at 15 g per liter. The medium was autoclaved again before use.

6. In the photosynthesis experiments, 0.2 ml (1.0 μCi) of radioactively labeled bicarbonate in 0.05*M* tris-HCl was dropped on the rock chip in a 2-ounce bottle. The bottles were closed with Bakelite screw caps. Dark controls were covered with aluminum foil. Lichens collected from the same vicinity were used for positive controls. Samples were exposed to ambient light for 24 hours and then fixed with Lugol's iodine. When they were returned to the laboratory the rock chips were washed in 1*N* HCl, then soaked in tap water for 30 minutes and rinsed with tap water several times to remove unassociated label. The chips were then transferred to scintillation vials with Aquasol (New England Nuclear) scintillation fluid and counted (Beckman LS-230 counter). For respiration experiments, 0.5 ml of sodium acetate (0.5 μCi) was added to each rock chip placed in a 16-ounce bottle which also contained a vial with 2 ml of 0.1*N* sodium hydroxide. Control specimens were fixed with Lugol's iodine. After 24 hours, the experimental rocks were fixed with Lugol's iodine, and the base was removed for scintillation counting in Aquasol. Control values for respiration averaged 14,436 count/min, whereas experimental values were 191,995 count/min.
7. For autoradiography, microcolonies were individually picked from rocks used in the labeling experiments. These were mounted on glass slides with gelatin. Medical x-ray film (GAFMED SR-2) was fastened to the slide surface so that the microcolonies were in direct contact with the emulsion. Controls included lichens for the photosynthesis experiments and the fixed specimens for the respiration experiments. The film was exposed for 14 days before development.
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Nitrogen Oxide Reactions in the Urban Plume of Boston

Abstract. *The rate of removal or conversion of nitrogen oxides has been determined from airborne measurements in the urban plume of Boston. The average pseudo–first-order rate constant for removal was 0.18 per hour, with a range of 0.14 to 0.24 per hour under daylight conditions for four study days. The removal process is dominated by chemical conversion to nitric acid and organic nitrates. The removal rate suggests an atmospheric lifetime for nitrogen oxides of about 5 to 6 hours in urban air.*

The nitrogen oxides, NO_x (*1*), play a pivotal role in the chemistry of the atmosphere. In the upper troposphere, NO_x may be the major source of O_3 (*2*). In polluted atmospheres, NO_x are precursors to O_3 and other manifestations of photochemical smog. The major products of NO_x reactions are inorganic and organic nitrates, principally nitric acid (HNO_3), peroxyacetyl nitrate (PAN), and particulate nitrate (NO_3^-) (*3*). The effects of PAN on vegetation and human health are well documented (*4*), and the role of HNO_3 in precipitation chemistry has been the focus of much attention recently (*5*). The behavior and effects of particulate NO_3^- in the atmosphere are not well understood at this time.

In earlier studies our group investigated the nitrogen balance and the distribution of NO_x reaction products in several urban atmospheres (*3*, *6*) and in smog chamber simulations (*7*). Using inert tracer data and our measurements of the oxidized nitrogen (all the oxides of nitrogen) distribution in the Los Angeles area, Chang *et al.* (*8*) derived a value of 0.04 hour^{-1} as a lower limit for the yearly average NO_x removal rate during daylight hours. They calculated an average NO_x residence time of 2.1 days or less. Calvert (*9*) used tracer and NO_x measurements from the Los Angeles Reactive Pollutant Program to estimate the NO_x removal rate at approximately 0.09 hour^{-1} during the midmorning to early afternoon. Since the major reaction products PAN and HNO_3 interfere with the NO_x measurement technique used in that program, this value represents only a portion of the true removal rate. During an airborne study of the Phoenix urban plume (*10*), we observed an NO_x upper-limit removal rate of 0.05 hour^{-1}. This rate is lower than one would expect from computer modeling and smog chamber simulations. A computer model of the kinetics of polluted atmospheres (*11*) suggests an NO_x removal rate of 0.10 to 0.12 hour^{-1} for the conditions of our Los Angeles and Phoenix studies. Smog chamber experiments suggest a removal rate of 0.2 to 0.4 hour^{-1} when simulated urban air is irradiated at realistic hydrocarbon/NO_x ratios (*7*).

The uncertainty in the NO_x removal rate and the need to study NO_x reactions under conditions other than the hot and dry environments of Los Angeles and Phoenix led to this investigation of the NO_x removal rate in the urban plume of Boston. Boston was selected because of its higher summertime relative humidity and because the prevailing westerly winds frequently carry the Boston urban plume over the ocean, effectively isolating it from the confounding effects of fresh emissions of NO_x and other pollutants. The experiments were performed in a Lagrangian manner (*12*) with the use of an instrumented research aircraft (*13*) with mobile laboratory ground support. The study was conducted between 27 July and 30 August 1978. The goal was to follow the polluted air parcel (0800 to 0900 EDT) from Boston as it reacted during transport downwind. Flight altitude was generally 150 to 300 m above sea level in order to sample the highest pollutant concentrations. The experiments of 14, 18, 23, and 30 August 1978 are the most appropriate for an analysis of NO_x reaction rate and are reported here. As an example of the experiments, the flights of 18 August are shown at the right in Fig. 1. The position of the air parcel leaving Boston at 0800 EDT is shown for each hour to 1600 EDT. Three flights, 20 through 22, were conducted during this day. The sample collection intervals used in data analysis are shown as solid lines. These specific locations were chosen after initial "scouting" traverses through the plume because they

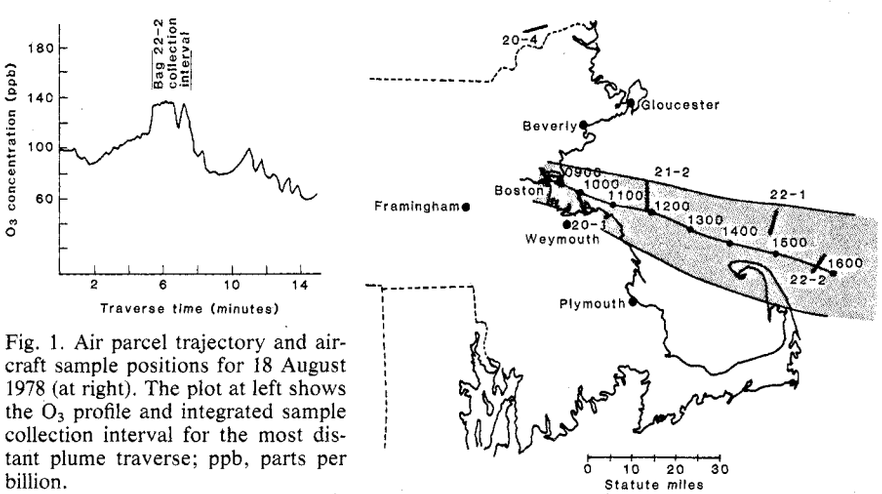

Fig. 1. Air parcel trajectory and aircraft sample positions for 18 August 1978 (at right). The plot at left shows the O_3 profile and integrated sample collection interval for the most distant plume traverse; ppb, parts per billion.

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Table 1. Summary of NO_x removal rates; ppm, parts per million.

Date (1978)	k_r ($hour^{-1}$)	Reaction time (hours)	Maximum downwind distance (km)	Peak $[O_3]$ (ppm)
14 August	0.20	3.0	83	0.189
18 August	0.24	7.0	122	0.129
23 August	0.15	8.0	142	0.154
30 August	0.14	5.5	95	0.101

yielded the highest concentrations of pollutants and tracers, thereby minimizing analytical imprecision. The O_3 profile during a complete traverse through the urban plume is shown at the left in Fig. 1. The interval over which the integrated sample 22-2 was collected is noted. Many samples were obtained during each of the three flights, but only those samples that matched the time and position of the selected air parcel are shown. Further details of the experimental protocol have been presented elsewhere (*14*).

The change in NO_x concentration during transport is dominated by dilution. In order to account for the effects of dilution, we use in situ tracers, that is, gases present in the urban air that are inert over the time scale of the experiment. For this study we used CO, C_2H_2 and CCl_3F (fluorocarbon-11) as dilution tracers. The strategy is to determine the ratio of NO_x to an inert tracer just downwind of the city before significant conversion or removal of NO_x has occurred. One can then use the measured downwind tracer concentrations to calculate the expected NO_x concentration, $[NO_x]_e$, at a given downwind distance by multiplication with the initial NO_x/tracer ratio. The tracer and NO_x concentrations must be corrected for background levels that are present in the plume dilution air. Therefore, background samples were collected upwind of the urban area or outside the urban plume. Plots of the logarithm of the ratio of expected NO_x to measured NO_x versus reaction time yield straight lines for each of the four study days, confirming that the reactions are first order in NO_x (*15*).

Least-squares straight lines with zero intercept (*16*) have been fitted to the data. The slopes of these lines yield pseudo–first order rate constants for NO_x removal, referred to in common usage as the removal rate, k_r. These removal rates are listed in Table 1, together with reaction time, maximum downwind distance, and peak O_3 concentration in the plume. By averaging the four daily rates or by fitting a single line to the entire data set, we obtain an overall daylight rate for NO_x removal of 0.18 $hour^{-1}$. Such a rate yields an NO_x lifetime ($1/e$) of 5.5 hours, with a range, based on the daily data, of 4.2 to 7.1 hours.

The NO_x removal rates reported here include both chemical conversion to products and physical removal processes. One can calculate a chemical conversion rate independent of the inert tracer measurements using F_n, the ratio of NO_x reaction products to total oxidized nitrogen (*17*). Losses due to deposition will lower the conversion rate estimate, but the species most likely to be deposited appear in both the numerator and denominator of the ratio so the effect should not be great, and we expect the lower-limit conversion rate estimate to be a reasonable approximation of the true conversion rate. The most accurate reaction product data were obtained on 18 August 1978 (*18*). The semilogarithmic plot of F_n versus reaction time yields a straight line whose slope provides a conversion rate estimate of 0.23 $hour^{-1}$. This is in excellent agreement with the overall NO_x loss rate on 18 August 1978 of 0.24 $hour^{-1}$.

I believe that the results reported here represent the most accurate determination of NO_x removal rate and lifetime in urban air. The reported rates are applicable to sunny, moderately polluted urban air. These results should be verified and extended by further studies under a variety of environmental conditions. The results from such experiments will permit the parameterization of the NO_x removal rate for inclusion in air quality models (*19*).

The NO_x removal rate and lifetime values should find widespread application in modeling polluted atmospheres and in attempting to unravel the complexities of precipitation acidity. As an example of this latter application, these results make it clear that NO_x is converted to products much more rapidly than SO_2, and so the area of effects due to acid deposition will be more localized for NO_x than for SO_2 (*20*).

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References and Notes

1. In this report NO_x is defined as NO + NO_2.
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10. C. W. Spicer, in *Atmospheric Pollution 1980*, M. M. Benarie, Ed. (Elsevier, New York, 1980), pp. 181–186.
11. I used a modified version of the mechanism described by D. F. Miller, A. J. Alkezweeny, J. M. Hales, and R. N. Lee [*Science* **202**, 1186 (1978)].
12. For most study days a specific air parcel, usually the air mass of 0800 to 0900 EDT, was sampled just downwind of the city at midmorning and then periodically during the day by successively farther downwind flights. Hourly meteorological data from several eastern Massachusetts stations were obtained by telephone several times each day. These data were used to construct working trajectories of the selected air parcel in order to vector the aircraft to the appropriate area. The plane then bracketed the predicted air parcel position with sampling traverses. For each sample, a "scouting" traverse located the maximum plume pollutant concentrations, and the integrated samples were collected in this area on the return traverse. At the conclusion of the field experiments, a more detailed trajectory analysis, based on wind data from ten eastern Massachusetts and Cape Cod weather stations, was undertaken. The more accurate air parcel positions resulting from this analysis were used to select the plume traverses that most closely matched the time and location of the specified air parcel.
13. A twin-engine Cessna 411 aircraft was used in these experiments. Two 100-A, 28-V d-c alternators connected to a 1-kVA power inverter supplied the electrical needs of the monitoring instruments and data acquisition system; d-c power was used to operate an aerosol sampler at a flow rate of 0.3 m^3 min^{-1}. Collections were on high-purity quartz filters; analysis for NO_3^- and SO_4^{2-} was done by ion chromatography (D-ION-X 10). Continuous measurements were made of the following: O_3 (Dasibi 1003AAS ultraviolet photometer), NO_x (Monitor Labs 8440HP chemiluminescence analyzer); HNO_3 [modified Monitor Labs 8440 HP, see D. W. Joseph and C. W. Spicer, *Anal. Chem.* **50**, 1400 (1978)]; condensation nuclei (Environment One); temperature (Metrodata M8 shielded thermistor); and dew point (Cambridge Systems hygrometer 137-C3). Integrated gas samples were collected in Tedlar bags and analyzed at our mobile laboratory at Beverly, Mass., airport for PAN and fluorocarbon-11 (Varian 1200 electron-capture gas chromatographs); C_2 to C_5 hydrocarbons (cryogenic preconcentration with Varian 3700 flame-ionization-detector gas chromatograph); and CH_4, CO, and total nonmethane hydrocarbons (Beckman 6800 flame-ionization-detector gas chromatograph). Continuous data were acquired on magnetic-tape and strip-chart recorders; these data were then averaged over the integrated sample (Tedlar bag) collection times. Supporting measurements made at the mobile laboratory include all the variables listed above, as well as wind speed and direction (MRI 1074-2), radiation intensity (Eppley Labs 180° pyrheliometer), SO_2 (Meloy 285 SA flame photometer), total suspended particulates (high-volume sampling on quartz filters), NH_4^+ (analysis of quartz filters by NH_3 gas–sensing electrode), and light-scattering aerosol (MRI integrating nephelometer).
14. C. W. Spicer, J. R. Koetz, G. W. Keigley, G. M. Sverdrup, G. F. Ward, "A study of nitrogen oxide reactions within urban plumes transported over the ocean" (Battelle Columbus final report

to the Environmental Protection Agency on contract 68-02-2957, Environmental Protection Agency, Research Triangle Park, N.C., June 1981).

15. The plots may be found in (*14*). Some curvature in the lines is expected during the early portion of the reaction as NO is converted to NO_2, with little net loss of NO_x. Since our measurements were initiated after this conversion was largely complete, the potential curvature was not observed on most days.
16. The intercept is forced to zero by our definition that $[NO_x]_e = [NO_x]$ measured at time $t = 0$.
17. $$F_n = \frac{HNO_3 + PAN + NO_3^-}{NO + NO_2 + HNO_3 + PAN + NO_3^-}$$
18. For these flights, the total NO_3^- concentration in the plume ranged from 0.005 to 0.015 part per billion, with the higher values occurring at the longer irradiation times. The ratio of gaseous NO_3^- to total NO_3^- was greater than 0.95.
19. Such a parameterization for SO_2 conversion in power plant plumes has been reported by N. V. Gillani and W. E. Wilson, Jr., *Atmos. Environ.*, in press.
20. The results of further studies of the NO_x conversion rate, the reaction product distribution, and the influence of NO_x reactions on precipitation acidity will be reported elsewhere (C. Spicer, in preparation).
21. I am indebted to G. Sverdrup, G. Ward, J. Koetz, and W. Keigley for their assistance in field operations and data reduction and to R. Hannigan for aircraft operation. This project was sponsored by the Environmental Sciences Research Laboratory of the Environmental Protection Agency under contract 68-02-2957.

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Observations of a Comet on Collision Course with the Sun

Abstract. *A brilliant new comet (1979 XI: Howard-Koomen-Michels) was discovered in data from the Naval Research Laboratory's orbiting SOLWIND coronagraph. An extensive sequence of pictures, telemetered from the P78-1 satellite, shows the coma, accompanied by a bright and well-developed tail, passing through the coronagraph's field of view at a few million kilometers from the sun. Preliminary orbital calculations based on the observed motion of the comet's head and morphology of the tail indicate that this previously unreported object is a sungrazing comet and may be one of the group of Kreutz sungrazers. It appears from the data that the perihelion distance was less than 1 solar radius, so that the cometary nucleus encountered dense regions of the sun's atmosphere, was completely vaporized, and did not reappear after the time of closest approach to the sun. After this time, however, cometary debris, scattered into the ambient solar wind, caused a brightening of the corona over one solar hemisphere and to heliocentric distances of 5 to 10 solar radii.*

Comets are commonly classified, according to the period of their orbital revolution about the sun, into two groups. Short-period comets, distinguished by orbits of moderate eccentricity and small inclination to the ecliptic plane, have periods ranging from a few to about 200 years. Further, their orbits are usually direct (prograde); that is, their orbital angular velocities are directed in the same sense as the angular velocities of the planets. Long-period comets, with periods ranging up to millions of years, have trajectories oriented arbitrarily with respect to the ecliptic and with equal probability of being direct or retrograde. Their orbits are characterized by large eccentricity ($\epsilon \approx 1$) and indeed are often more conveniently described as parabolas than as ellipses. A remarkable subset of the long-period comets is the group of sungrazers, associated with the name of the 19th-century astronomer H. Kreutz, who analyzed the apparition in 1882 of a spectacular member of this group and reviewed the data on a number of other suspected members (*1–3*). This cometary group, which has been studied in recent times by Marsden (*4*), is marked by perihelion distances of 1 to 2 solar radii (1 $R_\odot$ = 696,000 km), and probably owes its origin to fragmentation of some earlier protocomet, whose nucleus may have fractured under the stresses of a near encounter with the sun. A prominent recent member of the group was the well-observed comet Ikeya-Seki (1965 VIII).

It is a frustrating characteristic of the Kreutz sungrazers that their common orbital path is oriented with respect to the solar system in such a way that they are difficult to observe from the earth, particularly if perihelion passage occurs during the months from May to August. At that time the comet, viewed from the earth, appears to approach the sun from behind at small angular separation and to recede in nearly the same direction (*4*). Thus, only members bright enough to be observed in twilit skies are seen. Furthermore, in several instances a comet was discovered only because a total solar eclipse occurred at a time nearly coincident with the comet's perihelion passage. The question has been raised, therefore, whether the total number of comets in sungrazing orbits far exceeds the number observed.

Background. We report here the discovery of a new comet (*5*) under circumstances closely akin to a solar eclipse, namely in data collected by the SOLWIND orbiting coronagraph, designed and built by the Naval Research Laboratory and operating aboard the U.S. Air Force Space Test Program's P78-1 satellite.

The SOLWIND coronagraph (*6*) is a small video telescope designed to monitor activity in the sun's white light corona in the annular region between 2.5 and 10 $R_\odot$. To do this it employs an external occulting disk held by a post 0.76 m in front of the objective lens of a Lyot coronagraph, after the technique originated by Koomen *et al.* (*7, 8*). The occulter artificially eclipses the sun, preventing the blinding direct light of the sun's photosphere from reaching the focal plane, or even the objective lens. This permits recording of coronal forms with typically about 10^{-9} times the photospheric brightness. The occulter further provides a radially varying vignetting function with transmission gradient adequate to allow single-exposure imaging of the corona even though the coronal brightness varies by an order of magnitude in the range 2.5 to 10 $R_\odot$. The images are recorded by a digitally scanned secondary electron conduction (SEC) vidicon during a 2.5-second exposure, then read out into the satellite telemetry system for storage in onboard tape recorders and subsequent transmission during passage over a ground station. The satellite is in a 97-minute polar orbit, synchronized into the noon-midnight plane. In normal operation, SOLWIND records a full-frame coronal image every 10 minutes during the sunlit portion of each orbital revolution, then turns off automatically during satellite nighttime, resuming operation at the next orbital dawn. Data gaps of several hours occur when duty cycling with other instruments is necessary.

Observations. The observations were made on 30 and 31 August 1979, but they have only recently become available for analysis owing to delays in release of the data tapes to experimenters. Three images of the solar corona as it appeared at that time (Fig. 1) illustrate the salient characteristics of the data. The coronal image is recorded as a matrix of 256 by 256 picture elements (pixels), each digitized to 8 bits. Pixels are spaced on 1.25-arc-minute centers. Figure 1a shows the typical appearance of the corona at this solar maximum period. Streamers are seen in every quadrant, even near the poles. The most striking feature of Fig. 1b is that the comet's image has completely saturated the display photograph (although the vidicon was not saturated). The comet's head, first observed at 1856 UT near 6 $R_\odot$ elongation from the sun, is brighter than any coronal form we have seen in data examined thus far, after more than 2½ years of operation. Pre-

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