OZONE TRANSPORT FROM STRATOSPHERE TO TROPOSPHERE

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Abstract. ^{7}Be produced by the interaction of cosmic rays with oxygen and nitrogen, predominantly in the stratosphere, has been used to identify and measure stratospheric ozone at the ground level. Simultaneous measurements at Whiteface Mountain, New York, in July 1975 show that the maximum ^{7}Be concentrations are accompanied by increased ozone concentrations. Peaks in ^{7}Be concentrations occurred on July 5-6, 11-12, 16-17, 23, and 27. Ozone peaks were observed on July 7-9, 11, 18, 24, and 27. Isentropic trajectory calculations also showed that the trajectories reaching Whiteface Mountain on July 11-12, 15-16, 23, and 27 had stratospheric origin. One-day delay in ozone peaks on July 7-9, 18, and 24 is attributed to increased tropospheric ozone production. The observed relationship between ^{7}Be and ozone is used to deduce an upper limit of 37 ppb stratospheric ozone at Whiteface Mountain during July 1975. Thus, even during midsummer months, when stratospheric-tropospheric mass exchange is not at a maximum, stratospheric ozone may contribute substantially to the national ambient air quality standard of 80 ppb.

Ozone in concentrations exceeding the U.S. Environmental Protection Agency's national ambient air quality standard (80 ppb, hourly average) has been measured frequently in remote areas of the United States. Such occurrences are regional and seasonal, associated with high-pressure weather systems during the summer months (Coffey and Stasiuk, 1975; Worth et al., 1967). Peak ozone concentrations are generally observed on the back or stagnant side of the high-pressure system, where conditions may also be ideal for lower tropospheric ozone production through photochemical reactions involving NO_2 and both natural and man-made hydrocarbons.

A second source, the descending stratospheric ozone, has also been proposed as a significant contributor to tropospheric ozone (Danielsen, 1968). We have investigated this by using ^{7}Be as a natural tracer of stratospheric contributions to the troposphere at relatively isolated Whiteface Mountain, New York.

Interaction of cosmic rays with nitrogen, oxygen, and argon produces a large number of radioactive isotopes, with half-lives ranging from a few seconds to millions of years (Lal and Peters, 1967). Most of this production occurs in the stratosphere, but significant quantities (up to about 30%) of many isotopes, including ^{7}Be, are formed in the upper troposphere. Nuclides thus produced are quickly oxidized and may be attached to small aerosol particles. Bulk motion of the air masses eventually brings them to the lower troposphere. When nuclides with appropriate half-lives reach cloud levels, precipitation scavenging efficiently washes them down. (Dry fallout plays only a minor role.) This mechanism provides a constant background of cosmogenic nuclides in the troposphere.

Occasional large intrusions of stratospheric air into the troposphere cause a dramatic rise above this background in the concentrations of cosmogenic nuclides. Since ozone concentrations are significantly larger in the stratosphere (with maxima at about 27 km) than in the troposphere, a simultaneous increase in ozone concentration can be expected. Simultaneous measurements of cosmogenic nuclides and ozone can thus be used to study injections of stratospheric air masses into the troposphere. This approach has recently been applied at Zugspitze, Germany (Reiter et al., 1976), and at Quillayute, Washington (Ludwick et al., 1976).

During July 1975 we carried out continuous measurements of ozone, ^{7}Be (half-life, 53.5 days), total suspended particulates (TSP), precipitation, and barometric pressure at the observatory at the summit of Whiteface Mountain (elevation 1.5 km), a location remote from urban/industrial areas. Air particulates were collected over 24-hour periods (midnight to midnight) on 25-cm x 20-cm Whatman 41 filter papers using high-volume samplers. Four samplers were operated sequentially, each for a 24-hour interval, at a flow rate of about 75 m^3 of air per hour. The filter papers were then allowed to equilibrate for 24 hours at 21°C and 50% relative humidity and were weighed to determine the amounts of collected particulates.

Individual filter papers were then γ-counted in a 10-cm x 10-cm NaI(Tl) counter connected

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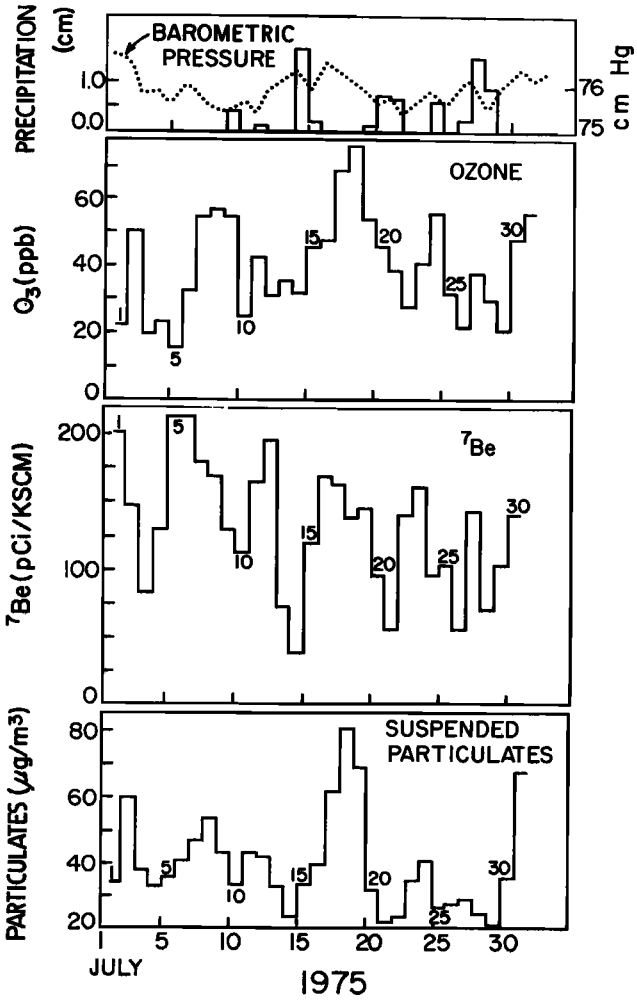

Fig. 1. Daily measurements of ozone, ^{7}Be, total suspended particulates, barometric pressure, and precipitation at Whiteface Mountain, New York (KSCM = 1000 m^3). Barometric pressures were measured at the base of Whiteface Mountain. Numerals in the figure indicate the days of July.

to a 200-channel analyzer. Activities of ^{7}Be were determined using a 477-keV γ-ray relative to a ^{7}Be standard counted in the same geometry as the filter papers. The γ-ray spectra were analyzed by a least-squares program. Absolute uncertainties in the ^{7}Be activities, based on possible errors, are estimated at about ±10%. Ozone was measured in a chemiluminescent analyzer, which was periodically recalibrated (Coffey and Stasiuk, 1975). Uncertainties in the ozone measurements are ±5%.

Ozone measurements, averaged on an hourly basis, varied between 1 and 100 ppb. Concentrations in excess of the 80 ppb air quality standard were observed 10 times. Since ^{7}Be measurements were carried out on particulates collected on a 24-hour basis (Fig. 1), ozone data are also shown as 24-hour averages. Diurnal fluctuations of the ozone concentrations were either absent or small, suggesting that local photochemical production of ozone at Whiteface Mountain is small. Continuous measurements of nitrogen oxides have also yielded values below the detection limit of about 3 ppb, indicating the air at this site is relatively clean.

To establish that the ^{7}Be we measured originated in the stratosphere, rather than in the upper troposphere, we calculated the trajectories of air reaching Whiteface Mountain between July 10 and 31. (Necessary meteorologic data were not available for July 1-10.) The isentropic trajectories, i.e., trajectories along surfaces of constant potential temperature, were calculated by Danielsen's methods (Danielsen, 1968) using wind, temperature, and humidity analysis data from the National Center for Atmospheric Research and the National Oceanic and Atmospheric Administration. These calculations showed that the trajectories reaching Whiteface Mountain on July 11-12, 15-16, 23, 27, and 29 had stratospheric origin, as shown by potential vorticities in excess of 10^{-8} cm sec deg/gm along the isentropic trajectory. ^{7}Be activity peaked on July 5, 11-12, 16-17, 23, 27, and 30. This correlation reinforces the use of ^{7}Be as a reliable tracer of stratospheric components of an air mass.

Fig. 1 shows the daily variations of ^{7}Be, ozone, TSP, precipitation, and barometric pressure. There are similarities between ^{7}Be, ozone and TSP. For example, ozone and TSP concentrations showed prominent peaks on July 2, 7-9, 11, 18, 24, 27, and likely on July 31. Multiple linear regression analyses of ozone against TSP and ^{7}Be, based on the entire 30 days' data, were performed. The correlation coefficient relating ozone with TSP was high (0.75) and that relating ozone and ^{7}Be, though also positive, was low (0.15). Since ^{7}Be is produced only in the stratosphere and upper troposphere, it will correlate with ozone only on those days when significant proportion of ozone measured at Whiteface Mountain originated in stratosphere. Hence a low correlation coefficient is to be expected when the entire 30 days' data are used.

Both ^{7}Be and ozone concentrations showed peaks on July 11 and 27. Since ^{7}Be is not produced in the lower troposphere, a ^{7}Be peak indicates the arrival of a fresh stratospheric air mass. As the local photochemical ozone production at Whiteface Mountain is small, the observed ozone levels of 42 and 37 ppb on July 11 and 27, respectively, may be of stratospheric origin or may be photochemically produced elsewhere and transported to Whiteface Mountain via air mass movement. Resolution of the tropospheric and stratospheric components, however, is a formidable task. Whereas the ^{7}Be peak indicates a stratospheric component, the ^{7}Be concentration cannot now be used to quantify this stratospheric ozone component, as neither the ^{7}Be/ozone mixing ratios nor the history of the ^{7}Be-ozone air mass (at and subsequent to tropopause injection) is known. A study of the trajectories of the air parcel reaching Whiteface Mountain may help delineate the tropospheric ozone component.

Backward trajectory calculations show that the air parcel arriving on July 27 came from the north-northwest, traveling over sparsely populated areas of the United States and Canada.

The level of TSP was also low, in agreement with this suggestion. The tropospheric component of ozone can thus be assumed to be low. We believe that the ozone concentration of 37 ppb on July 27 places an effective upper limit on the stratospheric contribution on that day. The air parcel reaching Whiteface Mountain on July 11 came from the west-southwest, passing through relatively more populated areas; hence it contained higher TSP and probably a somewhat greater tropospheric ozone component as well. The ozone concentration on July 11 was higher (42 ppb), supporting our interpretation. From these results we conclude that on July 11 and 27 up to 37 ppb of ozone at Whiteface Mountain originated in the stratosphere. This is the first identification of upper-limit quantification of the stratospheric ozone contribution at ground level.

Except for July 11 and 27, the ozone peaks were a day later than those of ^{7}Be. This is a tantalizing observation with no obvious explanation. This correlation cannot be explained on the basis of precipitation scavenging. In the lower troposphere all of the ^{7}Be is attached to TSP, only a small fraction of TSP act as carriers for ^{7}Be. However, the sources of ^{7}Be and TSP are unrelated: ^{7}Be is not produced in the lower troposphere, where most TSP originate. Furthermore, precipitation removes TSP, so that independent of any relationship both TSP and ^{7}Be are at a relative minimum. In the absence of precipitation ^{7}Be varied quite differently from TSP. For example, ^{7}Be peaked on July 5-6 and continually decreased until July 10, whereas TSP increased monotonically from July 5 to 8 and then decreased slowly. We propose the following hypothesis to explain the one-day delay in ozone peaks.

Behind a front there could be relatively clean air (as also indicated by low TSP) and a subsidence of stratospheric air containing ^{7}Be and ozone. Thereafter a continuous but slower buildup of TSP and ozone would occur due to increased tropospheric contribution, creating delayed ozone and TSP peaks. In our study this effect appears to be particularly noticeable when a ^{7}Be peak occurred on July 15-16 after a frontal passage. The ^{7}Be peak was accompanied by increased ozone concentrations due apparently to a stratospheric injection. On July 17 ^{7}Be began to decrease, but ozone continued to increase. Although the hourly ozone data indicate no significant diurnal variation on July 15, 16, and 17, the largest diurnal fluctuation during this study was observed on July 18.

We interpret these observations to mean that (1) the delayed ozone peak was largely due to the increased tropospheric contribution on July 17 and 18 and (2) the ozone measured on July 15 and 16 had a substantial origin in the stratosphere. What fraction of this ozone originated in the troposphere cannot be accurately determined. However, the 45 and 47 ppb concentrations on July 15 and 16, respectively, are in good agreement with the upper limit of 37 ppb deduced earlier in this paper.

In summary, from the observed ^{7}Be-ozone relationship on July 11, 16, and 27, we estimate that during this period the stratospheric ozone contribution was <37 ppb. Since stratospheric-tropospheric mass exchange is at a maximum in spring (Danielsen, 1968), substantially higher stratospheric ozone contributions can be expected then. Measurements in spring (preferably at varying altitudes), inclusion of ozone and ^{7}Be sinks, and accurate determinations of the ozone-^{7}Be mixing ratios in the stratosphere will help to more accurately quantify the stratospheric ozone at ground level.

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