1) Overland flow is a negligible fraction of total runoff and is transient and discontinuous (*13*). Subsurface flow is in intimate contact with the soil, and phosphorus is immobilized in the soil. This process has been confirmed for a number of chemical elements in laboratory column experiments with Minnesota forest soils (*14*).

2) Large portions of both watershed areas are lake surfaces (33 percent for Dogfish Lake and 21 percent for Meander Lake). Thus, inputs to the lakes from runoff are considerably diluted by precipitation falling directly on the lake surfaces.

3) Input stream waters are also diluted by the relatively large volume of lake water (for example, in the unburned area over the study period, the mean phosphorus concentrations of the input stream and lake were 26 and 14 parts per billion, respectively).

4) The fire occurred in early spring and vegetative regeneration was vigorous immediately after it [in one area just 5 months after the fire 190,270 new aspen suckers and 5,830 aspen seedlings per hectare were recorded (*15*)]. The prolific vegetative growth used some phosphorus released by burning and thus reduced losses to the aquatic environment.

Although our results are favorable for implementation of controlled burning in the study area, we stress that they should be used with caution. The Little Sioux wildfire occurred in early spring, just before the last snowfall, before new vegetative growth had begun, and when the forest floor was still cool and moist. The topography of the study area is not steep and practically no erosion occurred following the fire. The burned litter had no noticeable hydrophobic effects that might have inhibited water infiltration into the soil. A fire in summer or early fall might burn more intensely, exposing mineral soil to erosion and preventing recycling by vegetative uptake. The latter type of fire, or a fire in a large watershed with a small lake, might have detectable limnological effects. The effects of a forest fire on recycling processes differ with time of burning, topography, vegetative cover, soil type, relative size of the watershed and lake, and climate. Further studies are required to elucidate the relative importance of such factors, so that forest management policies involving fire can be wisely made and safely implemented.

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Stratospheric Nitric Oxide: Measurements during Daytime and Sunset

Abstract. *Measurements of the temporal variation in the stratospheric nitric oxide concentration covering a time period from 11:00 to 20:30 local time show the effect of solar ultraviolet sunset. The experimental results strongly support the theorized role of nitric oxide as a catalyst in the destruction of ozone and its importance in the stratospheric ozone balance.*

The importance of NO as a catalyst in the stratospheric O_3 balance has been discussed by several authors (*1*). Measurements of stratospheric NO concentrations to validate the conclusions of these theoretical models are difficult because of its rather low concentration. In addition, to make a proper comparison between theory and the experimental measurements, it is important to have the NO measurements as a function of solar elevation. It is known that NO enters into the stratospheric O_3 balance through the interaction of atomic oxygen and of the solar ultraviolet (UV) radiation with NO_2 via the following processes:

$$NO_2 + O \rightarrow NO + O_2 \quad (1)$$

$$NO_2 \xrightarrow{h\nu} NO + O \quad (2)$$

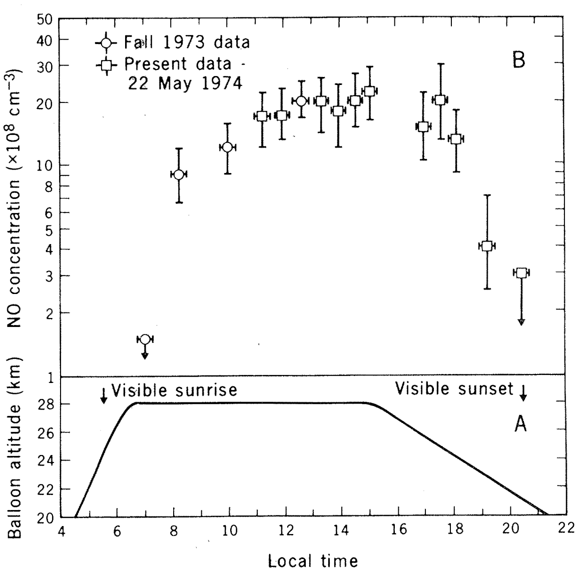
and

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (3)$$

where $h\nu$ is a photon. The reactions described in Eqs. 1 and 2 lead to the generation of NO when the solar UV radiation acts on the constituents of the stratosphere, whereas the reaction in Eq. 3 acts to remove the NO. Thus time-dependent measurements of NO (or NO_2) can provide a very important check of the models of the stratospheric O_3 balance in which the nitrogen oxides are considered to be effective catalysts for the destruction of O_3.

In our earlier report we described measurements of stratospheric NO, using the technique of opto-acoustic (OA) spectroscopy with a tunable spin-flip Raman (SFR) laser (*2*). Measurements were carried out during a balloon flight on 19 October 1973 from Palestine, Texas, and the measurements lasted from about 7:00 to 14:00 hours local time. This gave us the variation in the NO concentration from just before the sunrise till early afternoon. These experiments were terminated at 14:00 local time because of a battery failure. The measured noontime NO concentration of 2×10^9 molecule cm^{-3} at an altitude of 28 km is in reasonable agreement with the recent spectroscopic measurements of NO in which the sun was used as the source of blackbody radiation (*3*). Reasonable agreement also exists between the maximum NO concentration measured by us and that obtained recently by chemiluminescence measurement techniques (*4*) at lower altitudes. Our in situ measurement technique, however, has the singular advantage of making possible NO measurements regardless of the solar elevation. Thus our measurement technique is particularly well suited for the exploration of the diurnal variation in the kinetics of the NO in the stratosphere. The measurements from our first balloon flight (which was carried out in close collaboration with Sandia Laboratories) gave us the predawn, sunrise, and midmorning data on the NO concentration at 28 km. These measurements confirmed the importance of the reactions described in Eqs. 1 and 2. How-

Fig. 1. (A) Flight altitude as a function of time for the 22 May 1974 balloon flight from Holloman Air Force Base, New Mexico. (B) Concentration of NO as a function of time. Data from the present flight, covering a period from 11:00 to 20:30 M.S.T. (17:00 to 02:30 U.T.), are shown as squares. Data points from the earlier flight (*2*) are shown as circles and cover the sunrise period which was not accessed in the present flight. It is not possible to make a one-to-one comparison between the two sets of data because of differences in the time of the year (as well as differences in the geographical location of the balloon) when the two flights took place (see text).



ever, the early termination of that flight prevented collection of afternoon and sunset data and a complete investigation of the NO catalytic cycle described in Eqs. 1 through 3.

We report here measurements of the NO concentration which span a time frame from 11:00 to 20:30 local time. These data, together with the results of our first balloon flight (*2*), constitute the first measurements of temporal variation in the NO concentration in the stratosphere at an altitude of 28 km through a complete sunrise-to-sunset cycle. The measurements presented here were carried out during a balloon flight from Holloman Air Force Base, New Mexico, during the spring wind reversal in 1974 (in collaboration with Sandia Laboratories, Albuquerque, New Mexico; Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico; and the Air Force Cambridge Research Laboratory, Hanscom Air Force Base, Bedford, Massachusetts). The experimental apparatus, described in (*2*), was modified slightly for the present flight by the replacement of the long-path absorption cell with a CO_2 laser used for the detection of O_3. Other aspects of the NO measurement setup, that is, the SFR laser and the OA cell, remained unchanged. General experimental techniques for NO measurements are described in (*2*) and will not be repeated here.

The balloon was launched at 02:20 local time (08:20 U.T.) on 22 May 1974. As seen from the balloon flight profile shown in Fig. 1A, the flight altitude of $\sim$27 km was not reached until 06:45 local time. However, good NO measurements did not begin until 11:00 local time (M.S.T.) because of experimental problems (primarily electrical interference arising from another experiment, unrelated to the NO measurement apparatus, also carried on the same balloon payload). Subsequent to the determination of the problem, the NO measurements and the interfering experiments were carried out alternately to avoid electronic interference. The visible sunrise occurred at 05:37 M.S.T. (at the balloon altitude of $\sim$24.5 km), and the UV sunrise occurred at 06:00 to 07:30 M.S.T., depending upon the UV wavelength (*5*). From 11:00 M.S.T. on, the NO measurements continued until 20:30 M.S.T. The visible sunset at $\sim$21.5 km (balloon altitude at that time) occurred at 20:34 M.S.T., and the UV sunset occurred at $\sim$18:00 to 19:00 M.S.T. at the corresponding flight altitude (*5*). During its entire flight, the balloon stayed within about 75 km of the launch site at Holloman Air Force Base, and was visible throughout the daylight hours.

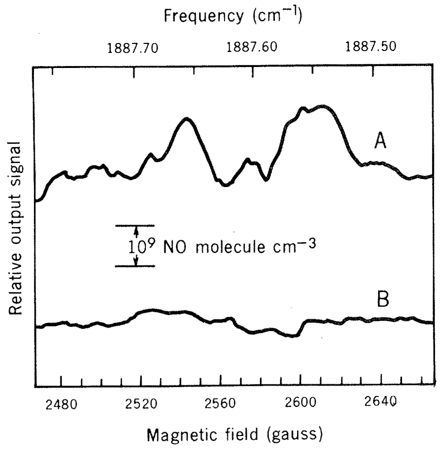


Fig. 2. Relative output signals from the OA cell as a function of the magnetic field which determines the SFR laser frequency. The NO absorption signals are expected to occur at 2545 and 2605 gauss. The concentration scale for NO in molecules per cubic centimeter is as shown: (A) NO run 1 taken between 11:00 and 11:28 M.S.T. (17:00 to 17:28 U.T.) at an altitude of $\sim$28.0 km. Balloon local temperature was $\sim$225°K. (B) NO run 13 taken between 20:13 and 20:40 M.S.T. (02:13 to 02:40 U.T.) at an altitude of $\sim$21.3 km.

The NO absorption lines used for OA spectroscopy with the SFR laser are the $\Omega = 3/2$, $m = 3.5$ and the $\Omega = 1/2$, $m = 3.5$ transitions of the $\nu = 0$ to $\nu = 1$ vibrational-rotational band at 1887.63 cm^{-1} and 1887.55 cm^{-1}, respectively [see table 1 of (*2*) for details]. In all, 16 NO runs were taken of which five were found to be difficult to analyze because of noise problems associated with the telemetry of the data from the balloon to ground. The remaining 11 runs have been analyzed. The NO absorption spectra for two of these runs are seen in Fig. 2, A and B, which show voltage output from the OA cell (which is proportional to the amount of the infrared energy absorbed in the OA cell) as a function of the magnetic field which determines the frequency of the SFR laser output. The two NO absorption lines at 1887.63 cm^{-1} and 1887.55 cm^{-1} are expected to occur (*2*) at magnetic field values of $\sim$2545 and $\sim$2605 gauss, respectively (*6*). Figure 2A shows the spectrum taken between 11:00 and 11:28 M.S.T. The two NO absorption lines are clearly seen. The calibration NO concentration scale is shown in Fig. 2, which gives a NO concentration of $(17 \pm 5)\times10^8$ molecule cm^{-3}. Figure 2B shows a similar trace, without any change in the detection sensitivity, taken between 20:13 and 20:40 M.S.T., well past the expected UV sunset at the balloon altitude of $\sim$21.3 km. No significant absorption peaks which can be correlated with the NO absorption lines, expected at 2545 and 2605 gauss are seen, leading us to infer a NO concentration of $<3\times10^8$ molecule cm^{-3}. [See (*2*) for unequivocal identification of NO absorption lines.] The disappearance of NO at sunset is thus ascertained.

In comparison with the quality of data obtained from the first flight (*2*), the data in Fig. 2, A and B, are somewhat noisier. This is so in spite of the fact that the on-ground preflight tests showed an improvement in the NO detection capability of our apparatus over that used for the first flight. This increased noise problem was found to be associated with the malfunction/interference problem alluded to earlier.

The data for all the NO runs are summarized in Fig. 1B where we plot the measured NO concentration at the flight altitude as a function of time. Figure 1B also shows four data points from the first balloon flight (all of which were taken at an altitude of 28 km) for completeness and comparison. It would be improper to compare the data from the two balloon flights on a one-to-one basis for the temporal variation of NO concentration because of the different time of year when the two flights were carried out and, to some extent, because of the different geographical regions where the measurements were made. However, for the overlapping time when the NO measurements are available from the two flights it can be seen that the measured NO concentrations from the two flights are within the experimental error bars shown. More precise comparisons with respect to the exact local visible and UV sunrise will be published elsewhere (*7*).

We see from Fig. 1B that the maximum measured NO concentration occurred at ~15:00 M.S.T. (21:00 U.T.) and was $(22 \pm 6) \times 10^8$ molecule cm^{-3}. The slow rise of the NO concentration from ~11:00 to ~14:00 local time seen for the first balloon flight of fall 1973 is confirmed by the similar data from the second set of measurements. This slow rise is explained in terms of a slow dissociation of N_2O_5 and is not unexpected (*8*). A more dramatic event in the measured NO concentration is seen to occur at times starting ~18:00 M.S.T. (00:00 U.T.). Within a time period of about 1.5 hours, the NO concentration dropped from $\sim 20 \times 10^8$ to $< 3 \times 10^8$ molecule cm^{-3}. This drop is associated with the reduction in the solar UV radiation reaching the environs of the balloon because the solar radiation traverses longer and longer paths as the sun is setting. This reduction in solar UV radiation diminishes the NO production rate as seen from the reactions described in Eqs. 1 and 2. The recombination of NO with O_3 described in Eq. 3 is expected to remove the NO with a time constant of the order of 100 to 1000 seconds for generally accepted rate constants and an O_3 concentration of $\sim 10^{12}$ molecule cm^{-3}. With the sun completely set and all the solar UV radiation gone, all the NO is converted into NO_2 as is seen from Figs. 1B and 2B. The measured concentration of stratospheric NO and its remarkable temporal variation is the first direct confirmation of the importance of the dynamic NO catalytic cycle in the stratospheric O_3 balance.

A further objective of the present balloon flight was to attempt to obtain similar data at a lower altitude next morning, thus adding a set of data in the vertical profiling of the NO concentration temporal variation. However, as seen in Fig. 1A, the balloon and payload rapidly lost altitude after sunset. It was not possible to hold the altitude beyond midnight, and the mission for the next day was aborted at 02:30 M.S.T. It is, however, clear that further future flights of the experiment with improved balloon altitude control will allow us to obtain much needed data on the stratospheric chemistry. The intrinsic spectroscopic nature of the technique should allow measurements of a variety of gaseous species of interest by the proper choice of a tunable laser.

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6. The magnetic field values in Fig. 2, A and B, are accurate; the frequency scale is approximate and is shown only for reference. The positions of the NO absorption lines at 2545 and 2605 gauss have been precisely determined (in the laboratory) for the particular SFR laser used in these experiments.
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Photochemical Smog Systems: Effect of Dilution on Ozone Formation

Abstract. *Dilution of a photochemical system containing hydrocarbons and oxides of nitrogen can lead to higher ozone concentrations than are observed in a static system. This effect was observed in an outdoor smog chamber with a hydrocarbon mix simulating urban systems.*

When studying urban photochemical smog systems with the use of chamber simulations, most researchers assume the worst case condition for O_3 production to be a system that is closed and static. This is not necessarily true under all conditions. Work described in this report shows that under some conditions a dynamically diluting system is capable of forming more O_3 than the static system, when each is charged with the same initial concentration of hydrocarbon and oxides of nitrogen ($NO_x = NO + NO_2$). This report shows the necessity of considering dilution, hydrocarbon reactivity, and diurnal solar radiation in photochemical smog reactions.

For the past 2 years the University of North Carolina has been operating a large dual-compartment (156 m^3 per side) outdoor smog chamber to investigate the effect of hydrocarbon control on afternoon concentrations of NO_2 and O_3. It was originally thought that the worst urban smog conditions could best be simulated in the outdoor chamber by a closed static system. This would represent an extremely stagnant air mass which could result in the maximum buildup of air pollutants over a city.

In order to evaluate this hypothesis, experiments were designed such that the same initial concentrations of nonmethane hydrocarbons (NMHC) and NO_x were introduced into both halves of the outdoor chamber. One side remained sealed off from the ambient atmosphere and was operated in the normal static mode, whereas the other side was slowly diluted with rural background air at a given time in the morning. The dilution air was not scrubbed to remove ambient hydrocarbons or oxides of nitrogen. At this location, background air has contained less than 0.02 part per million (ppm) of NO_x and has exhibited low reactivity (NO oxidation rate $\approx$ 0.2 part per billion per minute). The chamber halves have been labeled "red" and "blue" to help distinguish between the pollutant profiles graphically illustrated in Figs. 1 and 2. We discuss here two different dilution/static smog systems: (i) a reactive hydrocarbon-NO_x system (fast) with propylene as the hydrocarbon; dilution rate, 5.7 percent per hour (Fig. 1): and (ii) a less reactive hydrocarbon-NO_x system (slow) with urban mix as the hydrocarbon; dilution rate, 9.5 percent per hour (Fig. 2).

Let us consider first the reactive system. Both chamber sides have identical reactant profiles until 07:05 (Fig. 1), when dilution begins in the blue side. Propylene, NO_2, and NO are then slowly removed from the blue chamber by the dilution system. At the same time, however, NO_2 is being gen-