Reports

Ozone Concentrations in New Jersey and New York: Statistical Association with Related Variables

Abstract. *The concentrations of ozone at nine measurement sites in New Jersey and New York during the period 1 May through 30 September 1973 have been examined. Daily fluctuations in the ozone concentrations at any two sites are highly correlated. The concentrations are lower with low levels of solar radiation and also with high wind speed. The average ozone concentration shows only minor differences between weekdays and weekends, despite markedly different traffic patterns.*

Ozone is an important product of photochemistry in urban atmospheres. Much of what we know about its ambient concentrations is derived from measurements in the Los Angeles Basin (*1*). Since the emission ratios of many pollutants in the New Jersey–New York metropolitan region differ substantially from those in Los Angeles (*2*), and since the federal O_3 standard of 80 parts per billion (ppb) for the hourly mean is often exceeded in the New Jersey–New York area, it is important that the nature of O_3 production in this northeastern region be studied in detail. The results presented here represent a portion of the information which has been derived from a broadly based statistical and chemical study of the New Jersey–New York atmosphere. These results focus on the initial question of the general characteristics of ambient O_3 concentrations within this region.

The distributions of the daily maxima of hourly mean O_3 concentrations from 11 a.m. to 6 p.m. from nine sites in New Jersey and New York in 1973 are summarized in Table 1. [We have also examined data for 1972 (the only other year during which extensive measurements have thus far been made); the characteristics of the 1972 data are similar to those presented here.] Data for the period 1 May through 30 September were used since there is relatively little O_3 produced during the months October through April (*3*). The data were measured by the New Jersey Department of Environmental Protection in Ancora, Bayonne, Camden, and Newark; by the New York State Department of Environmental Conservation in Eisenhower Park, Mamaroneck, and Welfare Island (located in the East River, directly east of the Borough of Manhattan, New York City); by Esso Research and Engineering Company in Linden, New Jersey; and by Boyce Thompson Institute in Yonkers, New York (*4*).

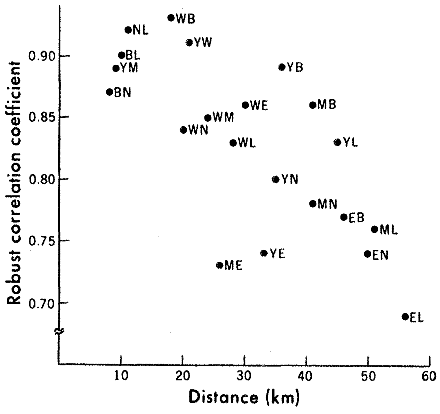

Fig. 1. Correlations between sites of the square roots of the daily maxima in the O_3 concentrations from 11 a.m. to 6 p.m. plotted against the distances between the sites. The two sites involved at a plotted point are coded by two letters: *B*, Bayonne; *E*, Eisenhower Park; *L*, Linden; *M*, Mamaroneck; *N*, Newark; *W*, Welfare Island; and *Y*, Yonkers.

The site with the highest percentage of days exceeding the standard was Ancora, a rural site located 32 km southeast of Philadelphia in a nonindustrial, low-traffic-density area (*5*). The O_3 concentrations at Ancora are quite similar to those at the Bayonne site, which is located in a small park in the midst of a highly industrialized, high-traffic-density area 18 km southwest of midtown Manhattan. The site with the lowest O_3 concentrations is Eisenhower Park, located on Long Island 30 km east of midtown Manhattan. These low values may be due to the incursion of strong sea breezes from the south. The intersite differences in the daily maximum O_3 distributions are considerably less than the intersite differences in the primary pollutant distributions. (Primary pollutants are those emitted directly from sources; secondary pollutants are those formed chemically in the atmosphere.) Proximity to strong sources of primary pollutants does not seem to be an overriding factor in determining O_3 concentrations as it would be, for example, with CO, hydrocarbons, and NO. In Fig. 1 correlation coefficients between sites (*6*) of the square roots (*7*) of the daily maxima are plotted against the corresponding distances between the sites for the seven sites in the New York City metropolitan region. The high correlations are best explained in terms of the regional character of meteorological and solar conditions, which greatly affect the O_3 concentrations. In addition, there is a tendency for the correlation to increase as the distance decreases. This is an indication that local conditions play a role, if not a dominant one, in O_3 production.

We have also studied the relationships between the nature of the diurnal O_3 patterns and wind speed, solar radiation, and day of the week. The results for the Bayonne site from 1 May through 30 September 1973, which are representative of the general results, are presented in Fig. 2. Each "average" diurnal curve in Fig. 2 is the result of calculating the mid-mean (*8*) of the square roots (*7*) of the O_3 measurements for each hour of the day over a subset

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Scoreboard for Reports: In the past few weeks the editors have received an average of 63 Reports per week and have accepted 11 (17 percent). We plan to accept about 10 Reports per week for the next several weeks. In the selection of papers to be published we must deal with several factors: the number of good papers submitted, the number of accepted papers that have not yet been published, the balance of subjects, and length of individual papers.

Authors of Reports published in *Science* find that their results receive good attention from an interdisciplinary audience. Most contributors send us excellent papers that meet high scientific standards. We seek to publish papers on a wide range of subjects, but financial limitations restrict the number of Reports published to about 12 per week. Certain fields are overrepresented. In order to achieve better balance of content, the acceptance rate of items dealing with physical science will be greater than average.

Table 1. Quantiles of the daily maximum O_3 concentration (1 May through 30 September 1973).

Measurement site	Median (ppb)	Upper quartile (ppb)	Upper decile (ppb)	Percentage of days exceeding standard
		New Jersey sites		
Ancora	74	100	125	44
Bayonne	64	96	121	38
Camden	66	88	106	31
Linden	54	78	104	22
Newark	46	75	108	21
		New York sites		
Eisenhower Park	33	60	85	13
Mamaroneck	45	68	101	20
Welfare Island	42	78	116	22
Yonkers	70	106	135	39

of days and then squaring the result to give the original parts-per-billion scale.

In Fig. 2A each curve corresponds to one of three groups of days stratified according to the total solar radiation between 4000 and 7700 Å from 7 a.m. to 1 p.m. in Central Park, New York City, as measured by the National Weather Service. (This period of the day was chosen since it constitutes the interval of major O_3 production. Central Park is the site nearest to Bayonne for which continuous solar radiation measurements are made.) The definitions of low, middle, and high solar radiation groups were chosen such that the groups contain approximately 25, 50, and 25 percent of the days, respectively. The results clearly demonstrate an association between O_3 production and solar radiation. This is consistent with the generally accepted view (*9*) that O_3 production is dominated by the reaction sequence

$$NO_2 \xrightarrow{h\nu} NO + O \qquad (1)$$

$$O + O_2 \rightarrow O_3 \qquad (2)$$

For the low-radiation days the afternoon peak in the O_3 concentration is greatly reduced. For middle- and high-radiation days the O_3 begins to rise at 7 to 8 a.m., peaks during the middle to late afternoon, and then decreases through the night. The peak value for the high-radiation days is not appreciably higher than for the middle-radiation days, whereas the area under the curve is clearly larger.

In Fig. 2B sunny days (days for which the sum of the Central Park total radiation from 7 a.m. to 1 p.m. is greater than 200 langleys) have been divided into three groups according to the mean wind speed (not the resultant wind speed) at Bayonne from 3 a.m. to 12 a.m. (This period includes the interval of primary pollutant buildup and major O_3 production.) The definitions of the low-, middle-, and high-wind groups were chosen such that the groups contain approximately 25, 50, and 25 percent of the sunny days, respectively. The afternoon peak in the O_3 concentration is higher with low wind speed, due presumably to the reduced dispersion of the pollutants involved in photochemistry. The O_3 curve for the days of low wind speed rises more rapidly from 7 a.m. to 1 p.m. and peaks earlier (1 p.m.) than the other two curves. Another interesting effect is the slightly higher O_3 concentration from 1 a.m. to 6 a.m. on the days with high wind speed. On nights with high wind speed the NO concentration is lower with the result that the O_3 is destroyed at a lesser rate by the fast reaction

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

Each week an "experiment" occurs in which the sources of the primary pollutants vary as a result of the changes in the pattern of motor vehicle traffic on different days of the week. It is important for a better understanding of photochemistry in urban atmospheres to thoroughly explore the effect of these experiments on the ambient concentrations of measured pollutants (*10*). In Fig. 2C "average" diurnal curves are shown for three groups of days: Mondays through Fridays, Saturdays, and Sundays. The most important fact is that the O_3 curves for these three groups of days differ only in relatively minor ways. For example, the afternoon peaks are nearly the same. One small, but noticeable, difference is that the 6 a.m. to 10 a.m. O_3 concentration increases from weekdays to Saturdays to Sundays. One possible explanation is that there is less destruction of O_3 due to the fast reaction (Eq. 3), since the ratio of NO to ($NO + NO_2$) decreases from weekdays to Saturdays to Sundays during the period from 6 a.m. to 10 a.m.

In summary, the federal O_3 standard is often exceeded at all the sites we investigated; the site that exceeds the standard most frequently is Ancora, the least urban. The regional character of the O_3 patterns is evident in the high correlations between pairs of sites; these correlations tend to decrease with increasing intersite distance. Low O_3 concentrations are associated with low levels of solar radiation and with high wind speed. Finally, average O_3 diurnal patterns on weekends differ from those on weekdays only in minor ways despite the markedly different traffic patterns.

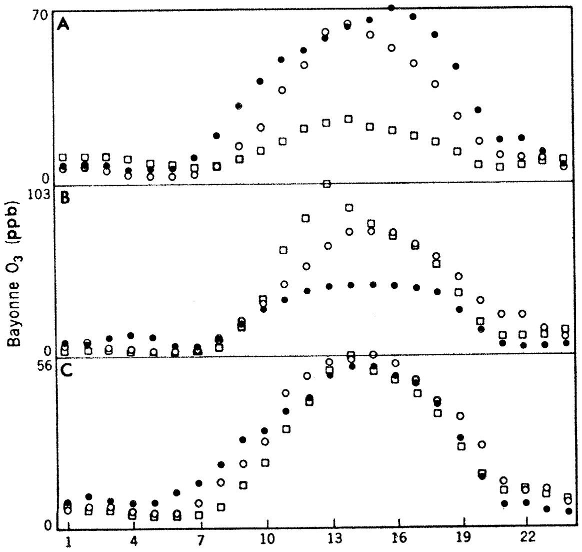

Fig. 2. Diurnal curves of Bayonne O_3 concentrations. (A) Days stratified according to the total solar radiation in Central Park, New York City, from 7 a.m. to 1 p.m. (in langleys): □ = 0 to 155, ○ = 155 to 335, ● = 335 and above. (B) Days stratified according to the average wind speed from 3 a.m. to 12 a.m. at Bayonne (in kilometers per hour): □ = 0 to 6.4, ○ = 6.4 to 16.1, ● = 16.1 and above. (C) Days stratified according to the day of the week: □ = Monday through Friday, ○ = Saturday, ● = Sunday.

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References and Notes

1. See, for example, G. C. Tiao, G. E. P. Box, M. Grupe, S. T. Liu, S. Hillmer, W. S. Wei, W. J. Hamming, *Univ. Wis. Dep. Statistics Tech. Rep. 346* (1973); *Air Quality Criteria for Photochemical Oxidants* (National Air Pollution Control Administration Publication AP-63, Washington, D.C., 1970).
2. "Final report: Emission inventory for the State of New Jersey" (IBM Corporation, Gaithersburg, Maryland, 1971); "Profile of air pollution control" (Air Pollution Control District, County of Los Angeles, Los Angeles, California, 1971); "New York City metropolitan area air quality implementation plan" (New York State Department of Environmental Conservation, Albany, 1972).
3. This seasonal pattern of O_3 production is evident in the data we have analyzed and has also been noted by J. S. Jacobson and G. D. Salottolo ["Photochemical oxidants in the New York–New Jersey metropolitan area" (Boyce Thompson Institute, Yonkers, New York, 1973)].
4. With one exception, the O_3 concentrations discussed herein were determined by the chemiluminescent technique. The Yonkers measurements are of "photochemical oxidants," a collection of oxidizing gases of which O_3 is the principal constituent [B. D. Tebbens, in *Air Pollution*, A. C. Stern, Ed. (Academic Press, New York, ed. 2, 1968), vol. 1, p. 43], as determined by KI oxidation. Any SO_2 interference was prevented by dichromate scrubbing of the incoming air sample. No correction for NO_2 was made, but tests show its effect on the oxidant concentration to be < 30 ppb at this site.
5. High O_3 concentrations in rural areas have also been reported; see, for example: W. Attmannspacher and R. Hartmannsgruber, *Pure Appl. Geophys.* **106**, 1091 (1973); L. A. Ripperton and J. J. B. Worth, paper presented at 2nd Joint Conference on Sensing of Environmental Pollutants, Washington, D.C., 11 December 1973; W. N. Stasiuk, Jr., and P. E. Coffey, *J. Air Pollut. Control Assoc.* **24**, 564 (1974); "High oxidant levels in Wisconsin" (Report of the Department of Natural Resources, State of Wisconsin, Madison, 15 February 1974).
6. We calculated robust 5 percent trimmed correlations, following the method of R. Gnanadesikan and J. R. Kettenring [*Biometrics* **28**, 81 (1972)].
7. Square roots were taken since statistical investigations revealed that they produced values for which an assumption of a normal probability distribution was justified.
8. W. H. Beyer, Ed., *CRC Handbook of Tables for Probability and Statistics* (Chemical Rubber Company, Cleveland, ed. 1, 1966), p. 2.
9. The chemistry of urban tropospheres has been discussed by the following: H. Niki, E. E. Daby, B. Weinstock, *Adv. Chem. Ser. 113* (1972), p. 16; T. A. Hecht and J. H. Seinfeld, *Environ. Sci. Technol.* **6**, 47 (1972); K. L. Demerjian, J. A. Kerr, J. G. Calvert, *Adv. Environ. Sci. Technol.* **4**, 1 (1974).
10. E. N. Lawrence, *Atmos. Environ.* **3**, 123 (1969); *ibid.* **5**, 935 (1971); E. A. Schuck, J. N. Pitts, Jr., J. K. S. Wan, *Int. J. Air Water Pollut.* **10**, 687 (1966); W. A. Lonneman, S. L. Kopczynski, P. Darley, F. D. Sutterfield, *Environ. Sci. Technol.* **8**, 229 (1974); and the New Jersey–New York data we have analyzed.

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Sulfates as Pollution Particulates: Catalytic Formation on Carbon (Soot) Particles

Abstract. *Experimental evidence (obtained by electron spectroscopy for chemical analysis) is presented which shows that finely divided carbon (soot) particles may play a major role in the catalytic oxidation of sulfur dioxide to sulfate in polluted atmospheres. The results obtained with sulfates produced in the laboratory by the oxidation of sulfur dioxide on graphite particles and combustion-produced soot particles are compared with the properties and behavior of ambient sulfates. The proposed sulfur dioxide oxidation mechanism is qualitatively consistent with field observations.*

Because of the adverse effects of sulfate particles as atmospheric pollutants, the study of the oxidation of SO_2 to sulfate is of prime importance in air pollution research. In the past most attention has been devoted to the study of the photochemical and solution chemical mechanisms for the oxidation of SO_2. There is, however, increasing evidence that these two kinds of processes alone cannot adequately account for the observations, and it is now thought that perhaps some catalytic reaction on suspended particulates is involved. The possible role of suspended metal oxides, for example, has been examined by some workers (*1*). However the concentrations of such oxides in the atmosphere are small. This report concerns the role that finely divided carbon (soot) particles, a common pollutant and a catalyst abundantly present in the atmosphere, play in the oxidation of SO_2. Even though the surface chemical and catalytic properties of carbon are known (*2, 3*), the relevance of soot-catalyzed reactions to air pollution chemistry has not been appreciated. We show here that the soot-catalyzed oxidation of SO_2 to sulfate is an important process and that the proposed oxidation mechanism is in qualitative agreement with the field observations. The experiments reported here were obtained by the technique of electron spectroscopy for chemical analysis (ESCA).

Carbon is the most abundant element associated with pollution particulates; actually, carbon constitutes about 50 percent of the total particulate emissions in urban atmospheres such as those in California (*4*). From our ESCA studies of ambient particulates, we find that perhaps as much as 80 percent of the particulate carbon is in the form of soot. Soot is basically carbon with a graphite-like structure, with some small soot particles consisting of only a few unit cells (*5*) and thus possessing extremely high surface area.

We studied the interaction of SO_2 with graphite particles with the experimental setup shown in Fig. 1a, which produces small graphite particles with a fresh (reactive) surface (diameter $\simeq$ 20 μm). The ESCA spectrum of graphite particles exposed to SO_2 reveals two sulfur (2*p*) peaks corresponding to sulfate and to sulfide (*6*). Blank filters without graphite particles, under identical SO_2 exposure conditions, do not collect measurable amounts of sulfate (or sulfide). These experiments show that even fresh graphite particles in air may bring about the oxidation of SO_2 to sulfate.

The similarity of soot particles to graphite with respect to the oxidation of SO_2 is demonstrated by the following experiments. Soot specimens from a premixed C_3H_8-O_2 flame collected on (silver membrane) filters were used for experiments with different SO_2 exposure conditions, in the apparatus shown in Fig. 1b. Dry air or prehumidified particle-free air or N_2 was used with an SO_2 concentration of about 300 parts per million (ppm) and an exposure time of 5 minutes. The ESCA spectra of soot exposed to SO_2 are shown in Fig. 1b. The sulfate peaks were always more intense in the case of prehumidified air than in the case of dry air. However, both dry and prehumidified N_2, when used instead of air, produced only very low, background level sulfate peaks. This result indicates that, in addition to soot particles, the O_2 in air is important for SO_2 oxidation. Although water molecules enhance the observed sulfate concentration in the air-SO_2-soot system, the contribution of sulfate produced by SO_2 oxidation via dissolved molecular oxygen in water droplets is not significant; that is, blank filters exposed to SO_2 and prehumidified air showed at most only low, background level sulfate peaks.

It is of interest to assess the role of soot-catalyzed oxidation in or near combustion devices where both SO_2 and soot concentrations are highest. Here, however, the SO_2 oxidation may be, at least in principle, caused by reactions with reactive combustion-produced radical species (*7*). The experimental arrangement is shown in Fig. 1c. Soot samples were collected while a constant SO_2 flow (300 ppm, 4 minutes)