United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/D-84-144 Aug. 1984

EPA

ENVIRONMENTAL RESEARCH BRIEF

Assessment of the Contribution of Stratospheric Ozone to Ground-Level Ozone Concentrations

A. P. Altshuller

Introduction

Several assessments of technical issues related to ozone and other photochemically generated products formed in the atmosphere have been requested by the Office of Air Quality Planning and Standards. This assessment is concerned with evaluating the contribution of O_3 transported from the stratosphere to ground level O_3 concentrations. The contributions of stratospheric O_3 during short episodic periods as well as to long term average O_3 concentrations is of interest. The episodic intrusions of stratospheric air have the potential to cause the O_3 concentrations at ground level to exceed the National Ambient Air Standard for ozone. Longer time-averaged concentrations of O_3 reaching the boundary layer from the stratosphere are of interest for several reasons. This O_3 (1) contributes to the total O_3 aloft which is available to be entrained downward into urban areas, (2) when entrained into rural areas upwind of urban areas it can contribute to the O_3 subsequently advected into urban areas, (3) when entrained downward in rural areas can contribute to adverse effects on field crops and forests.

Stratospheric O_3 intrusions were reviewed as an issue in 1977.[1] Since 1977, a number of additional investigations of O_3 concentrations aloft and at rural ground level locations have appeared which associate the O_3 measured with stratospheric intrusions. In addition, several tropospheric models have been developed which are concerned with the origin of O_3 in the troposphere. Therefore, the Office of Research and Development arranged that a scientific review on this subject be prepared.[2] This review updates earlier work and provides new insights into the problem. This assessment is based on studies discussed in this review[2] as well as papers published after the review was completed.

Discussion of Issues

Several issues have been identified for consideration in this assessment. Included are those issues concerning stratospheric sources of O_3. However, it often is difficult, if not impossible, to ascertain the origins of the O_3 measured aloft. Therefore, issues related to other sources of ozone contributing to the ozone measured aloft must be considered also.

Issue 1. To what extent are direct rapid intrusions of stratospheric O_3 down through the troposphere and down to ground level likely to result in O_3 concentrations in excess of the National Ambient Air Quality Standard for O_3?

Large amounts of O_3 are formed in the stratosphere.[3] Atomic oxygen, O, formed by the photolysis of oxygen molecules by the ultraviolet radiation penetrating the stratosphere combine with O_2 to form ozone, O_3. Ozone destruction also can occur by photolysis of O_3 by ultraviolet radiation of higher wave lengths. The resulting equilibrium for O_3 in the stratosphere depends on temperature and on altitude.[3]

Substantial evidence exists that O_3 observed in the upper troposphere has been transported down from the stratosphere as a result of stratospheric-tropospheric exchange processes.[1-3] The processes involved in such exchanges include (a) seasonal adjustments of tropopause level, (b) mean meridional circulation, (c) large scale eddies (tropopause folding events) and, (d) small scale eddies.[1,2] Over half of the transfer has been attributed to processes (a) and (b).[1] Such an evaluation was based on the estimate that, on average, less than one tropopause folding event occurs each day in the northern hemisphere. Subsequent work indicates that about four tropopause folding events occur,

on average, each day in the northern hemisphere.[2,4] This higher estimate results in the mechanism of transport associated with large scale eddies, tropopause folding events, being the most important mechanism for transport of O_3 from the lower stratosphere into the upper troposphere at mid-latitudes.[2]

Tropopause folding events occur near the mid-latitude jet stream under conditions having the potential for rapid and relatively undiluted transport of stratospheric air containing O_3 down into the upper troposphere.[2] Tropopause folding events are associated with the positions of 500-mb low pressure troughs and jet streams. As a result, the frequency of tropopause folding events will vary substantially with the month of the year, and with latitude and longitude. For example, no 500-mb low pressure troughs are likely to occur during the summer months between 20°N and 30°N latitude over the United States.[2,4]

The downward transport of O_3 in air originating in the stratosphere has been followed by instrumented aircraft subsequent to a number of tropopause folding events.[2,5] These aircraft flights provide O_3 profiles through portions of the troposphere. It has been observed that the air originating in the stratosphere frequently becomes horizontal in the upper troposphere although stratospheric air at times becomes a discrete horizontal layer as low as several kilometers above ground level.[5] The O_3 concentrations at the lower extremities of such layers usually are in the 60 to 80 ppb concentration level at or somewhat above the 3 km altitude level.[6] Stratospheric air has not been followed down to ground level.

Three-dimensional air parcel trajectories can be used to trace movements from the tropopause down to the 700-mb level, 10,000 ft, if appropriate meteorological observations are available.[5-6] The extent of the geographical area having the potential to be impacted can be estimated. The total integrated ozone flux from the 700-mb level downward over such geographical areas can be calculated.[6] This technique provides no information on the detailed movements of the air parcels within the planetary boundary layer or the losses of O_3 which may occur.

Four hypothetical mechanisms have been suggested to account for the ultimate fate of stratospheric O_3 injected into the troposphere.[5]

1. Dissipation of the intrusion by general mixing and diffusion into the troposphere above the planetary boundary layer, i.e., the free troposphere.
2. Persistence of the intrusion down to the planetary boundary layer where the lower portion of the intrusion is mixed down to the ground by turbulent eddies and convection at the top of the boundary layer.
3. Coupling of the intrusion to the frontal zone associated with a cold front with direct transport to the ground by frontal downdrafts.
4. The tropospheric air becomes entrained in organized frontal and prefrontal convection, which then transports it to the ground in connection with rainshowers or thunderstorm downdrafts.

Some theoretical and observational results support the existence of mechanisms 3 and 4. However, only limited field data is available relevant to the quantitative significance of these mechanisms.[5]

The discussion to this point has been concerned with information related to the downward movement of stratospheric O_3 in intrusion events. The other approach is to attempt to identify episodes of elevated O_3 concentrations at ground level which can be associated with stratospheric intrusions. Ten case studies have been identified in a compilation of the literature of episodic events ranging from 1964 to 1978.[2] The length of the records examined were highly variable. Records of several years or more were examined in five of the case studies. In one other case study, stratospheric intrusion has been claimed to impact on a site in the western United States over an extended period. This study will be considered in more detail in discussion of a subsequent issue.

The length of the reported episodic events varied from one hour or less to a few days. While several of the episodes were reported during the summer, most of the episodes identified occurred between November and March. Six of the ten episodes, involving ten days, were reported at locations within the United States. Three of the case studies reported in the United States involved measurements at elevated locations at or above 1.5 km.

The experimental evidence supporting claims that the elevated O_3 concentrations were associated with stratospheric intrusions reaching the surface vary considerably among case studies. The reliability of several of the case studies has been questioned.[2] The questioned reports involve episodes in which ground level O_3 concentrations in excess of 100 ppb were associated with stratospheric O_3 intrusions. These ground level O_3 concentrations were higher than expected according to the O_3 profiles obtained aloft during the actual tracking of stratospheric intrusions through the troposphere.

During only two of the episodes associated with stratospheric intrusions at ground level locations within the United States did the O_3 concentrations exceed 120 ppb. These two episodes occurred at Quincy, FL on March 3, 1964 and Santa Rosa, CA on November 19, 1972. The O_3 concentration at Santa Rosa reached 200-230 ppb for one hour during passage of a thunderstorm.[7] The elevated O_3 concentration was highly localized with no similar elevations of O_3 concentrations observed at the other monitoring sites in adjacent areas of northern California. The evidence presented to support this episode was based on isentropic trajectory analysis, the low water vapor mixing ratio, and the high potential vorticity along with an assumption that a growing, precipitating cloud entered a layer of stratospheric air aloft. The O_3 in the core of the downdraft was said to have arrived at ground level largely undiluted. This episode appears to be an example of mechanism 4 discussed above.

Tracer techniques involving isotopic species such as ^{90}Sr and ^{7}Be known to be present in the stratosphere have been utilized to estimate stratospheric contributions to surface O_3 concentrations. These techniques are based on the assumption that the aerosol particles containing the ^{90}Sr

and ^{7}Be behavior is similar enough to that of O_3 to serve as an adequate tracer for the transport of the O_3. This assumption has been questioned; and the possible limitations to these techniques will be discussed after some of the results obtained from their use are considered.

The concentrations of ^{90}Sr measured at ground level after nuclear weapons testing in the early 1960's has been used to estimate stratospheric contributions to ground level O_3 concentrations.[1] Maximum 24-hour average ^{90}Sr concentrations and ^{90}Sr to O_3 ratios measured during 1963 and 1964 indicated that the corresponding 24-hour average O_3 concentrations were in the range of 15 to 30 ppb. Maximum 1-hr O_3 concentrations associated with stratospheric intrusions could not be adequately estimated.

In more recent studies, a ^{7}Be tracer technique has been used.[8-10] The ^{7}Be is formed in the stratosphere through the collision of cosmic ray protons and neutrons with oxygen and nitrogen. The ^{7}Be isotope also can be formed (a) in the upper troposphere south of 30°N latitude and (b) in the upper troposphere on the warm-air (anticyclonic) side of the mid-latitude jet stream.[2] Because no mechanisms for ^{7}Be formation exist in the lower troposphere, a substantial downward gradient in ^{7}Be concentrations occurs from the tropopause to ground level.

The radioactive lifetime of ^{7}Be is 53 days,[2,11] while the residence-time in the free troposphere of the aerosols containing ^{7}Be has been estimated at 35±15 days. Ozone has been estimated to have average lifetimes at the same altitudes ranging from 1 to 4 months with its losses related to photochemical processes and deposition.[2,11] As a result, the concurrent presence and transport of ^{7}Be and O_3 through the troposphere to ground level was considered to have occurred.[8-10]

Measurements of ^{7}Be and of O_3 at the summit of Whiteface, Mt., NY have been reported for both July 1975[8] and June and July 1977.[9] Of the 30 days of measurement in July 1975 at Whiteface Mt., stratospheric origin was claimed for the air parcels on 7 days based on isentropic trajectory analysis and potential vorticities. The ^{7}Be concentrations on these seven days were in the 100 to 200 $fCim^{-3}$ range.

In a subsequent study[9] at the same location, quantitative estimates of the contribution of stratospheric O_3 concentrations was made for the 11 days out of a total of 26 days on which the 24-hour average ^{7}Be concentrations exceeded 200 $fCim^{-3}$. Isentropic trajectory analyses were not reported during this latter study. On these 11 days, the estimated stratospheric contributions to the observed O_3 concentrations averaged 28 ppb, and ranged from 19 to 47 ppb. These contributions averaged 51%, and on individual days ranged from 26 to 94% of the observed ozone concentrations. These estimates are based on a procedure utilizing an average ratio of ^{7}Be to O_3 of 10.8 $fCim^{-3}$ per ppb measured in samples collected above the tropopause near 40°N latitude during April to June 1978.[9]

If the 10.8 $fCim^{-3}$ per ppb ratio[9] is used with the results for the 7 days in July 1975,[8] the estimated stratospheric contributions to the observed O_3 concentrations averged 14 ppb, and ranged from 10 to 18 ppb. The estimated stratospheric contributions averaged 41% of the observed ozone concentrations, and on individual days ranged from 24 to 59%.

In a later study,[10] both 6-hour and 24-hour average ^{7}Be samples were obtained at sites in Houston, TX and San Antonio, TX between June and October 1978. Four stratospheric intrusion events were claimed to have occurred either in the San Antonio or Houston area, but not in both areas concurrently. These episodes were based on the ^{7}Be concentrations exceeding 400 $fCim^{-3}$ on either a 6-hour or 24-hour average. During the 6-hour periods of ^{7}Be measurement, 40 and 60 ppb of O_3 was attributed to stratospheric intrusions. However, in one of the episodes the observed O_3 concentration, 40 ppb, actually was less than the calculated O_3 attributed to stratospheric intrusion. Isentropic trajectory analyses were not reported in this study,[10] but are seen as essential in view of the absence of 500-mb troughs at these latitudes during the study period.[2,4]

Reservations have been expressed as to the ^{7}Be-to-O_3 ratio technique.[11] The reasons for these reservations are as follows: (a) ^{7}Be and O_3 are subject to different removal processes, (b) evidence is lacking that short-term intrusions routinely penetrate to ground level, (c) use of isentropic trajectory analysis is essential to verify that the air parcels reaching the surface came from the stratosphere rather than the upper troposphere, (d) no generally accepted ^{7}Be-to-O_3 ratios exist for the lower stratosphere and a fixed ratio is unlikely to exist in this region of the atmosphere, and (e) short sampling times for ^{7}Be are needed to properly resolve stratospheric contributions. These limitations must be taken into consideration in judging the validity of the quantitative estimates discussed above.

Summary—Well-authenticated episodes of stratospheric intrusions reaching ground level are rare. Episodes in which stratospheric intrusions contributed to O_3 concentrations at mountain locations[2,6,9] are more frequent than those reaching ground level. However, very occasional episodes involving intrusions reaching ground level as a result of mechanisms 3 and 4 discussed above cannot be discounted. Episodes in which stratospheric intrusions reaching ground level would contribute sufficient O_3 to lead to observed O_3 concentrations in excess of 120 ppb appear to be extremely infrequent.

Issue 2. To what extent does stratospheric O_3 contribute to longer time-averaged O_3 concentrations at ground level in non-urban areas?

Longer time-averaged O_3 concentrations in non-urban areas are of interest for several reasons: (a) in estimating typical inflows into individual urban areas, (b) to provide boundary conditions for regional scale O_3 models, (c) in estimating exposures of field crops and forested areas to O_3. In addition to improving our basic scientific understanding, identification and quantitation of individual sources of background O_3 are useful in assessing the extent to which the background O_3 concentrations may be controllable.

In early work on the O_3 background during the 1960's, it was assumed that the O_3 concentrations observed in non-

urban areas could be uniquely associated with stratospheric O_3 transport to ground level.[3] This conclusion was based on the recognition, at that time, of only one other source for O_3 production. The source was photochemical formation of O_3 within large urban areas. With the recognition during the 1970's that long-range transport of O_3 and its precursors could occur from anthropogenic sources, the determination of the contribution of stratospheric O_3 to the O_3 measured in non-urban areas became more complex.

Compilations of O_3 concentration levels in the free troposphere are available.[2] Based on ozonesonde measurements obtained between 1962 and 1975 at 5 km altitude, the seasonal average daily maximum ozone concentrations between 40°N and 60°N latitude in ppb were as follows: winter, 40; spring, 40 to 50; summer, 40 to 60; fall, 40. Similarly, ozonesonde measurements obtained between 1962 and 1965 at altitudes between 3 and 7 km have been considered separately to obtain mean annual O_3 concentrations over the eastern United States of 60 to 65 ppb, and over the western United States of 55 to 60 ppb. Aircraft measurements in 1978 of O_3 profiles over the central United States provided the following O_3 concentrations in ppb: May, 1.5 km, 55; 4 km, 72; October, 1.5 km, 33; 4 km, 46. Because of the multiple sources mentioned above, the O_3 concentrations in the free troposphere above the planetary boundary layer should not be assumed to necessarily equal the stratospheric O_3 contribution.

Observations of the average of daily maximum O_3 concentrations and the average of hourly O_3 concentrations at sites between ground level and 3 km in the northern and southern hemisphere have been compiled.[4,12-14] At non-urban sites in the United States between 1976-1978, O_3 concentrations in ppb by quarter of the year were observed over the following ranges: 1st quarter, 30 to 44; 2nd quarter, 33 to 52; 3rd quarter, 29 to 45; 4th quarter, 22 to 30. Because of the complexities in the origins of O_3, these observed O_3 concentrations should not be assumed to be predominantly stratospheric O_3.

A relatively complete set of air-quality measurements were obtained during an eight week period in July to September 1978 at a relatively remote location 40 km west-northwest of Pierre, SD.[15] Hourly average O_3 concentrations ranged from 10 to 56 ppb with a mean of maximum hourly O_3 values of 41 ppb. While the authors concluded that the dominant source of the O_3 appeared to be the stratosphere, they also pointed out that their measurements could not distinguish between O_3 from the stratosphere and O_3 from the upper troposphere. Based on (1) remoteness of the location, (2) the low concentrations measured of several species, (3) the small standard deviations of the concentrations of these species, and (4) the interpretation of ^7Be measurements, the authors considered that anthropogenic sources of O_3 within the boundary layer were not contributing significantly to the O_3 measured at this site. The highest O_3 concentrations were observed in the continental tropical air masses which usually arrived on the backside of the high pressure systems passing the site during the study period. An increase in ^7Be as well as O_3 was observed on the backside compared to the frontside of the high pressure systems.

Less than half of the variance in O_3 concentrations is explained by a linear relation with ^7Be.[4,15] Consequently, a detailed analysis of the meteorological conditions as related to the ^7Be and O_3 concentrations was undertaken.[4]

Three-dimensional air parcel trajectories[4] were calculated during the study period.[15] It was found that southwesterly air flow resulted in increasing O_3, while northwesterly air flow resulted in decreasing O_3. However, the higher ^7Be concentrations were observed with both southwesterly and northwesterly air flows. During southwesterly flows, no 500-mb low pressure troughs occurred.[4] It was postulated that the higher ^7Be concentrations from the southwest involved transport from the troposphere by subsiding circulation associated with high pressure systems.[4] Three weak stratospheric intrusion events associated with 500 mb low pressure troughs were identified in association with northwesterly air flow. During these weak intrusion events, the 24-hour average O_3 concentrations ranged from 32 to 34 ppb. During these intrusion events the 24-hour average ^7Be concentrations ranged from 125 to 175 $fCim^{-3}$.[4] If the stratospheric ^7Be-to-O_3 ratio of 10.8 $fCim^{-3}$ per ppb[9] can be applied to these events, the predicted stratospheric O_3 concentrations would range from 12 to 16 ppb. Half of ^7Be concentrations measured during the study were in the range between 40 $fCim^{-3}$ and 125 $fCim^{-3}$. Such low ^7Be concentrations suggest long residence times with dilution by air present in the lower free troposphere or the planetary boundary layer.

The ^{90}Sr ground level concentration measurements have been used to estimate long time-averaged O_3 concentrations.[1] The mean ^{90}Sr concentrations between January and June 1963 outside of the nuclear weapons test area, ranged from 5 $pCim^{-3}$ to 9 $pCim^{-3}$, corresponding to mean O_3 concentration from 7 to 12 ppb. Based on these measurements and other evidence, the background associated with stratospheric O_3 was assumed to be approximately 15 ppb.[1]

Summary—Based on the results discussed above, it appears that only a part of the observed O_3 concentrations even at relatively remote locations can be associated with stratospheric O_3 contributions.

Issue 3. Does *in-situ* O_3 production in the free troposphere contribute significantly to the O_3 from aloft reaching ground level?

In-situ photochemical formation of O_3 within the free troposphere can occur as the result of reactions involving methane and carbon monoxide with nitrogen oxides.[16] On a global basis, anthropogenic emissions of CO have been estimated to contribute from one-sixth of the total CO present in the free troposphere.[17-20] In the northern hemisphere, a range of contributions from anthropogenic sources of 31 to 54% has been estimated.[20] In the northern hemisphere, a contribution of about 10% to the free troposphere has been associated with anthropogenic sources of CH_4.[21] Over the United States, a recent estimate associates over 95% of the NO_x emissions with anthropogenic sources.[22]

Production of O_3 by photochemical processes in the free troposphere has been predicted to occur at significant rates for NO_x concentrations above 0.03 ppb.[16] The vertical profile of NO_x through the troposphere is critical to photochemical modeling in this region.[2] Over remote areas, a vertical profile has been observed with NO_x concentrations increasing from 0.01 ppb near ground level to 1 ppb at the tropopause.[23] However, the concentrations of NO_x near the surface in populated non-urban areas on continents are in the 1 to 10 ppb range.[24] Over these areas, a vertical profile of NO_x should decrease with increasing altitude. Several recent tropospheric models predict *in-situ* tropospheric formation of O_3.[25-27]

In a study[25] using a one-dimensional model, the observed latitudinal features for O_3 could not be reproduced unless free tropospheric photochemical production of O_3 were included. A net photochemical source of O_3 was predicted from 25°N to 65°N with very high rates of O_3 production in the free troposphere between 40°N and 60°N.

A two-dimensional tropospheric model has been tested using a number of assumptions as to sources of O_3.[26] The assumption of a stratospheric source of O_3—along with photochemical generation of O_3 in the upper troposphere, with NO_x sources from lightning and the stratosphere—reasonably well simulated profiles of O_3 over remote maritime regions. Inclusion of ground level sources of NO_x as necessary to obtain predicted O_3 profiles consistent with observed profiles at mid-latitudes in the northern hemisphere. Inclusion of ground level pollution sources of NO_x more than doubled the amount of O_3 in the lower troposphere in the summer at mid-latitudes in the northern hemisphere.

In a third modeling study, one- and two-dimensional tropospheric models were utilized.[27] When the one-dimensional model was applied to summertime conditions at 40°N, the O_3 concentrations in ppb predicted at several latitudes without and with ground level NO_x sources were as follows: 1 km, 15, 37; 4 km, 26, 50; 7 km, 43, 67 and 10 km, 63, 87. In the lower troposphere between 1 and 4 km the model predicts that half or more of the O_3 produced was associated with the ground-level NO_x emissions. The total O_3 concentrations predicted with inclusion of ground level NO_x emissions corresponded satisfactorily to the observed O_3 concentrations in the troposphere at mid-latitudes in the northern hemisphere in summertime. When the two-dimensional model was applied to summertime conditions in the northern hemisphere at mid-latitudes, the inclusion of upward transport of ground level emissions of CO and NO_x resulted in an increase of more than 20 ppb of O_3 in the total O_3 predicted. This result is in good agreement with the differences of 21 to 24 ppb in O_3 with altitude predicted for the same conditions with the two-dimensional model.

Additional evidence for tropospheric O_3 formation has been obtained from measurements of the small scale vertical variability of O_3 and CO in the troposphere.[27] A large scale region of positive correlation was observed between 20°N and 45°N from altitudes of 4 to 10 km. This strong positive correlation was associated with *in-situ* photochemical O_3 production in this same region of the troposphere.

Summary—A number of modeling studies predict substantial increments of O_3 associated with *in-situ* photochemical O_3 production in the free troposphere at mid-latitudes in the northern hemisphere, especially in the summertime. Two such studies predict a doubling in O_3 concentrations in the lower portions of the troposphere as a result of upward transport of ground level NO_x emissions.[20,21] A substantial portion of the precursors participating in *in-situ* tropospheric O_3 production are emitted by anthropogenic sources at the earth's surface.

General Discussion

There is little documented evidence that high episodic O_3 concentrations occur at ground level in urban or non-urban sites in the United States as a result of direct stratospheric intrusions of O_3. Only two episodes have been reported in which stratospheric O_3 intrusions have caused ground level O_3 concentrations to exceed 120 ppb.[2] In a number of other episodes during which both elevated ^7Be concentrations and O_3 were measured, application of the ^7Be-to-O_3 ratio technique indicates that, on average, about half of the O_3 measured actually originated in the stratosphere.

Several different processes contribute to the longer time-averaged O_3 concentrations at relatively remote locations. A part of the O_3 measured is likely to be of stratospheric origin. *In-situ* O_3 formation in the free troposphere also contributes to the O_3 concentrations at remote locations. There is evidence for local *in-situ* formation of O_3 even at relatively remote sites. Aircraft measurements of O_3 over ranchland and irrigated fields in rural northeastern Colorado indicated, that during some daytime periods, the entire rate of increase with time of O_3 in the lower half of the mixed layer could be accounted for by local photochemical O_3 production.[28] At Zugspitze Mountain at 2964 m MSL, in a clean remote area of the Bavarian Alps, the O_3 concentration was lower than that over an adjacent valley site at 740 m MSL.[2] The incremental monthly average daily maximum O_3 concentrations of 8 to 15 ppb on sunny days between March and September have been attributed either to local O_3 formation or to long range transport.[2] In contrast, over pine forests north of Houston, TX, net destruction of O_3 was indicated in measurements above the forest canopy.[29] This result is consistent with a recent review which concluded that biogenic hydrocarbons would not make a substantial contribution to O_3 formation.[30] Photochemical O_3 production also has been observed in traverses taken well out over the Gulf of Mexico[29], although at a slower rate than over northeastern Colorado.[28] Measurements of O_3 over the Pacific have been considered consistent with local photochemical O_3 over the remote marine boundary layer.[31]

A fourth process which could contribute O_3 to remote sites is transport upwards from the planetary boundary layer into the free troposphere transport over long distances in the free troposphere followed by downward transport back down into the boundary layer. Cloud venting through a well-developed convective, strato cumulus-topped layer can effectively transport O_3 and other species from the boundary layer into the free troposphere.[31] Thunderstorm systems can cause the exchange of air containing O_3 and other species from the boundary layer with air from the free troposphere.[32]

At non-urban locations in the eastern United States, additional processes contribute to O_3 measured. These processes involve O_3 formation and transport within the boundary layer in individual urban,[33-39] power plant,[40-45] industrial,[46] and petroleum refinery[47-49] plumes. During the movement of high pressure systems over the eastern United States the contributions of O_3 and precursors can contribute over multiday periods.[50,51] Most of the episodes of elevated O_3 concentrations studied in the eastern United States have been associated with these anthropogenic processes.[12,13,50-52]

An additional complication results from the varying lifetime of O_3 with season, and in different regions of the atmosphere. The lifetime of O_3 in the free troposphere due to photochemical destruction has been estimated to vary from 45 days in the summer to 105 days in the winter.[11] Within the planetary boundary layer, the lifetime of O_3 is shorter. Aloft at night, within the planetary boundary layer, a lifetime of about 30 hours was estimated from vertical profiles of O_3[53,54] and from 16 to 34 hours was estimated from O_3 measurement during a balloon flight. If transport from the top of the planetary boundary layer to ground level is slow, only a portion of the O_3 will reach ground level.

Conclusions

1. Only a small number of short-term direct stratospheric ozone intrusions to the surface have been adequately documented. Of these episodes, only a few have been associated with low-altitude ground level locations in the United States. Such intrusions to the surface appear to be rare and are usually observed at rural sites. Direct stratospheric ozone intrusions to the surface which result in ozone concentrations exceeding the National Ambient Air Quality Standard for O_3 of 120 ppb appear to be extremely infrequent.

2. Episodes of substantially elevated ozone concentrations in rural areas in the eastern United States predominately have been associated with anthropogenic sources of ozone.

3. Stratospheric ozone contributes to longer term average background ozone concentrations at ground level sites. Substantial contributions also can be associated with ozone formed in the free troposphere, and with ozone formed from a number of types of sources within the boundary layer. The average background ozone is likely to be the result of contributions from these processes which can vary diurnally, synoptically and seasonally.

4. Based on tropospheric model calculations along with ^{7}Be-to-O_3 and ^{90}Sr-to-O_3 ratios, it is estimated that during the summer months 15 ppb or less of the background ozone concentrations may originate in the stratosphere. In the early spring, the stratospheric ozone contribution to the background ozone is more significant

5 The contribution of stratospheric ozone plus the free tropospheric ozone to average seasonal ozone concentrations should be substantial, particularly over many of the rural areas in which major field crops are grown.

6. Tracer substances can be useful in identifying the origins of ozone measured in rural areas. However, a tracer such as ^{7}Be formed in the stratosphere and upper troposphere is only an indicator of a contribution of air from well aloft. The sources and removal processes for ozone can be much different than the aerosols to which ^{7}Be is attached.

Recommendations

1. Better estimates should be made of the contribution of various sources of ozone to the growing season average ozone concentration in representative crop areas.

2. Since a substantial fraction of the precursors to free troposphere ozone formation are anthropogenic in origin, hemispheric scale models should be utilized in developing control strategies, if needed, for the reduction of average growing season ozone concentrations.

3. A more complete evaluation of the limitations and applications of ^{7}Be as a tracer of stratospheric and free tropospheric ozone would be useful. A number of other tracer substances such as particle sulfur and lead from major sources of ozone should be utilized to aid in quantifying contributions to background ozone concentrations.

References

1. Mohnen, V.A. and Reiter, E.R. (1977) International conference on oxidants—1976. Analysis of evidence and view points. Part III. The issue of stratospheric ozone intrusion. EPA-600/3-77-115.

2. Viezee W. and Singh, H.B. (1982) Contribution of stratospheric ozone to ground-level ozone concentrations—A scientific review of existing evidence. SRI Project 3643. Prepared for Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

3. Junge, C.E. (1963) Air Chemistry and Radioactivity. International Geophysical Series Vol. 4, pp. 37-59. Academic Press, NY.

4. Viezee, W., Singh, H.B., and Shigeishi, H. (1982) The impact of stratospheric ozone on tropospheric air quality—Implications from an analysis of existing field data. Final Report to Coordinating Research Council, Inc., 219 Perimeter Center Parkway, Atlanta, GA 30346.

5. Johnson, W.B. and Viezee, W. (1981) Stratospheric ozone in the lower troposphere—I. Presentation and interpretation of aircraft measurements. *Atmos. Environ. 15,* 1309-1323.

6. Viezee, W. and Singh, H.B. (1982) A method to predict a stratospheric impact on boundary-layer and ground-level ozone concentrations. Draft Report. SRI Project 3643. Prepared for Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

7. Lamb, R.G. (1977) A case study of stratospheric ozone affecting ground-level oxidant concentrations. *J. Appl. Meteorol. 16,* 780-794.

8. Husain, L., Coffey, P.E., Meyers, R.E., and Cederwall, R.T. (1977) Ozone transport from stratosphere to troposphere. *Geophys. Res. Lett. 4,* 363-365.

9. Dutkiewicz, V.A. and Husain, L. (1979) Determination of stratospheric ozone at ground level using ^{7}Be/ozone ratios. *Geophys. Res. Lett. 6,* 171-174.

10. Husain, L., Rusheed, A., and Dutkiewicz, V.A. (1979) Sources of natural ozone: Stratospheric intrusions in Texas. In an Air Pollution Control Association specialty conference on: Ozone/oxidants. Interactions with the total environment. (Ed., E.R. Fredrick). Houston, TX.

11. Singh, H.B., Viezee, W., Johnson, W.B., and Ludwig, F.L. (1979) The impact of stratospheric ozone on tropospheric air quality. In an Air Pollution Control Association specialty conference on: Ozone/oxidants. Interactions with the total environment. (Ed., E.R. Fredrick). Houston, TX.

12. Evans, G., Finkelstein, P., Martin, B., Possiel, N., and Graves, M. (1983) Ozone measurements from a network of remote sites. *J. Air Poll. Control Assoc. 33,* 291-296.

13. Evans, G., Finkelstein, P., Martin, B., Possiel, N., and Graves M. (1982) The National Air Pollution Background Network 1976-1980. Environmental Monitoring Systems Laboratory Report, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

14. Computed from a tabulation of ozone meaurements at Whiteface Mt., NY provided by Dr. Volker Mohnen 1982.

15. Kelly, N.A., Wolff, G.T., and Ferman, M.A. (1982) Background pollutant measurements in air masses affecting the eastern half of the United States—I. Air masses arriving from the northwest. *Atmos. Environ. 16,* 1077-1088.

16. Fishman, J., Solomon, S., and Crutzen, P.J. (1979) Observational and theoretical evidence in support of a significant *in-situ* photochemical source of tropospheric ozone. *Tellus 31,* 432-446.

17. Seiler, W. (1974) The cycle of atmospheric CO, *Tellus 26,* 117-135.

18. Zimmerman, P.R., Chatfield, R.B., Fishman, J., Crutzen, P.J., and Hanst, P.L. (1978) Estimations on the production of CO and H_2 from the oxidation of hydrocarbon emissions from vegetation. *Geophys. Res. Lett. 5,* 679-681.

19. Kitada, T. and Peters, L.K. (1982) A three-dimensional transform-chemistry analysis of CO and CH_4 in the troposphere. In 2nd symposium: Composition of the nonurban atmosphere. May 25-28, 1982, Williamsburg, VA, Amer. Meteor. Soc., 45 Beacon St., Boston, MA 02108.

20. Hanst, P.L., Spence, J.W., and Edney, E.O. (1980) Carbon monoxide production in photooxidation of organic molecules in the air. *Atmos. Environ. 14,* 1077-1088.

21. Khalil, M.A.K. and Rasmussen, R.A. (1983) Sources, sinks and seasonal cycles of atmospheric methane. *J. Geophys. Res. 88,* 5131-5144.

22. Robinson, E. (1983) Natural emissions sources. Chapter A-2, Section 2.2, In: The acidic deposition phenomenon and its effects: Critical assessment review papers (Altshuller, A.P. and Linthurst, R.A., eds.) Vol. I. Public Review Draft.

23. Kley, D., Drummond, J.W., McFarland, M., and Liu, S. C. (1981) Tropospheric profiles of NO_x. *J. Geophys. Res. 86,* 3153-3161.

24. Altshuller, A.P. (1983) Atmospheric concentrations and distributions of chemical substances. Chapter A-5, Section 5.3. In: The acidic deposition phenomenon and its effects: Critical assessment review papers (Altshuller, A.P. and Linthurst, R.A., eds.) Vol. I Public Review Draft.

25. Hameed, S. and Steward, R.W. (1983) Latitudinal variation of tropospheric ozone in a photochemical model. *J. Geophys. Res. 88,* 5153-5162.

26. Gidel, L.T. and Crutzen, P.J. (1982) The role of various natural and anthropogenic NO_x emissions of atmospheric ozone in a two dimensional model. In 2nd symposium: Composition of the nonurban atmosphere. May 25-28, 1982. Williamsburg, VA, Amer. Meteorol. Soc., 45 Beacon St., Boston, MA 02108.

27. Fishman, J. and Seiler, W. (1983) Correlative nature of ozone and carbon monoxide in the troposphere: Implications for the tropospheric ozone budget. *J. Geophys. Res. 88,* 3662-3670.

28. Lenschow, D.H., Pearson, R., Jr., and Stankov, B.B. (1981) Estimating the ozone budget in the boundary layer by use of aircraft measurements of ozone eddy flux and mean concentration. *J. Geophys. Res., 86,* 7291-7297.

29. Lenschow, D.H., Pearson, R., Jr., and Stankov, B.B. (1982) Measurements of ozone vertical flux to ocean and forest. *J. Geophys. Res. 87,* 8833-8837.

30. Altshuller, A.P (1983) Review: Natural volatile organic substances and their effect on air quality in the United States. *Atmos. Environ. 17*, 2131-2165.

31. Gidel, L.T. (1983) On the maintenance of the marine boundary layer-free tropospheric gradient of transient tracers. *J. Geophys. Res. 88*, 5145-5152.

32. Lyons, W.A. and Calby, R.H. (1983) Impact of mesoscale convective precipitation systems on regional visibility and ozone distributions. Report to Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

33. Blumenthal, D.L., White, W.H., and Smith, T.B. (1978) Anatomy of a Los Angeles smog episode: Pollutant transport in the daytime sea breeze regime. *Atmos. Environ. 12*, 893-907.

34. Spicer, C.W., Joseph, D.W., Sticksel, P.R., and Ward, G.F. (1979) Ozone sources and transport in the northeastern United States. *Environ. Sci. Technol. 13*, 975-985.

35. Wolff, G.T., Lioy, P.J., Wight, G.D., Pasceri, R.E. (1977) Aerial investigation of the ozone plume phenomenon. *J. Air Poll. Control Assoc. 27*, 460-463.

36. Spicer, C.W. and Sverdrup, G.M. (1981) Trace nitrogen chemistry during the Philadelphia oxidant enhancement study (1979). Report to Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

37. Spicer, C.W., Koetz, J.R., Keigley, G.W., Sverdrup, G.M., and Ward, G.F. (1982) Nitrogen oxides reactions within urban plumes transported over the ocean. Report to Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

38. White, W.H., Anderson, J.A., Blumenthal, D.L., Husar, R.B., Gillani, N.V., Husar, J.D., and Wilson, W.E., Jr. (1976) Formation and transport of secondary air pollutants: Ozone and aerosols in the St. Louis urban plume. *Science 194*, 187.

39. Spicer, C.W., Joseph, D.W., and Sticksel, P.R. (1982) An investigation of the ozone plume from a small city. *J. Air Poll. Control Assoc. 32*, 278-281.

40. Davis, D.D., Smith, G., and Klauber, G. (1974) Trace gas analysis of power plant plumes via aircraft measurement. O_3, NO_x and SO_2 chemistry. *Science 186*, 733-736.

41 Gillani, N V., Husar, R B., Husar, J.D., Patterson, D.E., and Wilson, W E , Jr (1978) Project MISTT: Kinetics of particulate sulfur formation in a power plant plume out to 300 km *Atmos. Environ. 12*, 589-598

42. Gillani, N.V. and Wilson, W.E. (1980) Formation of ozone and aerosols in power plant plumes. *Ann. New York Acad. Sci. 338*, 276-296.

43. Miller, D.F., Alkezweeny, A.J., Hales, J.M., and Lee, R.N. (1978) Ozone formation related to power plant emissions. *Science 202*, 1186-1188.

44. Hegg, D.A., Hobbs, P.V., and Radke, L.F. (1976) Reactions of nitrogen oxides, ozone and sulfur in power plant plumes. EPRI EA-270. Prepared for Electric Power Research Institute, 3412 Hillview Ave., Palo Alto, CA 94304.

45. Ogren, J.A., Blumenthal, D.L., and Vanderpol, A.H. (1977) Oxidant measurements in western power plant plumes. Vol. 1. Technical analysis EPRI-421. Prepared for Electric Power Research Institute, 3412 Hillview Ave., Palo Alto, CA 94304.

46. Sexton, K. and Westberg, H. (1980) Ambient hydrocarbon and ozone measurements downwind of a large automotive painting plant. *Environ. Sci. Technol. 14*, 329-332.

47. Westberg, H.H., Allwine, K.J., and Robinson, E. (1977) Ambient hydrocarbon and ozone concentrations near a refinery: Lawrenceville, Illinois—1974. EPA-600/7-77-049.

48. Sexton, K. and Westberg, H. (1980). Ambient hydrocarbon and ozone concentrations near a refinery: Benicia, California 1975. EPA-600/7-80-028.

49. Sexton, K. and Westberg, H. (1983) Photochemical ozone formation from petroleum refinery emissions. *Atmos. Environ. 17*, 467-475.

50. Vukovich, F.M., Bach, W.D., Jr., Crissman, B.W., and King, W.V. (1977) On the relationship between high ozone in the rural surface layer and high pressure systems. *Atmos. Environ. 11*, 967-983.

51. Wolff, G.T. and Lioy, P.J. (1980) Development of an ozone river associated with synoptic scale episodes in the eastern United States. *Environ. Sci. Technol. 14*, 1257-1260.

52. Martinez, J.R. and Singh, H.B. (1979) Survey of the role of NO_x in nonurban ozone formation. SRI Project 6780-8. Report to Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

53. Research Triangle Institute (1975) Investigations of rural oxidant levels as related to urban hydrocarbon control strategies. EPA-450/3-74-036.

54. Sickles, J.E., II, Ripperton, L.A., and Eaton, W.C. (1977) Oxidant and precursor transport simulation studies in the Research Triangle Institute Smog Chambers. In: Proceedings of the International Conference on Photochemical Pollution and Its Control. pp. 319-328. Vol. I. (Dimitriades, B., ed.) EPA-600/3-77-012.

 * USGPO: 1984-759-102-10637