Tellus (1980) *32*, 456–463

Simultaneous presence of O_3 and CO bands in the troposphere

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(Manuscript received December 20, 1979; in final form March 7, 1980)

ABSTRACT

Vertical profiles of CO and O_3 in the troposphere and lower stratosphere have been constructed during a series of flights conducted in July and August 1974 over the American continents between 53° S and 67° N. The mixing ratios of both gases show large fluctuations with altitude in the Northern Hemisphere. Most of the observed bands of O_3 in the free troposphere are coexistent with elevated CO concentrations indicating that this O_3 is probably not of stratospheric origin, but most likely produced in the troposphere. From the observations, it is not clear whether these high concentrations of ozone were produced in situ in the remote troposphere or had been transported out of a polluted boundary layer. Isentropic trajectory calculations likewise indicate that the air containing these elevated ozone and carbon monoxide concentrations had been situated in the troposphere for at least 72 h prior to being sampled.

1. Introduction

Expanding upon the hypotheses of Crutzen (1972, 1973), the recent studies of Fishman and Crutzen (1978) and Fishman et al. (1979) have emphasized that a considerable fraction of ozone in the troposphere may be produced in situ by the oxidation of CO, methane, and non-methane hydrocarbons in the presence of the oxides of nitrogen (NO_x = NO + NO_2). In this paper, we present the first set of concurrent observations of CO and O_3 in the remote troposphere which utilize instrumentation having comparable time resolution for both species from which we have constructed vertical profiles at 34° N and 64° N. These profiles show the presence of well-defined bands of ozone in the troposphere which are concurrently observed with anomalously higher concentrations of CO. The positively correlated nature of the CO and O_3 mixing ratios indicates that the ozone observed in these bands could not have originated in the stratosphere and most likely confirms the existence of an in-situ source of tropospheric ozone in the remote troposphere.

2. Instrumentation

The data were obtained from several flights conducted in July and August 1974 between 53° S and 67° N providing a series of vertical profiles of ozone and CO in the troposphere. The measurements were carried out aboard a commercially-produced Hawker-Siddeley 125 airplane using continuously-monitoring CO and O_3 instruments having a comparable time resolution of 15–30 s. Thus, simultaneous vertical profiles of these two species could be constructed with a vertical resolution of 100–200 m, depending on the ascent or descent rate of the aircraft. The air was taken from the bleed air system which was not contaminated by the compressors and ventilation

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[2] The National Center for Atmospheric Research is sponsored by the National Science Foundation.

0040-2826/80/050456-08$02.50/0

system. The necessary tests had verified this during low altitude flights (3 km) by comparing measurements of CO and O_3 in air drawn in directly from outside with air from the bleed air system. No significant difference between the two sets of data could be found.

The CO measurements were conducted using a continuously monitoring CO instrument based on the HgO to Hg conversion at 200 °C, followed by the determination of the resultant mercury vapor using an atomic absorption spectrometer. Details of this system have been given previously by Seiler (1974). The lower detection limit of the CO instrument is approximately 0.2 ppbv, and its precision was determined to be ±2% at CO mixing ratios of 50 ppbv. The CO record does not interfere with other gases present in the troposphere such as hydrocarbons, O_3, etc., which may also react with mercury oxide. The instrument had been periodically calibrated during the flight using calibration gases stored under high pressures (>100 bars) in steel tanks. Before and after the flight the mixing ratio of this working standard has been compared with a primary standard available in this laboratory.

The O_3 measurements were carried out with an improved microcoulomb ozone sensor manufactured by the Mast Company. In this instrument, the sensing of O_3 in the air sample is accomplished by the oxidation-reduction of potassium iodide in solution providing a current between the two electrodes. The current had been recorded continuously on a strip chart recorder. The lower detection limit of this ozone sensor has been found to be approximately 1 ppbv with a precision of ±10%. As the measured current is directly proportional to the number of ozone molecules introduced into the solution, the O_3 sensor provides absolute O_3 numbers. Nevertheless, the O_3 sensor had been calibrated several times per year and the sensitivity was found to be proportional to the air pressure and increased linearly with increasing cabin pressure. At normal temperature and pressure the slope of the calibration curve is constant with time and the magnitude of the O_3 values agreed reasonably well with those measured by an O_3 analyser constructed by Fabian and Pruchniewicz (1973).

3. Results

Fig. 1 depicts part of the itinerary of the flights over the North American continent. During this

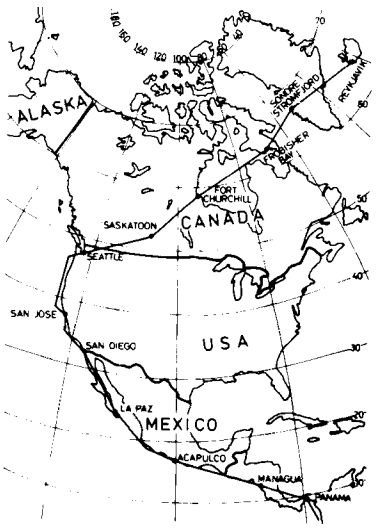

Fig. 1. Flight path of Hawker-Siddeley 125 airplane over North American continent between July 25 and August 1, 1974. Circles indicate locations into which refueling or overnight stops were made.

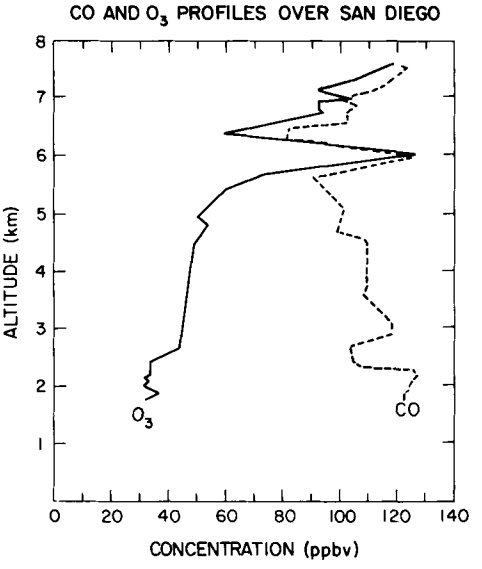

Fig. 2. Vertical profiles of O_3 and CO measured during descent into San Diego, California, (33° N) July 31, 1974.

time, flight levels ranged between 7 and 12 km. Carbon monoxide and ozone measurements at lower altitudes were made during the ascents and descents from airports; in addition to these measurements, several other vertical profiles were constructed during special ascents and descents over the ocean.

Fig. 2 shows the vertical distribution of CO and O_3 measured during the descent into San Diego (33° N, 118° W). Cruising altitude prior to descent was 7.6 km. After the initiation of descent at 1724 GMT, we note the general downward trend in both the CO and O_3 mixing ratios which reach relative minimum values of 81 and 57 ppbv, respectively, at 6.4 km. As descent continues, the CO mixing ratio jumps to 125 ppbv at 6.0 km while the ozone concentration increases to 126 ppbv at the same altitude. It is the simultaneous presence of the enhanced concentrations of CO and O_3 of this altitude of 6.0 km which is of particular interest in this study. Below about 5 km, there are no other lamina of either CO or O_3 which are as well-defined as the ones noted at 6.0 km.

At this point, it is important to point out that the enriched CO concentration observed at 6.0 km most likely would not have been detected by conventional gas chromatographic techniques. The duration of the higher concentration of CO found in this profile (as well as the elevated O_3 concentration) was approximately one minute, covering a vertical extent of only about 600 m. Conventional CO measurements using gas chromatography cannot make measurements more frequently than about every five minutes (Heidt, personal communication). Thus, it is quite probable that the CO band indicated in this profile would have gone undetected without a CO instrument which monitors continuously. In addition we note that previous observations of lamina containing elevated ozone concentrations (e.g., Danielsen, 1968; Danielsen and Mohnen, 1977) do not have concurrent measurements of CO which is an excellent tropospheric tracer, most likely of anthropogenic origin.

Even more structure is seen in the vertical distribution for O_3 and CO during descent into Frobisher, Canada (64° N, 68° W) on July 25, 1974. The sharp vertical gradient in both the CO and O_3 registrations depicted in Fig. 3 clearly indicates that the tropopause was located at an altitude of 10.3 km. Thus, the aircraft was

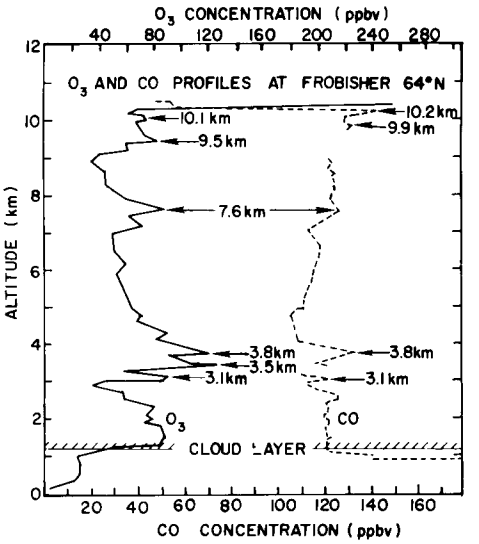

Fig. 3. Vertical profiles of O_3 and CO measured during descent into Frobisher, Canada (64° N), July 25, 1974. Arrows indicate significant altitudes at which anomalously high and/or low concentrations of these gases were observed. See text for discussion.

situated slightly above the tropopause during its cruising altitude of 10.5 km. Data in this profile are of particular interest because the rate of descent was slower than in the previous case resulting in much detail being present in Fig. 3. There are three regions of high variability of CO and O_3 as a function of altitude: one between 9.0 and 10.5 km; the second between 7 and 8 km; and the third located between 3 and 4 km. Above 9.0 km the CO and O_3 data are anti-correlated with O_3 minima at 9.9 and 10.2 km which are reflected in the CO data as relative maxima at these levels. In addition the O_3 peak at 10.1 km is associated with a corresponding decrease of CO concentration at that altitude. Unfortunately, the ozone peak measured at 9.5 km cannot be compared with the CO data as the CO instrument was going through an in-flight calibration.

The ozone peak centered at 7.6 km is clearly identified with a corresponding CO maximum at the same altitude. Likewise, it is seen that the strongest ozone band depicted in this profile, located between an altitude of 3 and 4 km, is found simultaneously in air in which the strongest CO band is identified in the profile. Within this altitude region, the ozone bands seen at 3.8 and 3.1 km correspond identically to CO peaks appearing at

these flight levels. The enhanced ozone concentration found at 3.5 km takes place during a calibration of the zero point of the CO instrument, but there are indications that the CO registration would have likewise shown a relative maximum value at this altitude.

4. Discussion

The vertical profiles shown in Figs. 2 and 3 clearly demonstrate that distinct lamina of enhanced ozone concentrations exist in the troposphere at various altitudes. The fact that elevated concentrations of CO are observed simultaneously with these ozone bands suggests that the air in which these anomalously high levels of O_3 and CO are measured most likely could not have originated in the stratosphere. Earlier stratospheric measurements (e.g., Seiler and Warneck, 1970; Seiler et al., 1978) as well as the stratospheric air depicted above 10.3 km in Fig. 3 show that stratospheric CO mixing ratios generally are less than 50 ppbv and that a negative correlation exists between stratospheric CO and O_3 concentrations. An examination of the meteorological data at the times when these profiles were constructed confirms the contention that the observed O_3 bands cannot be of stratospheric origin.

In Fig. 4, we show the 500 mb analysis at 12Z, July 31, 1974. The ozone band indicated at 6.0 km on Fig. 2 is located at a pressure of approximately 489 mb. Thus, the 500 mb analysis is quite representative of the isobaric level at which the

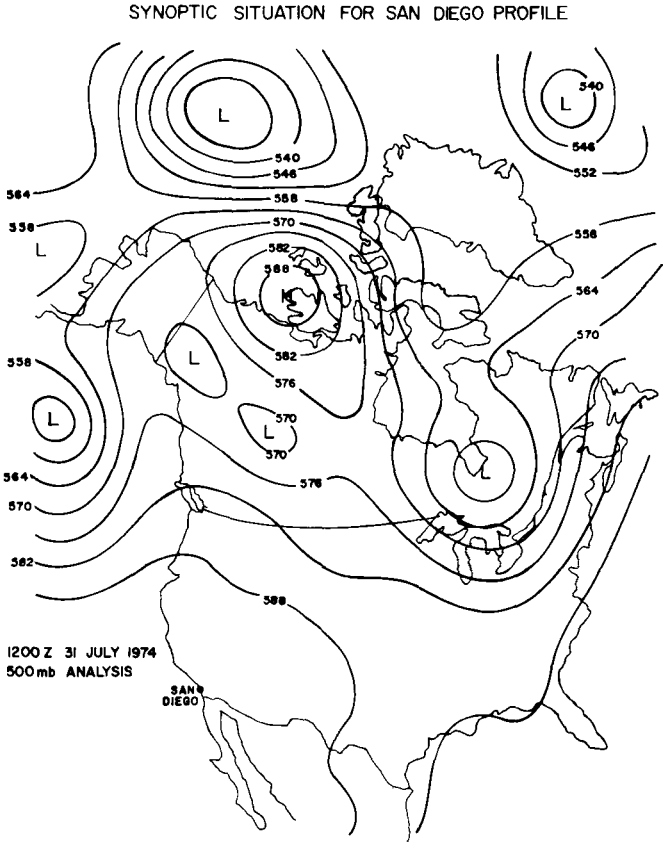

Fig. 4. Synoptic analysis of the 500 mb isobaric surface at 12Z, July 31, 1974 which corresponds closely with the altitude and time at which the predominant O_3 and CO bands were observed over San Diego.

enhanced ozone and CO laminae are observed. We note from this analysis (and from synoptic analyses at other levels not shown here) that the profile over San Diego lies outside of an area in which any significant meterological features are present. Examination of radiosonde data over San Diego at this time reveals that the potential temperature (θ) corresponding to an altitude of 6.0 km is approximately 326 K. Since air parcels move along surfaces of constant potential temperature under adiabatic conditions (Danielsen, 1961; Ucellini et al., 1979) we have constructed a backwards trajectory for the air arriving at San Diego at a θ-level of 326 K. We have utilized the computational algorithm developed by Haagenson and Shapiro (1979) which makes use of analyses constructed by the U.S. National Meteorological Center (NMC) and incorporating available radiosonde data to calculate these trajectories. These analyses are updated every twelve hours for the trajectory calculations. The recent history of the air arriving at 00Z, August 1, at an altitude of 6.0 km over San Diego (see Fig. 4) indicates that this parcel originated from a southerly direction and travelled nearly isobarically. According to the trajectory (see Table 1), the aforementioned air parcel reaching a pressure level of 489 mb at 00Z, August 1, 1974, traveled between a pressure 437 and 491 mb during the three days prior to reaching its destination. Trajectories calculated for air reaching San Diego at 12Z, July 31 and August 1 for θ-levels between 322 °K and 330 °K likewise indicate that air at these levels came from a southerly direction and must have been in the troposphere during the past 96 h. The trajectories calculated for lower levels in the atmosphere indicate that the air may have traveled over the continental U.S. or Mexico three or four days prior to reaching San Diego. Nonetheless, we conclude from these trajectory calculations that the O_3 band depicted in Fig. 2 could not have been a remnant of a stratospheric intrusion which is in agreement with the fact that a correspondingly elevated CO concentration was measured in this layer.

Table 1. *Isentropic trajectory calculation for San Diego*

$\theta = 326$ K (~6.0 km)				
Date	Time	Latitude	Longitude	Pressure
1 Aug	00 Z	32.8° N	117.7° W	489 mb
31 Jul	12 Z	30.8° N	117·2° W	491 mb
31 Jul	00 Z	29.1° N	118.2° W	498 mb
30 Jul	12 Z	27.7° N	119.0° W	454 mb
30 Jul	00 Z	26.8° N	120.4° W	478 mb
29 Jul	12 Z	27.0° N	122.1° W	428 mb
29 Jul	00 Z	27.8° N	123.3° W	437 mb

The 300 mb synoptic analysis corresponding to the time of the Frobisher profile depicted in Fig. 3 is shown in Fig. 5. The bands of enhanced ozone concentrations found between an altitude of 3 and 4 km are at a pressure level of approximately 674 mb and a θ-level of 298 K. The calculated isentropic trajectory along the 298 K θ-level (see Table 2) indicates that this air had been in the troposphere for at least the past 72 h and had maintained a pressure very near 700 mb. Thus, it is again clear that the O_3 band found at this altitude over Frobisher must be of tropospheric origin which is also consistent with the concurrent finding of an elevated CO mixing ratio. The O_3 band found at an altitude of 7.6 km over Frobisher is located at an isobaric level of approximately 373 mb corresponding to a θ-level of 314 K. The calculated trajectory for this O_3 band indicates that the air had come from the northwest and had descended from a pressure of 327 mb 72 h prior to reaching Frobisher. At 00Z, July 23 the calculated trajectory indicates that the air parcel had been located at 75.4° N, 121.7° W, The closest sounding to this location is found at Mould Bay (Northwest Territory), Canada, 76.2° N, 119.3° W and is shown in Fig. 6. As is clearly seen from this temperature profile, a well-defined tropopause is indicated at 295 mb which suggests that the air located at a pressure of 315 mb at this location was situated slightly below the tropopause. The calculated value of potential vorticity, which can be used as a stratospheric tracer, at this altitude and location likewise suggests that the air parcel is probably not of stratospheric origin.

Thus, we conclude from the isentropic trajectory analyses that none of the three predominate ozone bands found in the profiles depicted in Figs. 2 and 3 had descended from the stratosphere within 72 h prior to their being observed. This is consistent with the concurrent observation of elevated CO concentrations accompanying the O_3 measurements. On the other hand, it is difficult to determine the precise origin of the observed O_3 and CO bands

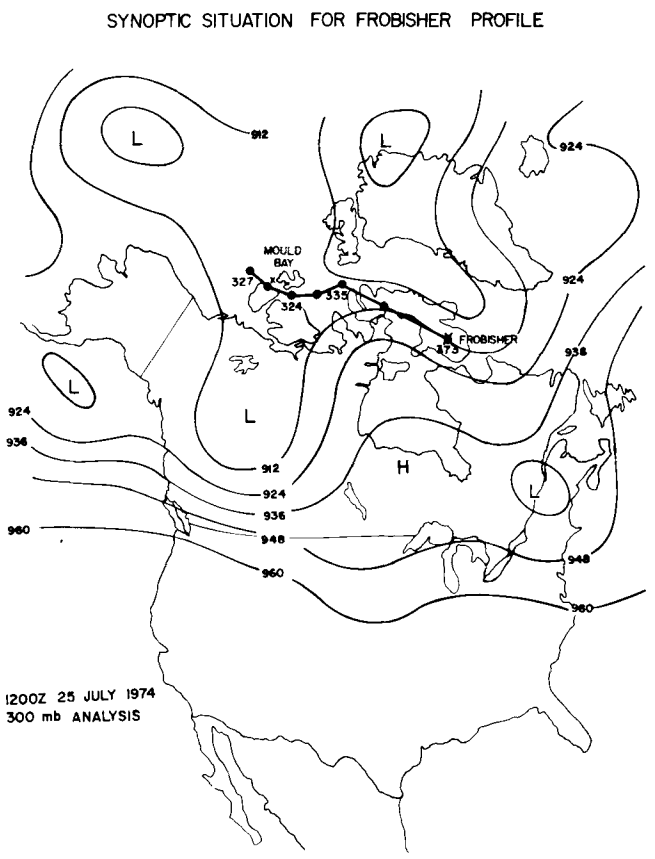

Fig. 5. Synoptic analysis of the 300 mb isobaric surface at 12Z, July 25, 1974 which corresponds closely to the time when the Frobisher vertical profiles were constructed. Superimposed on this analysis is the isentropic trajectory calculated for a θ-level of 314 K which is depicted by the heavy solid line. The circles on this trajectory represent the location of the air at 12-h intervals prior to arrival at Frobisher. The pressure at which the 314 K θ-surface is located is given at 24-h intervals by the numbers beneath the appropriate circle on the trajectory. The location of Mould Bay, Canada is marked by an X.

from these trajectories since none of them seemingly passed over densely populated prior to their being observed.

One possible explanation for the simultaneous presence of enhanced CO and O_3 layers is the in-situ photochemical production of tropospheric ozone by the oxidation of CO and hydrocarbons in the presence of nitric oxide. This hypothesis is consistent with the observations and raises another point about the origin of these bands. It is of particular interest in the Frobisher profile (Fig. 3) that CO concentrations increase dramatically below about 1.5 km whereas the O_3 mixing ratio decreases substantially in this lowest layer. The vertical distribution of these gases in this region of the atmosphere is consistent with the conventional understanding of both the O_3 and CO cycles which suggests that O_3 is destroyed in the boundary layer by destruction at the earth's surface (e.g., Fabian and Junge, 1970; Fabian and Pruchniewicz, 1977) and that nearly all of the sources of CO are located in the boundary layer (Seiler, 1974). Under such constraints, the observed CO bands depicted in these profiles must have originated in the boundary layer. However, the transport of air parcels from the boundary layer to the free troposphere which

Table 2. *Isentropic trajectory calculations for Frobisher*

Date	Time	Latitude	Longitude	Pressure
		$\theta = 298$ K (~3.5 km)		
25 Jul	12 Z	64.0° N	68.0° W	674 mb
25 Jul	00 Z	67.3° N	76.5° W	691 mb
24 Jul	12 Z	71.1° N	79.5° W	685 mb
24 Jul	00 Z	74.0° N	81.6° W	682 mb
23 Jul	12 Z	74.8° N	84.9° W	708 mb
23 Jul	00 Z	75.5° N	78.5° W	713 mb
22 Jul	12 Z	75.6° N	75.6° W	683 mb
		$\theta = 314$ K (~7.6 km)		
25 Jul	12 Z	64.0° N	68.0° W	373 mb
25 Jul	00 Z	71.7° N	78.3° W	427 mb
24 Jul	12 Z	75.3° N	90.6° W	335 mb
24 Jul	00 Z	75.1° N	101.2° W	356 mb
23 Jul	12 Z	75.2° N	110.3° W	324 mb
23 Jul	00 Z	75.4° N	121.7° W	315 mb
22 Jul	12 Z	76.1° N	129.3° W	327 mb

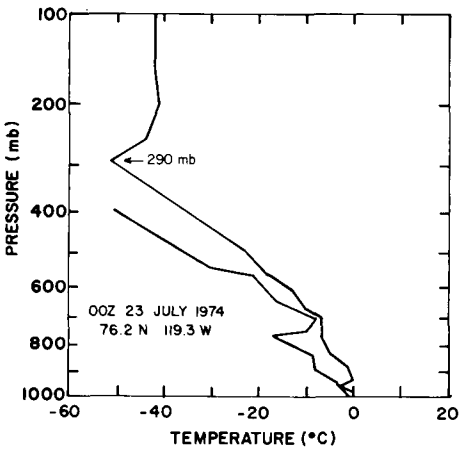

Fig. 6. The temperature and dewpoint soundings over Mould Bay, Canada for 00Z, July 23, 1974.

are identified by relatively higher CO concentrations should have resulted in the concurrent observation of relatively lower concentrations of ozone unless the ozone had been produced either in the free troposphere or in a polluted boundary layer and then subsequently released to the free troposphere along with other pollutants. If the former hypothesis is correct, then the elevated O_3 concentrations measured concurrently with relatively higher CO mixing ratios must define remote ("unpolluted") areas in which in-situ production of ozone is occurring. In either case, it is quite likely that the elevated CO concentrations are also serving as tracers of enriched layers of hydrocarbons and NO_x which likewise have their origins in the boundary layer. Unfortunately, no concurrent measurements of the other trace gases are available.

5. Conclusion

We have presented two sets of vertical profiles which show the simultaneous presence of well-defined laminae of O_3 and CO in the free troposphere. Although the appearance of ozone bands in the troposphere has been reported previously (Danielsen, 1968; Danielsen and Mohnen, 1977), these data represent the first time that concurrent observations of CO using an instrument with a comparable response time has been reported. The fact that CO and O_3 concentrations both increased in these bands suggests that the air could not have originated in the stratosphere. This finding is substantiated by isentropic trajectory calculations which likewise indicate that the air in which the anomalously high O_3 and CO concentrations were located could not have descended recently from the stratosphere.

One explanation which is quite consistent with the findings presented in this paper is that the "tropospheric" ozone observed in these bands was produced in situ. Thus, the elevated CO concentrations measured concurrently may be indicative of air which may also contain enhanced concentrations of hydrocarbons and NO_x which provide a favorable environment for photochemical production of ozone. Another possible explanation is that both the CO and O_3 were produced in the boundary layer and then injected into the free troposphere by some dynamic process such as convection.

Either mechanism is likewise consistent with the observations and theoretical calculations which support the existence of a significant in-situ production mechanism of tropospheric ozone (Crutzen, 1972, 1973; Fishman and Crutzen, 1978; Fishman et al., 1979). Although many more

concurrent observations of ozone, CO, NO_x and hydrocarbons are necessary before the relative importance of the in-situ source of tropospheric ozone can be properly assessed, the data presented in this paper indicate directly for the first time that such a production mechanism probably exists and demonstrates that some of the ozone observed in the remote troposphere does not originate in the stratosphere.

6. Acknowledgements

This work was initiated at the Max-Planck-Institute for Chemistry as part of the program of the SFB 73 and was partially funded through the DFG. Additional support for this research has been provided through EPA Grant 804-921-03 to Colorado State University. The authors would like to acknowledge the helpful and critical discussions with Dr Paul Crutzen of NCAR.

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ОДНОВРЕМЕННОЕ ПРИСУТСТВИЕ ПОЛОС O_3 И CO В ТРОПОСФЕРЕ

По данным ряда полетов, проведенных в июле и августе 1974 года над континентами Америки между 53° ю.ш. и 67° с.ш., были построены вертикальные профили CO и O_3 в тропосфере. Отношение смеси для обоих газов в Северном полушарии проявляет большие флуктуации с высотой. Большинство наблюдаемых полос O_3 в свободной тропосфере существует вместе с повышенными концентрациями CO, указывая на то, что этот озон вероятно не стратосферного происхождения, но может образовываться на месте фотохимическими процессами в незагрязненной тропосфере. Расчеты изэнтропических траекторий также указывают, что воздух, содержащий эти повышенные концентрации O_3 и CO, находился в тропосфере не менее 72 часов до момента забора проб.