Occurrence of High Ozone Concentrations in the Air near Metropolitan Washington

Abstract. Relatively high concentrations of surface ozone and the indication that ozone is the inciting agent in fleck injury to tobacco were reported previously (*1*). Considerable interest therefore attaches to weather parameters on the high-ozone days which may throw light on the source and on the physicochemical processes affecting the ozone level. A source in the direction of nearby Washington, D.C., and photochemical production of the oxidant are indicated. Days with appropriate wind direction but low peak ozone concentration are discussed in terms of coexisting weather parameters. The weather ensemble found on high-ozone days is considered in relation to instances of fleck injury for which peak ozone levels were not measured.

A continuous recorder of atmospheric ozone was operated in a tobacco field at Beltsville, Md., 6 mi northeast of the District of Columbia, from 16 Sept. to 22 Oct. 1958 (*1*). Air-intake level was 3½ ft above ground, or about 1 yd below the tops of the tobacco plants. The instrument, a prototype of model 725-2 ozone recorder of the Mast Development Corporation (Davenport, Iowa), measures coulometrically the oxidation of buffered potassium iodide solution (*2*). This instrument is being subjected to tests for specificity by other workers; our report, therefore, is based primarily on relative values of ozone concentration. These are supported by the degree of transverse cracking observed in shaded, looped strips of rubber exposed in the tobacco field daily during September at a height of 2 ft (*1*).

On 5 of 32 days of measurement, the ozone or ozone-equivalent concentration (hereinafter termed simply "ozone level") reached peak values ranging from 31 to 50 parts per hundred million (pphm) by volume (*1*). All these peaks occurred between 0955 and 1505 local standard time (EST). On four days secondary maxima were observed 1 or more hours before or after the peak. Additional data pertaining to the ozone levels have been reported previously (*1*). The daily peak levels over the whole period of record may be summarized, on a relative scale of 0 to 100, as follows: on 5 high-ozone days, the range was 62 to 100; on 27 other days, the range was 4 to 38, and on 18 of these days, the range was 14 to 24.

The 1300 EST surface weather charts for the five high-ozone days show a ridge of high pressure to the southeast or south of Beltsville and a trough of low pressure to the northwest. On two days the Washington, D.C., area was occupied by a saddle of high pressure, with the ridge line about 100 mi to the southeast or the south. On another day the ridge, which extended southwestward from a nearby center, was just east of Washington. On the two remaining days the ridge lay several hundred miles to the south or the southeast, and an approaching trough was 100 to 400 mi to the northwest.

On each of the high-ozone days, the surface winds during the 2-hour period preceding the peak ozone level were from a sector that includes the eastern portion of the Washington metropolis, south of Beltsville (Table 1). This finding is contrary to that reported in a study of ozone at a place 30 km west-southwest of Paris, where *low* levels of ozone concentration were associated with winds from the city (*3*), in the months January to June. Haagen-Smit advanced the hypothesis that ozone is formed in the photochemical reaction of nitrogen dioxide and certain hydrocarbons found in automobile exhausts and elsewhere; this hypothesis, which is supported by several chamber experiments, has been invoked to explain high levels of ozone found at times in the Los Angeles basin (*4*).

Metropolitan Washington can be classified as, at most, light industrial, and at the air temperatures dealt with there should have been little or no contribution to air pollution from domestic heating; the density of Washington automobile traffic, on the other hand, is notorious. We believe the nature of pollution sources, and particularly the absence in Washington of a "coal" atmosphere (*5*), can help to explain the difference in the occurrence of ozone near Paris and near Washington. Since no other sources of ozone in suitable strength are known (*6*), we tentatively adopt Haagen-Smit's hypothesis to explain the origin of high levels of ozone at Beltsville.

It is considered unlikely that stratospheric ozone was an important source on the five high-ozone days because the indicated ozone levels at Beltsville reached an order of magnitude higher than levels in the lower troposphere commonly attributed to downward mixing from the high-altitude source (*5*). This would still be true even though the indicated ozone levels should prove to be high by a factor of 3. The convective layer at the time of peak ozone levels at Beltsville was bounded on top by a layer of considerable stability. Analysis of the upper-air sounding for Washington indicates that on three days (26 September and 10 and 16 October) the surface-based morning inversion had not been penetrated by the developing convective layer at the time of occurrence of the peak ozone level. On the other two days (23 September and 9 October) the surface-based inversion had been dissolved, but the convective layer was bounded above by a markedly stable subsidence layer.

The District of Columbia lies in the sector south through west-southwest of Beltsville, the nearest boundary being from 6 to 9 mi away. Satellite communities and the highways converging upon the district of course subtend a somewhat broader sector. Weather parameters listed in Table 1 were examined for the 11 days when the surface wind direction within the hour preceding peak ozone level at Beltsville fell between southeast and south-southwest. No cases of south-west-to-west surface wind were encountered. The purpose was to discover why the ozone level on these 11 days failed to reach the high relative values (62 to 100) previously discussed. A comparison with values in Table 1 for high-ozone days follows: Wind speed (see *i*) was higher by at least a factor of 2 on two days; solar radiation (see *f*) was lower (range, 53 to 75 langleys) on four

Table 1. Some meteorological parameters on five high-ozone days, Beltsville, Md.

No.	Parameter and Range
	At time of peak ozone level
a.	Temperature, tobacco field, 80° to 84°F
b.	Temperature, airport, 72° to 79°F*
c.	Relative humidity, tobacco field, 54 to 66 percent
	During 2-hr period preceding peak
d.	Surface wind, airport, direction, SE to SSW*
e.	Surface wind, airport, speed, 3 to 8 knots (3 to 9 mi/hr)*
f.	Solar radiation, Silver Hill, 81 to 118 langleys
	2 Hours before peak
g.	Depth of convective layer, 200 to 4700 ft
h.	Wind near top of convective layer, direction, S to SSW
i.	Wind near top of convective layer, speed, 2 to 6 knots (2 to 7 mi/hr)
	*Daily values, airport**
j.	Maximum temperature, 78° to 90°F
k.	Average temperature, 66° to 78°F
l.	Temperature range, 23° to 29°F
m.	Precipitation, none on day of high value and on preceding day.

* Data measured at Washington National Airport, 14 mi south-southwest of Beltsville.

days; wind speed was higher and solar radiation was lower on two days; wind direction aloft (see *h*) was north of west on two days; no difference was found on one day.

Thus, dilution of precursor material for the photochemical reaction, insufficient irradiation, or wind direction aloft from a quarter other than Washington may account for the findings on 10 of the 11 days when winds at the surface were southerly but ozone levels were low at Beltsville.

While the weather parameters on the remaining day (16 September) appeared to be similar to those for the five high-ozone days, the 0600 sounding at Silver Hill, Md. (*7*), differed; instead of a surface-based inversion, the sounding showed a 500-ft-deep isothermal layer, with an inversion immediately above, and southwest wind of 22 knots 700 ft above the surface. The temperature in the tobacco field at 1152, the time of peak relative ozone level (34), was the highest in the period of ozone record (97°F). While the velocity rate of ozone decomposition increases rapidly with temperature (*8*), it is believed that the antecedent high wind speed aloft was the primary limiting factor in this case.

Weather-fleck injury to tobacco, of the kind previously reported at Beltsville in association with high ozone levels (*1*), was observed northeast of Hartford, Conn., on 15 Sept. 1958 (*9*). Physiological insult by ozone was presumed to have occurred the day before. Weather parameters applicable to the Hartford area on this day were found to be similar to those associated with instances of high ozone level at Beltsville (Table 1). Likewise it was found that the weather parameters for Washington, D.C., on 14 September, fell into the same ranges, if, as was assumed, the maximum ozone level occurred about 1030 (the ozone recorder was not operated on that day). Whether fleck was observed at Beltsville the following day (*1*). While the test data indicate the ranges within which certain weather parameters make possible the occurrence of high-ozone levels downwind of a metropolis, further work is necessary to establish critical limits (*10*).

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References and Notes

1. H. E. Heggestad and J. T. Middleton, *Science* 129, 208 (1959).
2. The ozone recorder used in this study was on loan to the U.S. Public Health Service, for test, and became available through the courtesy of C. Stafford Brandt of the Robert A. Taft Sanitary Engineering Center (Public Health Service), Cincinnati, Ohio.
3. I. Rasool, *Compt. rend.* 242, 2168 (1956).
4. A. J. Haagen-Smit, *Science* 128, 869 (1958); see also C. E. Bradley and A. J. Haagen-Smit, *Rubber Chem. and Technol.* 24, 750 (1951).
5. C. E. Junge, "Atmospheric chemistry," in *Advances in Geophysics*, H. Landsberg and J. Van Mieghem, Eds. (Academic Press, New York, 1958), vol. 4, pp. 49–57, 95.
6. The amount of ozone produced by point dischargers in normal electrostatic fields would seem inadequate; however, further investigation may be warranted. See H. Cauer, "Some problems of atmospheric chemistry," in *Compendium of Meteorology*, T. F. Malone, Ed. (American Meteorological Society, Boston, 1951), p. 1126.
7. Silver Hill, Md., lies 13 miles south of Beltsville.
8. E. Warburg, in J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green, New York, 1922), vol. 1, p. 901.
9. H. C. Nienhuys (H. Duys and Co., Inc., Westfield, Mass.), personal communication.
10. The portion of the research reported here by Weather Bureau personnel was supported by the Public Health Service through contract with the Weather Bureau for studies of community air pollution.

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Molecular Structural Factors in Competitive Inhibition of Sugar Transport

Abstract. The high potency of phloretin as a competitive inhibitor of the human red cell's monosaccharide transport system is not shared by any of several molecular fragments of phloretin, but is duplicated in certain artificial estrogens resembling phloretin in respect to the spacing between terminal phenolic —OH groups. Related molecules which are slightly less extendible are comparatively inactive.

The glucoside phlorhizin, the classical agent for inducing experimental glycosuria through inhibition of sugar reabsorption in the renal tubules, similarly interferes with the passage of monosaccharides through the surface of human erythrocytes (*1*) and mouse ascites tumor cells (*2*). But the glucose moiety of the phlorhizin molecule does not appear to be involved in this action, since (at least in the red cell system) slowing of sugar transfer is much more pronounced with the aglucon (phloretin) than it is with the glucoside (*3*). The systematic manner in which the degree of this inhibition is determined by the sugar and phloretin concentrations (*4*) accords well with the mass action law as applied to a case of direct competition between inhibitor and substrate (sugar) for some "carrier" site on the cell surface.

A novel type of substrate stereospecificity has recently been reported for this sugar-transfer system (*5*), such that the critical requisite for reaction with aldoses is evidently the energetic stability of the sugar in the particular pyranose "chair" conformation designated as "C1." But both rings of the phloretin molecule are aromatic (hence essentially planar), and neither assumes any of the conformations in which the substrate sugar rings could be stable. Therefore a quite different factor must underlie the even tighter association with phloretin which is implied by the inhibition kinetics. Hence the present study (*6*) was directed toward identification within the phloretin molecule of the atomic groupings critical to the high, specific inhibitory potency, in the hope of developing a clue about the physicochemical structure at the hypothetical carrier sites.

To this end, various agents (*7*) were compared as inhibitors of the red cell's monosaccharide transport system, principally in terms of decrease in the rate of egress from the cells of D-glucose; as illustrated in earlier reports (*4, 8*), estimation of rates is simpler with this procedure than with "entry" experiments. Washed human erythrocytes equilibrated with the sugar at about 0.15*M* were transferred, at 37°C, to a much larger volume of sugar-free medium. The relatively slow sugar exit which ensues is accompanied by rapid osmotic equilibration of the water, and the resultant cell shrinkage was followed in the very dilute cell suspension by continuous optical densitometry (method of Ørskov, *9*). The usual medium was a mixture of the chlorides of Na, K, Ca, and Mg in a molar proportion of about 150:6:3:2 and at a total tonicity of 300 to 305 milliosmole/lit. when buffered at *p*H 7.4 with 32m*M* tris(hydroxymethyl)-aminomethane.

A priori, the length of the phloretin molecule raises the likelihood that activity might persist in the absence of one end or the other. But examination of assorted fragments from each end of the phloretin structure (the two columns of the upper section of Fig. 1) has revealed no agent of comparable potency; and the residual activity shown at higher concentrations appears to be independent of sugar concentration, so that it cannot be based on competition with the substrate. Moreover, when a combination of overlapping moieties (phloretic acid and phlorpropiophenone) was used, only a direct additivity of the separate inhibitory effects was observed, with no appreciable synergism. The much higher potency of the intact molecule thus focused attention on the orientation and spacing of the terminal groups. Simple α,ω-dihydroxyl derivatives of hydrocarbons of similar length (nonamethylene glycol or decamethylene glycol) were almost totally inactive; but among other diphenolic forms (lower section of Fig. 1), certain ones proved to be extremely potent in slowing sugar transfer.

The most effective inhibitor found was the synthetic estrogen, diethylstilbestrol; at physiological *p*H, it was about half again as potent as phloretin, while its saturated homologue, hexestrol (not quite so potent an estrogen) was some-