OZONE, TROPOSPHERIC

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In the early part of the 20th century, ground-based and balloon-borne measurements discovered that most of the atmosphere's ozone is located in the stratosphere with highest concentrations located between 15 and 30 km (9.3 and 18.6 miles). For a long time, it was believed that tropospheric ozone originated from the stratosphere and that most of it was destroyed by contact with the earth's surface. Ozone, \( \text{O}_3 \), was known to be produced by the photodissociation of molecular oxygen, \( \text{O}_2 \), a process that can only occur at wavelengths shorter than 242 nm (see article on stratospheric ozone). Because such short-wavelength radiation is present only in the stratosphere, no tropospheric ozone production is possible by this mechanism (1). In the 1940s, however, it became obvious that production of ozone was also taking place in the troposphere. The overall reaction mechanism was eventually identified by Arie Haagen-Smit of the California Institute of Technology, in highly polluted southern California. The copious emissions from the numerous cars driven there as a result of the mass migration to Los Angeles after World War II created the new unpleasant phenomenon of photochemical smog, the primary component of which is ozone. These high levels of ozone were injuring vegetable crops, causing women's nylons to run, and generating increased respiratory and eye-irritation problems for the populace. Our knowledge of tropospheric ozone increased dramatically in the early 1950s as monitoring stations and research centers were established throughout southern California to see what could be done to combat this threat to human health and the environment.

See also AIR POLLUTION; AIR POLLUTION: AUTOMOBILE AIR QUALITY MODELING.

OZONE AS A POLLUTANT

Of the six major air pollutants for which the National Ambient Air Quality Standards (NAAQS) have been designated under the Clean Air Act, the most pervasive problem continues to be ozone. The most critical aspect of this problem is the formation of ozone downwind of large urban areas where, under certain meteorological conditions, emissions of nitric oxide (\( \text{NO} \)) and nitrogen dioxide (\( \text{NO}_2 \)), known together as \( \text{NO}_x \), and volatile organic compounds (\( \text{VOCs} \)) can result in ambient ozone concentrations up to three times the standard of 120 parts per billion, by volume (ppbv) over a 1-hour period. In other major urban areas such as Mexico City, Mexico, and Athens, Greece, high concentrations of ozone are also prevalent, prompting the establishment of a World Health Organization guideline of 150–200 \( \mu \text{g m}^{-3} \) (77–102 ppbv) exposure over 1 hour. Thus, the exposure of large populations worldwide to such deleterious conditions has prompted considerable research on the international level. Eventually, it is hoped that our knowledge and technological advances will lead to an elimination of high ozone concentrations. On the other hand, it is also now recognized that there are
of the engines, especially the amount of nitrogen oxides they emit (which will be driven by the technology of the engines). For a "middle" value of assumed nitrogen oxide emissions, the models suggest an increase in stratospheric odd nitrogen at northern mid-latitudes of some 50% to 75% and 50% to 100% for a fleet of Mach 2.4 and 1.6 aircraft, respectively, over that which would otherwise be found for the year 2015. There is a range in the predicted changes, however, depending on what atmospheric model is used. Northern mid-latitude water vapor changes would be considerably smaller, however, being of the order of 15% to 25% and 5% to 25% (51).

These models may also be used to calculate the projected effect of aircraft operations on stratospheric ozone amounts. These calculations involve the full range of stratospheric chemical processes. Recent recognition of the role of heterogeneous chemistry in converting nitrogen oxides to nitric acid now leads to model results that suggest only a small effect of these aircraft on ozone. The magnitude (and indeed, for some models, the sign) of this effect depends strongly on the exact altitude of injection (the higher the ejection, the more likely it is to have a deleterious effect on ozone) and the nature of the emission of the aircraft engines (51).

The possibility also exists that the increased water vapor and nitrogen oxides in the stratosphere due to aircraft exhaust could lead to increased formation of PSCs. Stratospheric models are only beginning to address this question, and additional work on enhanced PSC formation and its potential impact on ozone distributions will be needed to make accurate predictions (51).

Relationship with Ultraviolet Radiation at Earth's Surface

It has long been understood that if there is a reduction in the amount of ozone in the stratosphere and all other factors remain the same, there will be an increase in the amount of ultraviolet radiation that reaches the Earth's surface. This has been very difficult to demonstrate in practice, however, as except for the Antarctic ozone hole, the changes in ozone have been sufficiently small that it is difficult given the instrumentation available to pick out a small trend in surface UV flux from the data. Two major factors contribute to this. First, clouds, aerosols, and local pollutants can also affect the penetration of ultraviolet radiation, so the ozone effect can be masked. Second, the instrumentation used is frequently of a type in which the stable long-term calibration needed to deal with small long-term changes cannot be assured.

Recently, however, there has been some relatively conclusive evidence for changes in surface ultraviolet radiation over a several-year period. These results were obtained by scientists in Canada, who used the ground-based Brewer spectrophotometer in Toronto from 1989 to 1993. They found evidence that the intensity of the light near 300 nm increased by 35% per year in winter and 7% per year in summer, whereas there was no trend in the radiation between 320 and 325 nm. These results are consistent with our understanding of the propagation of ultraviolet light through the atmosphere and the ultraviolet absorption cross sections of ozone (52). There is also evidence for a long-term increase in UV measurements made at the Jungfraujoch Observatory in Switzerland through the 1980s (5).

BIBLIOGRAPHY

many regions where high ozone levels are found and that
a significant perturbation to the global distribution of tropo-
ospheric ozone has already occurred because of human
activity.

The Chemistry of Ozone Formation

Photodissociation of NO₂ by (visible) sunlight is the only
significant anthropogenic source of O₃ in photochemical
smog:

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} (\lambda < 420 \text{ nm}) \]  \hspace{1cm} (1)

immediately followed by

\[ \text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M} \]  \hspace{1cm} (2)

where the M in reaction no. (2) represents any nonreactive
molecule that absorbs some of the excess energy of the
intermediate product formed in the reaction (2). The
critical aspect of the VOCs is the role that they play in
the oxidation of the NO, emitted by combustion processes,
to NO₂, the precursor of O₃ via the above two reactions.

In a perfect world, all VOCs in fossil fuel would be oxi-
dized in the combustion chamber to produce CO₂ and H₂O
as it generates heat that can be transformed to energy. In
reality, however, VOCs are not entirely oxidized during
the combustion process, causing the release of partially
oxidized and fragmented hydrocarbons to the atmosphere.
As a result, VOCs emitted into the air are subjected to an
atmospheric oxidation process considerably slower than
what should have occurred in the combustion chamber of
an automobile or steam plant. The atmospheric oxidation
of a VOC is initiated by reaction with the hydroxyl radical
(OH):

\[ \text{RH} + \text{OH} \rightarrow \text{R} + \text{H}_2\text{O} \]  \hspace{1cm} (3)

where RH denotes any hydrocarbon compound. The prod-
uct is another radical, denoted R, and water vapor. The
radical quickly combines with an oxygen molecule in a 3-
body reaction:

\[ \text{R} + \text{O}_3 + \text{M} \rightarrow \text{RO}_2 + \text{M} \]  \hspace{1cm} (4)

to form another oxygenated radical, RO₂, called a peroxy
radical. The peroxy radicals are the key for converting NO
to NO₂:

\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]  \hspace{1cm} (5)

In addition, RO attaches to an oxygen molecule to form
another peroxy radical:

\[ \text{RO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{RCHO} \]  \hspace{1cm} (6)

where RCHO is an aldehyde. The HO₂ likewise reacts
with NO to form another NO₂ molecule:

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  \hspace{1cm} (7)

where the two NO₂ molecules photolyze and eventually
produce ozone:

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} (\text{2 times}) \]  \hspace{1cm} (1)

Additional ozone molecules can also be produced through
the oxidation of RCHO (5). In this reaction sequence, it is
important to note that the nitrogen oxide emitted as a
pollutant is still available to make more ozone. If NO
were not present in the atmosphere, ozone would not be
formed. In fact, the presence of VOCs, by themselves,
would result in a destruction of ozone because they, or
some of their daughters of the oxidation process, could re-
act with any ozone present in the atmosphere.

On the other hand, if only nitrogen oxides and ozone
were present in the atmosphere, an equilibrium would
quickly be established because O₃ reacts quickly with NO:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  \hspace{1cm} (8)

and the ratio between NO, NO₂ and O₃ is quickly estab-
lished by the rates of the reactions among these species:

\[ [\text{NO}] / [\text{NO}_2] = j_l / (j_3) k_s \]

where the brackets denote the concentration of a particu-
lar species, j_l the rate of photolysis of NO₂, and k_s the rate
of reaction in equation no. 8; the relationship among these
three gases defined by this ratio is often referred to as the
photostationary state, and has had an important implica-
tion for understanding the formation of ozone near urban
areas and subsequent strategies developed for the control
of ozone concentrations.

Effect of VOC and NO₃ Controls on Ozone Concentrations

One of the first approaches to abate the ozone pollution
problem was to conduct a series of “smog chamber” stud-
ies so that the amount of ozone could be quantified under
controlled conditions. The peak 1-hour concentrations
were measured in a chamber into which VOCs and NO
were placed and then irradiated with a simulated amount
of sunshine. The results are often displayed in the form
of isopleths such as those shown in Figure 1. Such iso-
pleths were generated by the use of computer models such
as the EKMA (Empirical Kinetic Modeling Approach) (4)
where the calculations have been tested against smog
chamber data. Figure 1a shows the peak O₃ formed from
irradiation of mixtures of VOC and NO₃ at the initial con-
centrations shown on the axes. Figure 1b reflects that
same data in three dimensions. The overall shape of the
“ozone hill” in Figure 1b is useful in examining whether
controlling VOC or NO₃, or both, would be most effective
in reducing O₃.

Low VOC/NO₃ ratios (eg, point D) are thought to be
indicative of typical polluted air masses in many urban
centers. If the ratio is zero, the photostationary state rela-
tionship shows that an increase in NO (because nearly all
direct emissions of NO₃ are in the form of NO) results in
a decrease in O₃. Figure 1b supports this relationship by
showing that O₃ increases initially along the path from
point D to F until the crest of the hill is reached. At these
low VOC/NO₃ ratios, a much more efficient way to control
O₃ is traveling along path DE: reduction of VOC.
At high VOC/NO\textsubscript{x} corresponding to point A, decreasing VOC alone at constant NO\textsubscript{x} along the AB line gives only slowly decreasing O\textsubscript{3}. However, decreasing NO\textsubscript{x} at constant VOC (ie, along line AC) is very effective in rolling down the "ozone hill." Thus, in this case, the chemistry of the polluted air masses is NO\textsubscript{x}-limited and NO\textsubscript{x} control is most effective. This region of high VOC/NO\textsubscript{x} is typical of suburban, rural, and other downwind areas.

Because the ozone problem was so acute in Los Angeles, the strategy of reducing VOC emissions was adopted for ozone control. The success of the program is illustrated in Figure 2 (from (5)) where the number of days in the southern California region in excess of 200 ppbv (the 1-hour concentration required for issuance of a Stage I-alert) has diminished significantly since 1976, shortly after the mandate of catalytic converters on auto-
mobile exhaust systems was put into effect. VOCs from automobile exhaust were converted to carbon dioxide (CO₂) as they passed through the tailpipe and therefore ozone production could not take place.

In other urban areas, however, the success of VOC control is not as evident. One study for the Atlanta metropolitan area (6) examined 9 years of O₃ and other data between 1979 and 1987 and concluded that the 40% reduction of anthropogenic VOCs during that time had a negligible impact on the ambient ozone concentrations in the Atlanta area. VOC emissions from natural sources, primarily trees, are probably larger than the anthropogenic VOC emissions in the metropolitan Atlanta region except very near the urban core area in 1988 (7). Therefore, reducing emissions from anthropogenic sources had a relatively small impact on the total amount of VOCs present over the entire region.

**Tropospheric Ozone in the Nonurban Atmosphere**

Another reason that the Los Angeles area was so prone to high O₃ concentrations was the prevalence of weather conditions that restricted ventilation of the emissions to higher altitudes and transported them away from the central urban area. In particular, when regions are subjected to strong thermal inversions, that is, when a layer of warm air sits on top of layer of a cooler air, vertical transport and hence ventilation of the pollutants is severely restricted. Although the Los Angeles basin is very susceptible to such regimes, the eastern United States is also prone to such a situation when the region is dominated by the presence of a large high-pressure area. Such occurrences often happen in the summer, primarily when the movement of weather systems is blocked by the quasi-permanent feature known as the "Bermuda High." Under such conditions, high concentrations of O₃ can build up over vast regions of the eastern United States (8). A particular example is shown in Figure 3 for a day during 1988, perhaps the worst year for high concentrations of ozone in the eastern United States.

Using the summer of 1988 as a base case, the U.S. EPA has conducted a series of detailed computer simulations of the meteorology and atmospheric chemistry taking place during that time. From the information obtained by these computer simulations, they are able to forecast what impact controls on NOₓ and VOC emissions would have on ozone concentrations in the eastern United States (9). They conclude that control on both classes of emissions is necessary. In the most polluted areas (eg, the New York metropolitan area in their simulation), VOC controls are most effective for reducing ozone. When the entire eastern United States is considered, on the other hand, NOₓ emissions are more important for lowering overall ozone concentrations.

**THE GLOBAL DISTRIBUTION OF TROPOSPHERIC OZONE**

The distribution of tropospheric ozone can be determined from the analyses of satellite data sets obtained independently from two different instruments: The Total Ozone Mapping Spectrometer (TOMS) and the Stratospheric Aerosol and Gas Experiment (SAGE). Between October 1978 and May 1993, TOMS functioned on the Nimbus 7 satellite and provided daily maps of the distribution total ozone. Another TOMS was launched on the Russian Meteor-3 satellite in 1991 and additional TOMS instruments are scheduled to be launched periodically (at ~2-year intervals) through the end of the century. After that time, NASA’s Earth Observing System (EOS) should be operational and total ozone will be measured as part of EOS. Total ozone is defined as the integrated amount of ozone between the surface and the top of the atmosphere. A unit of measure for total ozone is a quantity known as the Dobson Unit (DU), where 1 DU = 2.69 × 10¹⁶ molecules of O₃ cm⁻². A typical amount of total ozone found in the atmosphere is 300 DU, and approximately 90% of this ozone is located in the stratosphere.

At middle and high latitudes, the distribution of total ozone is primarily governed by the prevailing large-scale circulation patterns. These patterns can vary substantially on a daily basis, and intense gradients of total ozone have been observed with differences of 200 DU at locations less than a few thousand km apart. At these higher latitudes, total ozone amounts can range between ~225 DU and ~500 DU. Only recently have values as low as 100 DU been observed during austral spring in conjunction with the Antarctic ozone hole.
At lower latitudes, however, the total ozone distribution patterns exhibit much smaller gradients than at middle and high latitudes. The intense gradients of as much as 200 DU found at the higher latitudes are replaced by much more subtle gradients of no more than 20–30 DU. Because the primary intent of the measurement of total ozone was to study the distribution of stratospheric ozone, very little research was conducted using the information provided by TOMS in the tropics. Subsequently, however, it was shown (10) that the variations in total ozone at low latitudes were primarily the result of variability of ozone in the troposphere even though only ~10% of the total ozone was in the troposphere.

The use of TOMS for tropospheric studies was taken a substantive step further when data from SAGE were used to derive the amount of ozone in the stratosphere. Ozone measurements from the SAGE instruments (SAGE was launched in February 1979 and operated through November 1981; SAGE II was launched in November 1984 and is still operating) provide the vertical distribution of ozone in the stratosphere. From these profiles, the amount of ozone in the stratosphere can be integrated and then subtracted from the co-located total ozone amount derived independently from the TOMS on the same day (11). A schematic representation of the method used to derive the tropospheric residual is shown in Figure 4.

The distribution of the integrated amount of tropospheric ozone (Fig. 5) shows distinct plumes that seem to result from pollution originating in North America, Asia, Africa, and Europe. In the three northern continents, the plumes originate over the eastern portions of each landmass and are transported by the prevailing westerly winds for several thousand kilometers. At low latitudes, the highest concentrations of pollution are off the west coast of Africa. At these latitudes, the prevailing low-level winds are trade winds (easterlies), which would carry the emissions from central and western Africa to the eastern tropical South Atlantic Ocean (12). The prevailing upper-level winds are westerlies, so any ozone that gets to altitudes of ~5 km or higher is transported long distances to the east. Evidence of the long-range transport of emissions from biomass burning in Africa and South America to Australia is evident in long-term Australian data sets of not only ozone, but also carbon monoxide and elemental carbon, two other products of widespread burning (13).

**TROPOSPHERIC OZONE TRENDS IN THE NONURBAN TROPOSPHERE**

The global distribution of tropospheric ozone shown in Figure 5 illustrates its wide range (approximately a factor of 3) of abundance. Therefore, unlike trace gases such as chlorofluorocarbons, nitrous oxide, or carbon dioxide, which exhibit very small spatial gradients, an assessment of the global rate of increase of tropospheric ozone is difficult to determine from measurements at only a few loca-
tions. Outside of urban areas, only a few stations around the world have continuous long-term measurements of tropospheric ozone. Among these stations are the ones set up by the U.S. National Oceanographic and Atmospheric Administration (NOAA), which has maintained a carefully calibrated monitoring program at Barrow, Alaska; Mauna Loa, Hawaii; American Samoa; and South Pole since the early 1970s (13–15). The monthly mean concentrations from Mauna Loa and Barrow are shown in Figures 6a and 6b. The linear least-squares fit illustrating the trend between 1973 and 1992 for these two data sets is also plotted on these figures. Even though both of these stations show a significant increase over this period (see Table 1), the measurements at Barrow show that the long-term trend of 0.67% per year has a strong seasonal dependence; the increase during the summer is 1.73% per year whereas there is almost no trend (−0.07% per year) during the winter (16). The data from American Samoa exhibit a negligible trend, and the South Pole data display a significant decrease since 1975. The reason for these trend differences at these remote sites is not clear and is currently being studied.

Several recent studies have reexamined ozone measurements from the late 19th century and early 20th century to determine tropospheric ozone trends over longer time periods (17–19). These studies have carefully examined calibration procedures used last century and have determined that a significant increase in tropospheric ozone has occurred over the past century. The German scientist Christian Fredrich Schönbein, a professor of chemistry at the University of Basel, Switzerland, is credited with the discovery of ozone in 1839. One of the goals of Schönbein's research was to show that ozone is a permanent and natural component of the atmosphere. He devised a method to measure ozone that was capable of measuring very low levels simply and easily in the atmosphere. The method he developed employed the use of Schönbein paper, which was a strip of paper saturated in potassium iodide. In the presence of ozone, the potassium iodide oxidizes to potassium iodate. In the process of con-

Figure 6. (a) Monthly mean surface ozone at Mauna Loa with the linear trend; (b) monthly mean surface ozone at Barrow. Also shown are the linear trend for the entire data record and the seasonal trends for the winter (January–March, solid circles) and the summer (July–August, open circles) (16).
version, the paper changes color to various hues of blue. The more ozone in the air, the bluer the paper. Schönbein calibrated the amount of color change into a measurement standard called Schönbein units, which allowed him and his colleagues to put out a new piece of Schönbein paper each day and measure the relative amount of ozone in the atmosphere (20).

More than three decades of measurements using Schönbein's technique were obtained at the Montsouris Observatory outside Paris. The instrument used at this meteorological site was recalibrated and the observations were converted to units of measurement consistent with modern measurements (18). The results from this data set are compared with modern observations obtained in Germany in Figure 7. This and other analyses (17–19) strongly suggest that ozone at the surface has risen from ∼10 ppbv to more than 30 ppbv in nonurban Europe and the eastern United States. Although ozone at the surface has likely increased significantly on the time scales of years and decades since the inception of the industrial era, tropospheric measurements above the surface are extremely scarce and difficult to interpret because of the different methods of measurement used since the 1960s. Most of the measurements are from ozonesondes (an
ozone sensor placed on a balloon), but several types of sensors have been used and each type is susceptible to interference from other trace gases in the atmosphere (21). Despite the uncertainty in the measurements, it is generally believed that ozone has increased throughout the entire troposphere since the 1960s, when ozonesonde measurements started on a fairly regular basis (21,22).

THE GLOBAL TROPOSPHERIC OZONE BUDGET

Historical Perspective: The Natural Sources of Tropospheric Ozone

The components of the global tropospheric ozone budget can be broken into four general categories: transport from the stratosphere, destruction at the earth’s surface, photochemical destruction, and in-situ photochemical production (23). The primary mechanism by which ozone is transported from the stratosphere into the troposphere is through meteorological events referred to as stratospheric intrusions. These events occur in conjunction with the movement of air associated with rapid changes in the intensity and position of the jet stream, the fast-moving westerly river of air that often delineates the position of strong frontal boundaries at middle latitudes. Under these conditions, the tropopause (i.e., the boundary between the troposphere and the stratosphere) often becomes contorted; its position becomes difficult to define, and it often takes on a “folded” depiction. Because of this, stratospheric intrusions are also synonymous with tropopause folding events (24).

The topic of stratosphere-troposphere exchange was an intense research area in the 1960s and early 1970s because of the concern about transport of radioactive debris created by atmospheric nuclear bomb testing from the stratosphere into the lower atmosphere and eventually its deposition to plants, animals, and human populations. During this time, the North American Ozonesonde Network was established for the primary purpose of understanding how stratospheric air was transported into the troposphere. From these data, it is generally thought that ~10% of the stratosphere is exchanged annually with the troposphere (25). From these estimates, the global source of tropospheric ozone from the stratosphere, which was assumed to be the primary natural source of tropospheric ozone, could be computed.

One of the other aspects of the global budget of tropospheric ozone is its sink, the process by which it is destroyed once it is in the troposphere. The early measurements of ozone’s vertical distribution always showed that the lowest concentrations were near the earth’s surface, implying a sink for ozone as it came in contact with the ground. These measurements generally showed much sharper vertical gradients over land and vegetated surfaces than over water and ice surfaces. Thus, one way to determine this deposition sink globally was to make a series of field measurements over a representative sample of surfaces and extrapolate these measurements to the rest of the world. Using this methodology, the globally averaged destruction rate of tropospheric ozone generally converged to a value near ~8 × 10^19 molecules of O_3 cm^{-2} s^{-1}. The accuracy of these estimates was claimed to be ~30% (23). These calculations were consistent with the few attempts to extrapolate the global input from the stratosphere resulting from stratosphere-troposphere exchange studies, which indicated that a global average of ~8 × 10^19 molecules of O_3 cm^{-2} s^{-1} came from the stratosphere (24). Thus, up until the early 1970s, it was generally believed that the tropospheric ozone budget was balanced by the natural input from the stratosphere and the destruction at the earth’s surface (26,27). The potential impact of local-scale photochemical generation (as was known at the time for areas such as southern California) was believed to be insignificant.

A series of papers published shortly thereafter challenged this assumption (28,29) and proposed that a natural source of tropospheric ozone of comparable magnitude to that of input from the stratosphere existed in the background atmosphere as a result of methane oxidation. For the first time, the paradigm of the tropospheric ozone budget was challenged, resulting in a lively debate in the scientific literature (30–32). These theoretical studies

Table 1. Trends in Deseasonalized Surface Ozone Mixing Ratio %/yr

<table>
<thead>
<tr>
<th>Station</th>
<th>Period</th>
<th>Annual</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrow</td>
<td>3/73–2/92</td>
<td>0.67 ± 0.30</td>
<td>−0.07 ± 0.81</td>
<td>0.85 ± 1.26</td>
<td>1.73 ± 0.58</td>
<td>0.50 ± 0.61</td>
</tr>
<tr>
<td>Mauna Loa</td>
<td>10/73–9/92</td>
<td>0.37 ± 0.26</td>
<td>0.56 ± 0.67</td>
<td>0.55 ± 0.87</td>
<td>0.34 ± 0.78</td>
<td>0.04 ± 0.63</td>
</tr>
<tr>
<td>Samoa</td>
<td>1/76–12/91</td>
<td>0.03 ± 0.44</td>
<td>0.22 ± 0.86</td>
<td>0.00 ± 0.94</td>
<td>−0.82 ± 1.36</td>
<td>0.22 ± 1.35</td>
</tr>
<tr>
<td>South Pole</td>
<td>1/75–2/92</td>
<td>−0.68 ± 0.23</td>
<td>−0.22 ± 0.56</td>
<td>−0.66 ± 1.03</td>
<td>−1.42 ± 0.72</td>
<td>−0.66 ± 0.73</td>
</tr>
</tbody>
</table>

* 95% confidence interval is based on Student's t-test.

![Figure 7](image-url) The annual mean ozone concentrations at Montsouris Observatory outside Paris (1876–1910) and Arkona, East Germany (1956–1984). The average ozone concentration at the beginning of the 20th century near Paris was less than 10 parts per billion whereas in 1985, the typical ground-level concentrations in central Europe were approaching 30 parts per billion, implying an increase of about 200% during the century (18).
concentrated primarily on the generation of ozone from the oxidation of methane and carbon monoxide, the two most abundant trace gases that could lead to the photochemical formation of tropospheric ozone. None of these studies through the early 1980s actually considered the large amounts of ozone generated on the urban and regional scales that the U.S. EPA had focused its research on since the 1950s.

Current Understanding of the Tropospheric Ozone Budget

The global distribution of tropospheric ozone presented earlier in this chapter illustrates its heterogeneity and underscores the difficulty of quantifying a global budget using the simplistic assumptions about ozone's vertical distribution that had been employed when budgets neglecting photochemical processes were formulated. It is clear from the depiction in Figure 5 that local scale photochemical generation of ozone has had a considerable impact on its global distribution, as evidenced by the dominant plumes originating over North America, Europe, Asia, and Africa. A proper calculation of the tropospheric ozone budget must quantify these local- and regional-scale processes that feed into the global budget. One simplified study investigating photochemical processes from industrial emissions of volatile organic compounds and nitrogen oxides on scales of ~1000 km (621.5 miles) showed that the ozone generated on these scales should at least be comparable to the amount generated in the background through methane and carbon monoxide oxidation (33). In addition, the data now indicate that large quantities of ozone generated in the tropics as emissions from the intense tropical sunshine (34,35). Furthermore, some recent analyses of ozonesonde data have concluded that very little (perhaps as small as 5%) ozone near the ground had originated in the stratosphere and only ~25% of the ozone observed at 300 mb had originated in the stratosphere (36). This analysis agrees with more recent estimates of stratosphere-troposphere mass exchange suggesting that the amount of ozone from the stratosphere is likely to be only ~30% of the amount derived from the earlier estimates determined in the 1970s.

These studies, as well as the documented increase in tropospheric ozone over time scales of decades (16,18) provide fairly strong evidence that its distribution has changed significantly over the last century and that the tropospheric ozone budget is now likely to be controlled by anthropogenic pollution from both industrialized and tropical regions of the world. Studies are currently under way to provide more quantitative information; our understanding of tropospheric ozone will greatly improve as more data are analyzed and more sophisticated global models are developed to study the problem.

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