portional to the actual utilization patterns of carbon throughout the system. For example, the loading of DOC to lakes can be many orders of magnitude higher than that of POC, and its demands on the respiratory capacity of the ecosystem are virtually unknown. A simple linear correlation between the retention period and cycling index (r^2 = .86, where r is the correlation coefficient) suggests the overriding influence of flushing rate on the structure of the lake.

These results support the concept that lake ecosystems may be considered as unique aggregations of similar components. The individual linkages—for instance, of nutrients and producers or predators and prey—operate within a certain range in all lakes (although the factors actually determining the couples are complex). Lakes differ in the relative combination of these similar structural elements as one factor or another is selectively enhanced, according to the nature of the inputs, lake morphometry, or flushing rate.

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Ozone Formation Related to Power Plant Emissions

Abstract. *A curious and unambiguous event of excess ozone formation downwind of a power plant has been analyzed. A kinetic model used to simulate the event indicates that the excess ozone can be reconciled entirely on the basis of excess nitrogen oxides in the polluted air.*

The chemistry of emissions from electricity-generating plants that use fossil fuels has become an important and controversial subject. One aspect of the controversy involves "O_3 bulges," a phenomenon first reported by Davis *et al.* (*1*). According to their report, O_3 concentrations in the domain of aged yet well-defined plumes sometimes exceeds the concentrations in the ambient air. The finding was in contrast to all other monitoring data that had shown the expected trend of O_3 depletion in the paths of power plant plumes. More recent studies gave mixed results. No evidence of O_3 bulges was found in studies conducted in

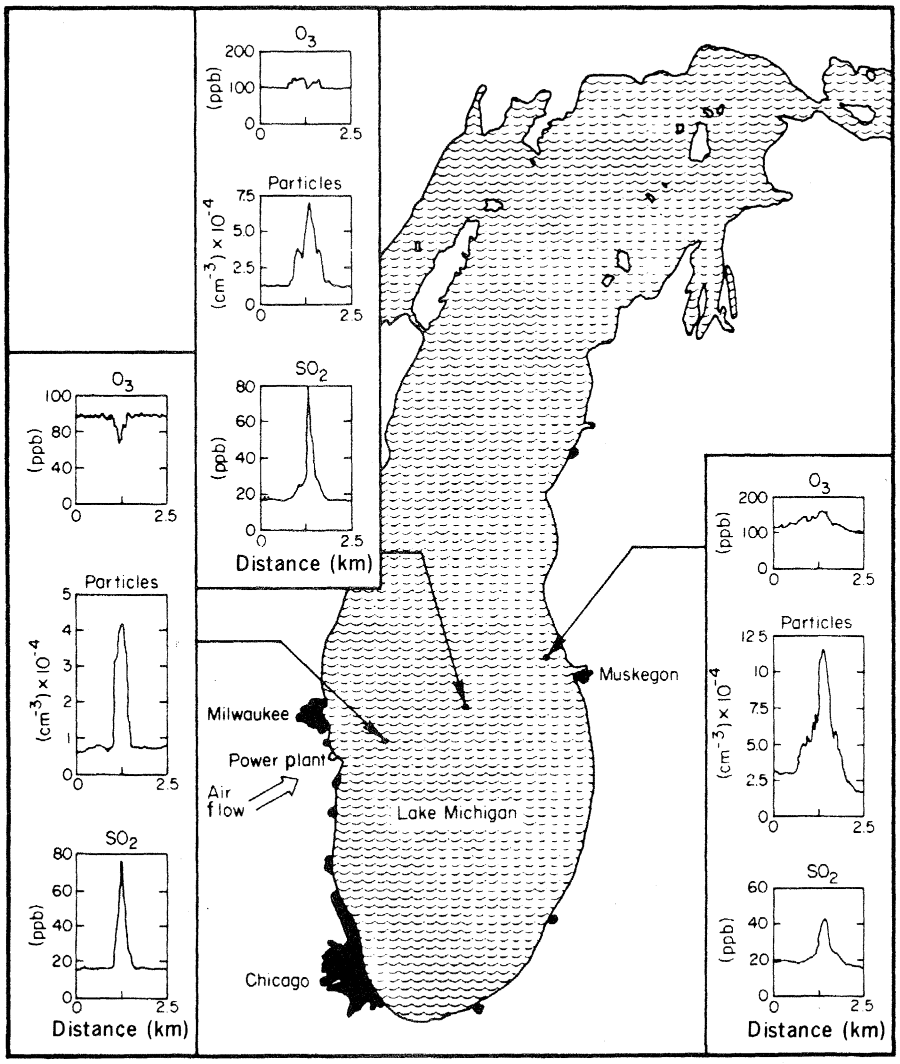
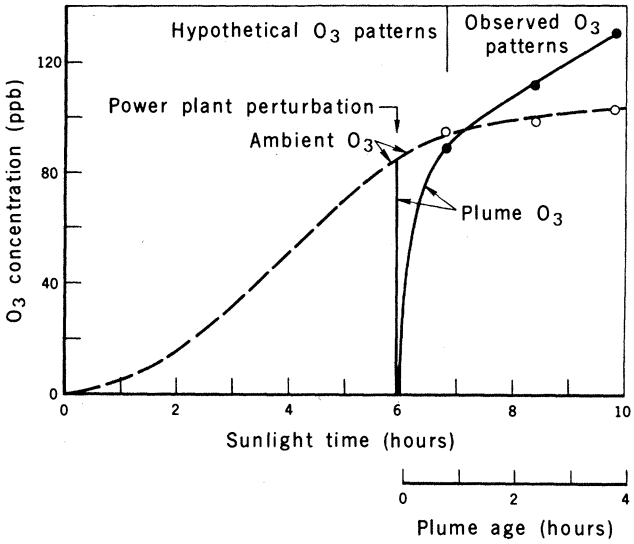


Fig. 1. Aerometric data showing the concentrations of SO_2, particles larger than 0.01 μm, and O_3 in a power plant plume traveling 300 m above Lake Michigan.



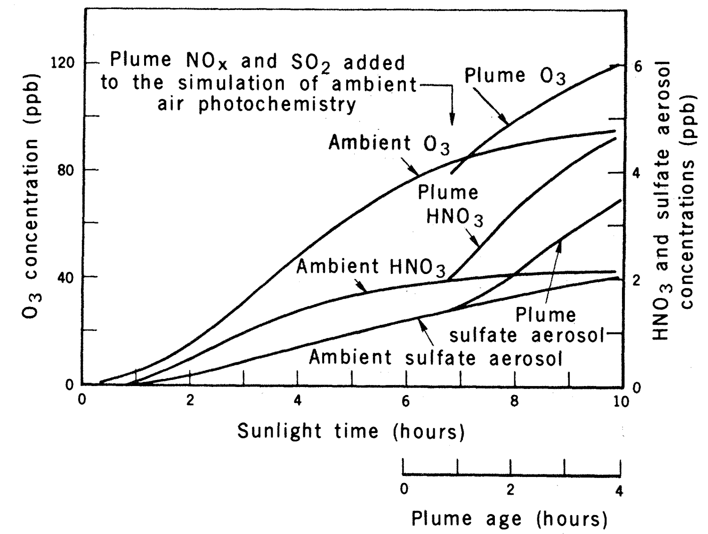


Fig. 2. (left). Trends in the average O_3 concentrations as observed in the air downwind of a power plant. The estimated release time for the observed plume was 12:26 p.m. on 20 July 1977; *ppb*, parts per billion. Fig. 3. (right). Theoretical predictions of the excess O_3, HNO_3, and sulfate aerosol in the air downwind of a power plant.

western states (*2*), but recent data of Gillani *et al.* (*3*) and additional investigations by Keifer *et al.* (*4*) showed further evidence of excess O_3 in plumes.

Explanations for the phenomenon have been speculative, and the possibility arose that scientists might by unaware of an important O_3-forming mechanism in the atmosphere. Indeed, in the first and subsequent reports by Davis' group, a new chain mechanism was proposed to account for the extra O_3. By a sequence of reactions beginning with the addition of OH to SO_2, peroxysulfate radicals repeatedly oxidized NO to NO_2, a condition that must be met to cause O_3 to increase in polluted air (*5*). However, smog chamber experiments (*6*) and theoretical considerations (*7*) of the SO_2 scheme indicated that appreciable O_3 could not be formed by the proposed route.

In this report we present an alternative explanation in support of new and unambiguous data collected by aircraft over Lake Michigan. The formation of excess O_3 in plumes is shown to be consistent with conventional mechanisms of atmospheric chemistry, although subject to certain atmospheric conditions. According to that theory, the key to the developments of excess O_3 is the concentrations of nonmethane hydrocarbons (NMHC) and nitrogen oxides (NO_x). With additional NO_x from a power plant, O_3 can be expected to increase downwind if the $NMHC/NO_x$ ratio remains relatively large. Although we can generalize about the requisite conditions for such events, the exact conditions can be stated only after additional atmospheric data have been obtained.

Data were collected on 20 July 1977, on board a DC-3 aircraft specially equipped for atmospheric monitoring (*8*). The Lake Michigan area was selected for plume studies because of advantages offered by the stabilizing influence of the lake. During summer months, warm air from the land becomes stabilized when advected over the lake and a virtual "decoupling" of the boundary layer takes effect (*9*). Plume dispersion becomes relatively uniform, deposition is minimal, and plume chemistry can be assessed with the use of one-dimensional kinetics formulations. The large uninterrupted fetch over the lake also allows plume tracking in the absence of downwind pollutant sources.

The meteorological situation on 20 July typified the stabilization feature described above; winds were steady from about 245°. The plane flew three north-south tracks, 300 m above the surface, at selected positions over the lake, moving downwind with the advected air mass as shown in Fig. 1.

A plume from the Oak Creek power plant was intersected at each pass. Data in Fig. 1 show the concentration profiles of SO_2, O_3, and particles larger than 0.01 μm for the plume and ambient air. The plume age is estimated to be 52 minutes at the first intersection, 141 minutes at the second, and 233 minutes at the third. At the first cross section, the O_3 concentration followed the usual pattern of dropping below the ambient value as a result of the reaction with NO in the plume. By the time of the second and third cross sections, the O_3 concentration was above ambient values. The concentration of particles increased substantially as the plume reacted in the atmosphere. The average O_3 trends in the plume and the ambient air are plotted on the right side of Fig. 2 as a function of plume age. The O_3 curves upwind of the first intersection of the plume are hypothetical, and they are included (left side of Fig. 2) to complete the picture of O_3 depletion that occurs as a plume is first dispersed into the atmosphere.

Our objective was to determine if acceptable models of atmospheric chemistry could describe the patterns of O_3 formation depicted in Figs. 1 and 2, with particular emphasis on reproducing the trends in the data that were recorded during the flight. A "lumped" photochemical model (*10*) was used, and a variable light intensity function was included to approximate the diurnal ultraviolet intensity recorded on 20 July 1977. The first step was to model the photochemistry representing background air for the day in question. The second step was to introduce into the reacting background mixture the average NO_x and SO_2 concentrations of the plume as observed at the first downwind cross section (*11*). No attempt was made to simulate the period when the plume was first dispersed into the air because no information was available to guide such an exercise (*12*).

The results of a representative kinetic simulation are shown in Fig. 3. A profile of the ambient O_3 concentration is shown together with profiles for predicted concentrations of ambient sulfate aerosol and HNO_3. Profiles are also shown for the secondary pollutants that were predicted to result from the interaction of plume emissions with the simulated atmosphere. The most pertinent feature of the simulation results is the prediction for excess O_3 formation in accord with the observed data. Although the absolute O_3 concentrations predicted by the model are slightly lower than the atmospheric data, the predicted trends for an O_3 bulge are in satisfactory agreement in view of the crudeness of the model. The model predicts a relatively large excess of HNO_3 in the aged plume and also substantial increases in sulfate aerosol formation. The increase in the rate of production of these secondary pollutants is due primarily to the elevated NO_2 and SO_2 concentrations in the plume rather than to increases in the radical concentrations responsible for NO_2 and SO_2 oxidation. (*13*).

If the O_3 ozone bulges (and the rest) are not quirks but are consistent with conventional smog kinetics, then why might the occurrences be so infrequent? There seem to be several conditions which must be realized concomitantly in order for O_3 bulges to manifest themselves. First, conditions must be optimal for intense photochemical activity—warm temperatures, intense ultraviolet radiation, and adequate reaction periods under such conditions. Second, the plume must remain intact during such episodes, and that is infrequent because the afternoon heating, particularly over landmasses, usually causes enough turbulence to dissipate the plume before the O_3 bulge develops. The most restrictive requirements are for NO_x concentrations in the dispersed plume to be substantially above ambient NO_x concentrations and for favorable $NMHC/NO_x$ ratios to be present. The latter condition requires additional clarification.

Many smog chamber studies have shown that under nearly static reaction conditions O_3 concentrations depend on the absolute concentrations of both NMHC and NO_x. As a general rule, the studies show that, for constant NMHC concentrations, the curves relating O_3 formation with NO_x concentrations go through a maximum when the initial NO_x concentration is approximately one-eighth the initial NMHC concentration [$NMHC/NO_x = 8/1$ parts per million of carbon divided by parts per million of NO_x (by volume)] (*14*). When the $NMHC/NO_x$ ratio is $< 8/1$, peak O_3 concentrations are inversely proportional to the NO_x concentration; conversely, when $NMHC/NO_x$ is $> 8/1$, peak O_3 concentrations are directly proportional to the NO_x concentration. The laboratory findings are applicable to the plume conditions under discussion. On the basis of independent measurements taken for this area on other flights, the $NMHC/NO_x$ ratio over Lake Michigan was expected to be high (~30/1), and, because NO_x (from the plume) was added to the atmosphere under favorable photochemical conditions, the O_3 concentration in the plume increased. Accepting that reasoning, the O_3 bulge, as a corollary, offers actual evidence of the role of NO_x in O_3 formation, and it supports the idea that increased NO_x emissions are apt to cause elevated O_3 concentrations in nonurban areas where there are natural concentrations of NMHC and where low NO_x concentrations normally prevail.

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5. In the polluted atmosphere where NO_x is present, O_3 is produced mainly by the photodecomposition of NO_2, which generates NO and O atoms. The O atoms, in turn, react with O_2 to give O_3. Because of the rapid reaction of NO with O_3 to reproduce NO_2 and O_2, a photostationary state develops whereby the O_3 concentration is proportional to a sunlight intensity term and the ratio of NO_2 to NO. Thus, to increase the O_3 concentration, it is necessary to convert NO to NO_2 without expending O_3 stoichiometrically. Peroxy-type radicals are primarily responsible for the conversion.
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10. The kinetic model may be described as follows (units are ppm^{-1} min^{-1} unless noted; *hν*, M, and O_2 are assumed; PAN, peroxyacetyl nitrate; ald, aldehyde; and R, alkyl group):

Reaction	Rate constant
$NO_2 \rightarrow NO + O$	0 to 0.39 min^{-1} (k_1)
$NO + NO_2 + H_2O \rightarrow 2HONO$	2.2×10^{-9}
$HONO + HONO \rightarrow NO + NO_2$	1.4×10^{-3}
$HONO \rightarrow HO + NO$	$0.2 k_1$ min^{-1}
$NO + O_3 \rightarrow NO_2$	2.3×10^1
$NO + HO \rightarrow HONO$	8.9×10^3
$NO_2 + HO \rightarrow HONO_2$	1.9×10^4
$CO + HO \rightarrow HO_2$	4.4×10^2
$NO + HO_2 \rightarrow NO_2 + HO$	1.2×10^3
$NO_2 + HO_2 \rightarrow HONO$	4.8×10^1
$HONO + HO \rightarrow NO_2$	8.5×10^3
$NO_2 + O_3 \rightarrow NO_3$	4.6×10^{-2}
$NO_3 + NO \rightarrow 2NO_2$	1.3×10^4
$NO_3 + NO_2 \rightarrow N_2O_5$	5.6×10^3
$N_2O_5 \rightarrow NO_2 + NO_3$	1.7×10^1
$NO + NO \rightarrow 2NO_2$	1.5×10^{-4}
$N_2O_5 + H_2O \rightarrow 2HONO_2$	1.0×10^{-5}
$CH_4 + HO \rightarrow RO_2$	1.2×10^1
$ald \rightarrow 1.2\ HO_2 + 0.3\ HCO_3 + 0.5\ RO_2$	$2 \times 10^{-3} k_1$ min^{-1}
$ald + HO \rightarrow 0.7\ HO_2 + RCO_3 + 0.3\ HCO_3$	2.0×10^4
$RO_2 + NO \rightarrow NO_2 + HO_2 + ald$	1.5×10^3
$RCO_3 + NO \rightarrow NO_2 + RO_2 + CO$	1.5×10^3
$RCO_3 + NO_2 \rightarrow PAN$	5.0×10^2
$HCO_3 + NO \rightarrow NO_2 + HO_2 + CO$	1.5×10^3
$NMHC + HO \rightarrow RO_2$	1.1×10^4
$O \rightarrow O_3$	3.3×10^6
$HO_2 + HO_2 \rightarrow H_2O_2$	5.3×10^3
$HO_2 + RO_2 \rightarrow RO + HO$	1.0×10^2
$RO_2 + RO_2 \rightarrow 2RO$	1.0×10^2
$RO \rightarrow HO_2 + ald$	5.0×10^3
$HO + HO_2 \rightarrow H_2O$	1.2×10^4
$HO + HO \rightarrow H_2O + O$	3.4×10^3
$NO + O \rightarrow NO_2$	3.6×10^3
$NO_2 + O \rightarrow NO_3$	1.3×10^4
$ald + O \rightarrow HO + HCO_3$	7.4×10^2
$HO + SO_2 \rightarrow$ sulfate	1.6×10^3
$RO_2 + SO_2 \rightarrow RO +$ sulfate	2.4
$HO_2 + SO_2 \rightarrow HO +$ sulfate	1.2

11. Species concentrations in the simulation model corresponding to the first downwind plume traverse are as follows [concentration units are parts per million (by volume)]: $NO = 2.4 \times 10^{-3}$, $NO_2 = 1.12 \times 10^{-2}$, $NO^3 = 9.7 \times 10^{-7}$, $N_2O_5 = 8.6 \times 10^{-7}$, $HNO_2 = 9.35 \times 10^{-5}$, $HNO_3 = 1.98 \times 10^{-3}$, $PAN = 4.77 \times 10^{-3}$, $CO = 4.99 \times 10^{-1}$, $NMHC = 1.2 \times 10^{-1}$, $CH_4 = 1.69$, $ald = 3.38 \times 10^{-2}$, $H_2O = 2.0 \times 10^4$, $SO_2 = 4.2 \times 10^{-2}$, sulfate $= 1.4 \times 10^{-3}$, $O = 4.6 \times 10^{-10}$, $O_3 = 7.9 \times 10^{-2}$, $H_2O_2 = 6.6 \times 10^{-3}$, $OH = 3.7 \times 10^{-8}$, $HO_2 = 7.7 \times 10^{-5}$, $RO = 1.1 \times 10^{-9}$, $RO_2 = 6.0 \times 10^{-5}$ $HCO_3 = 1.3 \times 10^{-5}$, and $RCO_3 = 1.0 \times 10^{-5}$.
12. We made many assumptions in the simulations. Although we make no attempt to rationalize them all, several assumptions were supported by the results of sensitivity analyses carried out on various upwind variables (that is, mixing volume, NMHC concentration, NMHC reactivity, light intensity, and morning NO/NO_2 ratios); thus, reasonable changes in these parameters did not qualitatively change the predictions obtained for the downwind plume.
13. In theory, the concentration of radicals (HO, HO_2, RO_2) responsible for homogeneous SO_2 oxidation will be suppressed by NO in a plume, in much the same way as the O_3 concentration is suppressed by NO. Thus the fractional rate of SO_2 oxidation will depend on the extent to which an air parcel recovers from the deficit in those radicals. Recovery is indicated when the ambient O_3 concentration is restored (or exceeded as in the unusual case sited here); under such conditions SO_2 oxidation is expected to proceed at relatively high rates, as observed within some urban plumes. See A. J. Alkezweeny and D. C. Powell, *Atmos. Environ*, **11**, 179 (1977).
14. For example, see B. Dimitriades, *Environ. Sci. Technol.* **1**, 80 (1977).
15. We are indebted to R. Easter and K. Busness for their assistance. This project was sponsored by the U.S. Department of Energy under the MAP3S program, contract EY-76-C-06-1830.

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