danielsen and Mohnen, 1977; Gidel
and Shapiro, 1980). The corresponding ozone destruction
rates at the earth's surface are estimated to be about
17×10^{10} and $5-6 \times 10^{10}$ molecules $cm^{-2} s^{-1}$ (Galbally and Roy,
1980; Lenschow et al, 1985; Fishman, 1985). The average
photochemical destruction of ozone in both hemispheres by
reactions R1 and R2 are about equal to 7×10^{10} and 5×10^{10}
molecules $cm^{-2} s^{-1}$ in the northern and southern hemisphere.
From mass balance considerations a net photochemical
production of ozone of about 2×10^{11} molecules $cm^{-2} s^{-1}$ must
take place in the troposphere of the northern hemisphere.
Also in the southern hemisphere some net ozone formation in
the "NO-rich" upper troposphere and transport from the
northern to the southern hemisphere, adding up to about
5×10^{10} molecules $cm^{-2} s^{-1}$, seems to be required for a
satisfactory ozone budget.

5. CONCLUSIONS

In this paper we have shown that anthropogenic activities most likely have caused large increases in ozone concentrations in the northern hemisphere. These changes not only have affected heavily polluted industrial areas, but also the background free troposphere. The processes that produce enhanced ozone concentrations are basically well known, viz. the photochemical oxidation of hydrocarbons in the presence of NO_x.

The maximum possible, global ozone production by oxidation of all hydrocarbons and carbon monoxide which are emitted into the atmosphere is about equal to 10^{16}g of ozone annually ($\approx 10^{12}$ molecules $cm^{-2}s^{-1}$). Only a small fraction ($\leq 10\%$) of this ozone production can actually take place, because in much of the free atmosphere there is very little NO. Future human developments, that are accompanied by enhanced NO_x production, will consequently lead to considerable increased tropospheric ozone concentrations. This may even be of climatic significance (Fishman et al, 1979; Ramanathan and Dickinson, 1979; Wang, this volume).

Because of the potential for large future changes in atmospheric concentrations, and because of the central role in atmospheric chemistry, the study of atmospheric ozone remains a topic of intensive interest. It is remarkable to note that the importance of this gas was already "smelled" more than 100 years ago by researchers, even before its chemical composition was established.

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