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Twelve Month Interim Report on the Subject Grant

"Diagnostic Studies of the H_xO_y-N_xO_y-O_3 Photochemical System Using Data from NASA GTE Field Expeditions"

NASA Grant NAG-1-786

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During the first year of the three-year granting period the major focus of the research effort funded by NASA has been on the analysis of data gathered during the Spring, 1984 GTE CITE-1 and the Summer, 1986 GTE CITE-2 field expeditions.

In the case of the Spring CITE-1 flights data from the field exercise was obtained from a GTE Data Archive Tape. Chemical and supporting meteorological data taken over the Pacific Ocean was statistically and diagnostically analyzed to identify the key processes affecting the concentrations of ozone and its chemical precursors in the region. The analysis has been completed and a paper has been submitted to the Journal of Geophysical Research. Reviews for the paper have been recently received and we are now making our final revisions to the paper.

Our analysis of the GTE CITE-2 data is being carried out in collaboration with Dr. D.D. Davis and other GTE scientists. Initial results of our analysis were presented at the Fall meeting of the American Geophysical Union in San Francisco and we have begun work on a paper describing our results. This paper should be completed and submitted to the Journal of Geophysical Research by the end of the summer.

(NASA-CR-183038) DIAGNOSTIC STUDIES OF THE HxOy-NxOy-O3 PHOTOCHEMICAL SYSTEM USING DATA FROM NASA GTE FIELD EXPEDITIONS Annual Interim Report (Georgia Inst. of Tech.) 56 p N88-25984
CSCL 13B G3/45 Unclas 0148373

In addition to the work described above, six other papers have been completed with partial support from the subject grant. Titles of all papers completed with funds from NASA during the granting period are:

1. Acid dew and the role of chemistry in the dry deposition of reactive gases to wetted surfaces, W.L. Chameides, *J. Geophys. Res.*, *92*, 11,895-11,908, 1987.

2. Absorption cross sections and kinetic considerations of the IO species as determined by laser flash photolysis/laser-absorption spectroscopy, R.E. Stickel, A.J. Hynes, J.D. Bradshaw, W.L. Chameides and D.D. Davis, *J. Phys. Chem.*, in press, 1988.

3. High ozone events in Atlanta, Georgia, in 1983 and 1984, R.W. Lindsay and W.L. Chameides, *Environ. Sci. Technol.*, *22*, *No. 4*, 426-431, 1988.

4. Ozone precursors and ozone photochemistry over the eastern North Pacific Ocean during the spring of 1984 based on the NASA/CITE 1 airborne observations, W.L. Chameides and D.D. Davis, *J. Geophys. Res.*, in revision, 1988.

5. Ozone trends in Atlanta, Georgia: Have emission controls been effective? R.W. Lindsay, J.L. Richardson, W.L. Chameides, submitted to *JAPCA*, in review, 1988.

6. The biochemistry of ozone deposition to plant leaves: The role of ascorbic acid, W.L. Chameides, submitted to *Environmental Science and Technology*, in review, 1988.

7. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, W.L. Chameides, R.W. Lindsay, J.L. Richardson and C.S. Kiang, submitted to *Science*, in review, 1988.

Copies of papers 1, 2, 3, and 4 listed above have already been forwarded to NASA in our six month Interim Report. Copies of papers 5, 6, and 7 are included in this report as an appendix.

Plans for research during the next 12 months of the granting period include:

1. Completion of our analysis of the GTE CITE-2 data. Two major studies on this data are envisioned: a comparison of measured and theoretically calculated NO/NO_2 ratios and a diagnostic analysis of ozone photochemistry implied by the observations. The latter study will include a comprehensive propagation of error analysis to determine the accuracy and precision with which we are able to calculate ozone photochemical tendencies from a set of state-of-the-art chemical

measurements.

2. An initial study of the data obtained during the GTE ABLE-2A and 2B experiments aimed at determining to what extent long-range transport of pollutants can affect oxidant levels in remote Brazilian locations.

3. Preparation of a paper in collaboration with Dr. D.D. Davis and other GTE scientists comparing measured and model-calculated OH levels from the Spring CITE 1 mission.

APPENDIX B

Ozone Trends in Atlanta, Georgia:
Have Emission Controls Been Effective?

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April 6, 1988

Abstract: Nine years of summertime ozone data from the Atlanta Metropolitan Area are analyzed and compared to local emissions of volatile organic carbon and nitrogen oxides. Trends from 1979 to 1987 were studied for the number of days per year ozone exceeded the NAAQS standard, the second-highest ozone level observed per year, and the first quartile summertime average ozone observed, as well as the mean difference between the ozone level observed downwind and upwind of the city. Because this last parameter is sensitive to chemical factors but relatively insensitive to meteorological variations its trend may provide a better indication of how effective emission controls have been in reducing O_3 in the Atlanta area. In spite of sizeable reductions reported for volatile organic carbon emissions over the past several years the data give no indication that ozone levels have decreased and in fact imply that summertime ozone production may have increased. The results suggest the need for a reevaluation of our nation's strategy for O_3 abatement in Atlanta and comparable cities.

I. Introduction

In 1952 Haagen-Smit first used the term "photochemical smog" to describe the mix of air pollutants that arise in the Los Angeles area from the oxidation of volatile organic carbon (VOC) and nitrogen oxides (NO_x) in the presence of sunlight and water vapor.[1,2] Photochemical smog is now recognized to be responsible for the high O_3 levels ($[O_3]$) typically found in all areas with large VOC and NO_x emissions and adequate sunlight. In an effort to prevent $[O_3]$ from exceeding the 120 ppbv National Ambient Air Quality Standard (NAAQS), the U.S. Environmental Protection Agency (EPA) in conjunction with state and municipal agencies have mandated reductions in anthropogenic VOC and NO_x emissions. Because O_3 production in most American cities is believed to be limited by VOC rather than NO_x, EPA has focussed primarily on VOC reductions.[3] It is estimated that nationwide from 1976 to 1985, VOC emissions have been reduced by 19% and NO_x emissions by only 1%.[4]

To determine if emission controls have successfully reduced $[O_3]$, data from numerous American cities have been analyzed. While some investigators have found evidence for a downward trend in $[O_3]$, others have concluded that $[O_3]$ has either remained constant or increased slightly.[4,5,6] One possible reason for these conflicting results is that meteorological factors have a major impact on $[O_3]$; the meteorological fluctuations that a city typically experiences can cause large year-to-year variations in $[O_3]$ and these variations can obscure the presence of a small secular $[O_3]$ trend due to changes in VOC.[7,8]

In this work we analyze O_3 data gathered from 1979 to 1987 in Atlanta, Georgia, a city in the southeastern U.S. characterized by frequent O_3

episodes. Our analysis is unique in that we have been able to determine the trend in a parameter which we believe to be sensitive to O_3 chemistry but relatively insensitive to meteorological factors. This parameter can therefore be used with less ambiguity to determine if emission controls enforced over the last several years have been effective.

II. VOC and NO_x Emissions

Figure 1a shows the total (point and area sources) annual VOC and NO_x emission rates as a function of year for the eleven county Atlanta metropolitan area as obtained from the National Emissions Data System (NEDS) maintained by EPA. The data indicate that VOC declined steadily from 1979 to 1982, increased by 25% from 1982 to 1983, and then returned to a decline. The large increase in VOC from 1982 to 1983 is not reflected in the raw fuel usage for the area which increased by only 3% and appears to be an artifact caused by a change EPA made in 1983 to the algorithm used to calculate VOC emissions from gasoline-powered motor vehicles; for the same fuel consumption rates the new algorithm calculates significantly more VOC emissions than the old algorithm.[9] To correct for this artifact and obtain a consistent trend, the VOC emission factor from gasoline-powered vehicles was increased by 0.05 tons/gallon for the years 1979 to 1982. This "adjusted" VOC trend is also illustrated in Figure 1a.

VOC emissions appear to have been reduced significantly in the Atlanta metropolitan area. From 1979 to 1985, VOC emissions dropped by 37% (22% before adjustment) in the eleven county area. In Fulton County, the most populous and centrally located of the eleven counties, VOC emissions dropped by 55% (44% before adjustment) reflecting its slower growth rate compared to the suburban counties. Changes in NO_x emissions have been more modest: a 4% increase in the eleven counties and a 16% decrease in Fulton county. If VOC-emissions are the limiting chemical factor in O_3 production in Atlanta, then these sizeable VOC reductions should have caused a significant reduction in O_3. Whether or not this has been the case is addressed below.

III. O_3 Concentrations and Trends

Our O_3 analyses for the Atlanta area are based on hourly-averaged $[O_3]$ observed by the Georgia Department of Natural Resources (DNR) from three stations in the Atlanta area (South Dekalb, Conyers, and Dallas) during the months of June, July, and August from 1979 to 1987. Figure 2 shows the locations of the three stations and of Hartsfield Atlanta International Airport where the surface winds used in our analysis were measured. (Note that in 1979 observations to the northwest of the city were actually made at New Hope, a location relatively close to Dallas. Furthermore, in 1980 the Conyers station was down for much of the year, causing a small gap in our data.) All O_3 measurements were made using the photoluminescence method, with calibration by UV photometry.

Figure 1b illustrates the annual variations in one of the parameters EPA uses to follow ozone trends: the number of days each year that the daily maximum $[O_3]$ exceeds the NAAQS. The year-to-year variations in this parameter are fairly large but a slightly significant upward trend is discernible; the slope is 14 ± 12%/yr. The years 1983, 1986, and 1987 appear to have been high in O_3, while 1982, 1984, and 1985 were low; interestingly EPA obtained a similar pattern for the nation as a whole with a high number of exceedances in 1983.[4]

Another parameter followed by EPA is the second highest daily maximum (SHDM) [O_3] observed at a location for the year. Although not illustrated in Figure 1, the pattern of year-to-year variations in the SHDM [O_3] in Atlanta is quite similar to that obtained for the number of NAAQS exceedances in Atlanta: a maximum in 1983 and minima in 1982 and 1984/85. There is no evidence of a secular trend; the slope is 0.2 ± 1%/yr.

Figure 1c illustrates the variations in the summertime average of the first-quartile in daily [O_3] maxima from the three stations; since the parameter is less sensitive to outliers that the two discussed above it is a more robust statistic.[5] The pattern of variations in the first-quartile average is also quite similar to that of the number of NAAQS exceedances; however there is no evidence for a significant secular trend. Slopes of 1.7 ± 1.6, 0.3 ± 1.5 and 0 ± 1.9%/yr were calculated for South Dekalb, Conyers and Dallas, respectively.

The lack of a significant downward trend in any of the above parameters would appear to imply that reductions in VOC emissions have not been effective in reducing O_3. However some caution should be exercised in interpreting these results since variations in the above parameters can be unrelated to chemical factors. For instance note that each of the above parameters is strongly affected by meteorological variations. In Atlanta, as in most cities, the days with the highest [O_3] often have stagnant winds, so summers with long periods of near-calm winds and warm temperatures tend to have higher average [O_3] and a higher number of NAAQS exceedances[10] regardless of how ozone-precursor emissions varied for the year.

Furthermore [O_3] in an urban area is a function of the amount of O_3 that is advected into the city; we have found for instance that in 1983 and 1984 air entering Atlanta during an O_3 episode day contained, on average, about 85 ppbv O_3.[10] Given the magnitude of this value, it is not inconceivable that yearly variations in average $[O_3]$ maxima in the city could be simply due to changes in the $[O_3]$ being advected into the city and have nothing to do with local emissions.

In order to unambigiously determine if emission controls have effectively limited ozone production in a location, one must study the trend in a parameter which is directly linked to the local ozone production rate. An analysis of a parameter having these properties is presented below.

IV. $\Delta(O_3)$ Trend

In a previous study[10] based on Atlanta O_3 data from 1983 and 1984, we found that $[O_3]$ measured at Conyers and Dallas could be used to indicate the intensity of O_3 production in the Atlanta area. Note in Figure 2 that when the winds are out of the northwest, Conyers lies downwind of the city and Dallas lies upwind of the city. On the other hand when the winds are out of southeast, Dallas is downwind while Conyers is upwind. Thus $\Delta(O_3)$, defined as the difference between the daily maximum $[O_3]$ measured at Conyers and at Dallas, should reflect the increment of O_3 added to an air mass as it advects over the city.

In Figure 3 $\Delta(O_3)$ is plotted as a function of the six-hour (1200-1700) vector-averaged wind direction for summer days from 1979 to 1987. Because our focus is on those processes that cause O_3 episodes, only days during which at least one of the two stations recorded a daily maximum $[O_3]$ above 80 ppbv are included in the figure. Furthermore, because the use of $\Delta(O_3)$ as an indicator of photochemical activity can only be valid when there is a significant flow of air over the city, all days with winds less than 2 m/s were excluded from the figure. The overall trend in $\Delta(O_3)$ as a function of wind direction is easily discernible in Figure 3; $\Delta(O_3)$ is most positive when the winds are out of the northwest and most negative when the winds are out of the east-southeast. However, not all days follow this trend; there are some days when $\Delta(O_3)$ has the opposite sign - negative for west winds and positive for east winds - implying that O_3 was actually consumed as it passed over the city. In general these days appear to have occurred when there was significant cloud cover over the city and therefore little photochemical activity or when there were wind reversals so that air already polluted by the metropolitan area was brought back into the city. In the trend analysis described below we have excluded these days from our calculation.

In Figure 1d the annually averaged values for $\Delta(O_3)$ for west winds (i.e., winds having directions from 260-320°) and for east winds (i.e. winds having directions of 70-130°) are plotted for the years from 1979 to 1987. Because the individual points in Figure 1d are not functions of the number of O_3 events per year and because they were calculated for days with specific meteorological conditions (i.e., a specific wind direction and minimum wind velocity), the year-to-year meteorological variations that determine how many O_3 episodes a city experiences each year are factored out of the trend. The fact that the year-to-year variability in $\Delta(O_3)$ is much smaller than and different from the variability in the parameters plotted in Figures 1b and 1c tends to support this contention. For this reason we believe that $\Delta(O_3)$ represents a more accurate indication of the secular trend in ozone production in Atlanta and of how effective VOC-emission reductions have been in reducing O_3 in the urban area.

The slopes of the $\Delta(O_3)$ trends in Figure 4 are +3.9 ± 2 and +2.1 ± 2.2%/yr for west and east winds, respectively, indicating a slight upward trend in ozone production in Atlanta over the eight year period. The possibility that $\Delta(O_3)$ has decreased over the period can be excluded at the 90% and 80% confidence levels for west and east winds, ($N = 8$, $R = .58$ and .36). While we do not understand why a larger and more significant slope was obtained for west winds than for east winds, it should be noted that the west-wind analysis included almost three times as many data points (145 days) as that of the east-wind analysis (58 days) and is therefore more robust.

V. Conclusion

An analysis of eight years of ozone data gathered in the Atlanta metropolitan area indicate that the sizeable VOC-emission reductions reported by NEDS for the area have not been accompanied by a significant reduction in O_3. While VOC emissions appear to have decreased significantly over the last several years, summertime $[O_3]$ has not decreased and there are indications that O_3 photochemical production in the area during O_3 episodes has actually increased. For each 10^5 ton reduction in VOC emissions in the eleven county metropolitan area, ozone production over the five years of overlapping data is calculated to have increased by 12 ± 8 and 1 ± 8 ppbv for west and east winds, respectively. While we do not mean to imply a causal relationship between the VOC decrease and O_3 increase with this statistic, it does serve to illustrate the fact that our strategy for reducing O_3 in Atlanta appears to have been largely ineffective

Why has O_3 production not decreased over the last nine years? One possibility is that the NEDS VOC inventories are incorrect and VOC emissions in the Atlanta area have not decreased significantly since 1979. If, on the other hand, VOC emissions have decreased significantly then it would appear that, contrary to the results of numerical and smog chamber simulations,[3] O_3 in the Atlanta area is relatively insensitive to VOC levels.

In light of the above result it is interesting to note that while natural emissions of VOC (primarily isoprene and terpene) from trees can be quite large[11], these sources have been largely ignored in the development of our current O_3 abatement strategies.[12] In fact, in the Atlanta area biogenic emissions of VOC appear to be comparable in magnitude to the NEDS estimate of VOC emissions from anthropogenic sources. Using 1976 LANDSAT photographs obtained from Dr. N. Faust of the Georgia Tech Engineering Experiment Station and urban growth rates supplied by the Atlanta Regional Commission, we estimate that approximately 60% of the 11 county Atlanta metropolitan area was covered by forest in 1985, roughly 20% each by deciduous, coniferous, and mixed forests. Combining these results with measured daytime and nighttime emission factors for isoprene, α-pinene and β-pinene from each forest type[11], we calculated a total summertime biogenic VOC source for the area of about 400 tons C/day, a result consistent with measurements made in a 1981 Atlanta area field study.[13] The NEDS estimated anthropogenic VOC source for 1985 is also about 400 tons C/day (see Figure 1). This result suggests that natural VOC compounds may play a significant role in the formation of O_3 in the Atlanta area. The fact that natural VOC measured levels in the Atlanta area tend to be much lower than anthropogenic VOC's does not necessarily mean that natural VOC can be neglected since they tend to be more reactive. The size of the natural VOC source suggests that the supply to the area may be very much larger than has been previously assumed;[12] perhaps large enough to make

NO_x rather than VOC the limiting chemical precursor to O_3 production. If this were the case, NO_x emission controls would be more effective in reducing $[O_3]$ than VOC.[14]

Our results indicate that efforts to limit VOC emissions in Atlanta have not been effective in reducing summertime O_3 photochemical production. Trend studies by other investigators suggest similar results for other locations.[5] We believe that a careful reevaluation of the nation's strategy for reducing O_3 is needed. This reevaluation should perhaps include a more careful assessment of VOC emission trends, of the relative importance of VOC and NO_x in limiting O_3 production, and of what role, if any, natural hydrocarbons play in urban and regional O_3 episodes.

VI. Acknowledgement: This work was supported in part by funds from Grant ATM 8600888 from the National Science Foundation and Grant NAG-1-786 from the National Aeronautics and Space Administration. In addition the authors would like to thank R. Collum, W. Estes, and D. Kemmerick of the Georgia Department of Natural Resources for the use of their data and their helpful comments, N. Faust of the Georgia Tech Research Institute for his help with the LANDSAT photographs, and Dr. C.S. Kiang of the Georgia Institute of Technology, School of Geophysical Sciences for his advice and encouragement.

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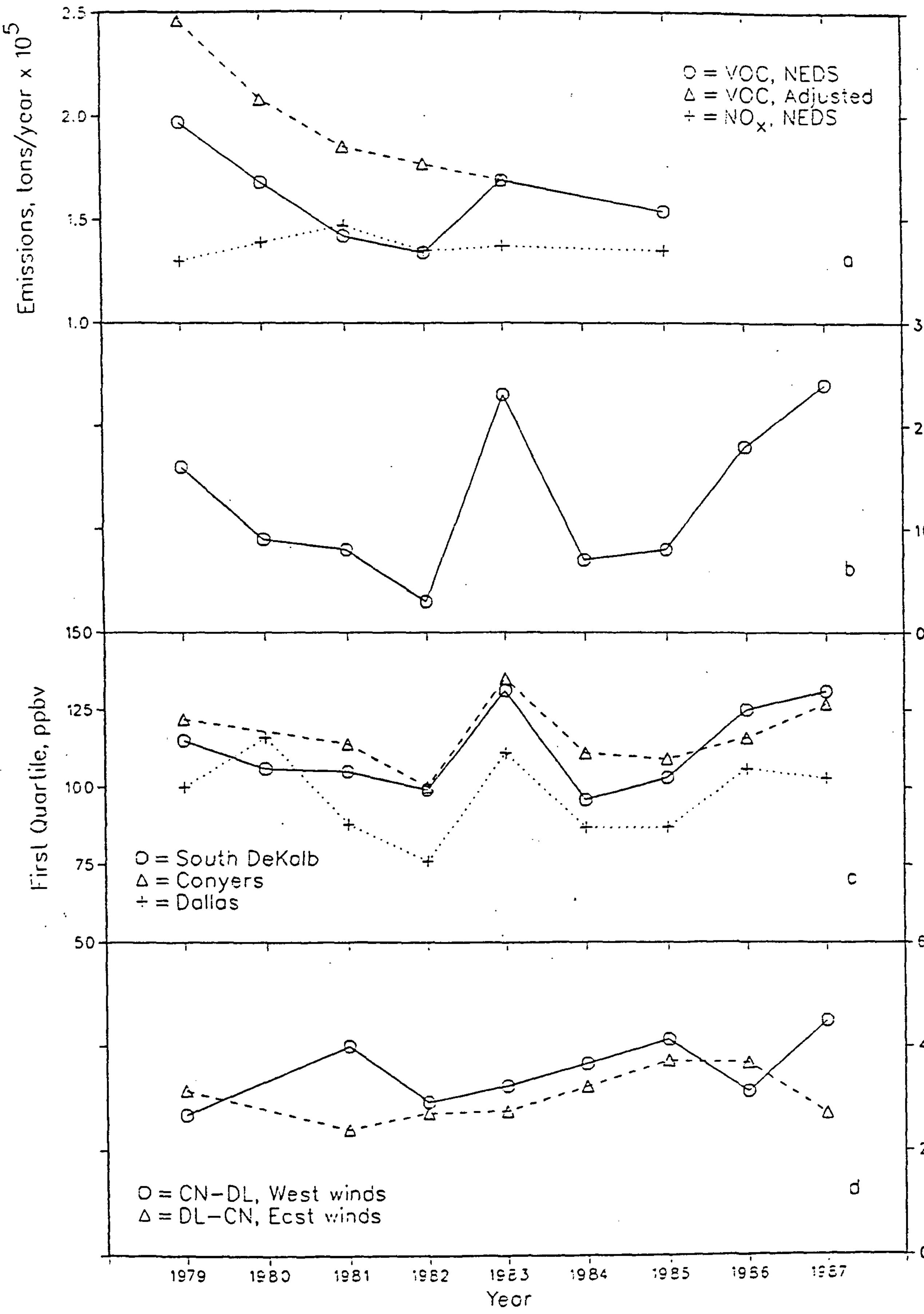
Figure Captions

Figure 1., a) Annual VOC and NO_x emissions from NEDS and the adjusted VOC emissions, b) number of days any of the three stations measured ozone concentrations above 120 ppbv, c) annual top quartile of ozone concentrations for each of the three stations, and d) $\Delta(O_3)$ for west and east winds as shown in Figure 3.

Figure 2., Map of Atlanta area showing the locations of the three ozone monitoring stations and that of the Atlanta Hartsfield International Airport where the winds were measured. Also shown is the outline of the city's urbanized area.[4]

Figure 3., The difference between the maximum ozone concentrations at Conyers and and Dallas ($\Delta(O_3)$) versus wind direction. Only days when one of the two stations recorded over 80 ppbv are shown. The winds were six-hour vector-averaged (1200-1700 EST) and must have averaged over 2 m/s. The boxes enclose the data points that were used for the analysis illustrated in Figure 1d. West winds, 206° - 320°, included 145 days and east winds, 70°-130°, 58 days, both over eight years.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Δ = VOC, Adjusted
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10
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Days above 120 ppbv
b
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75
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Δ = Conyers
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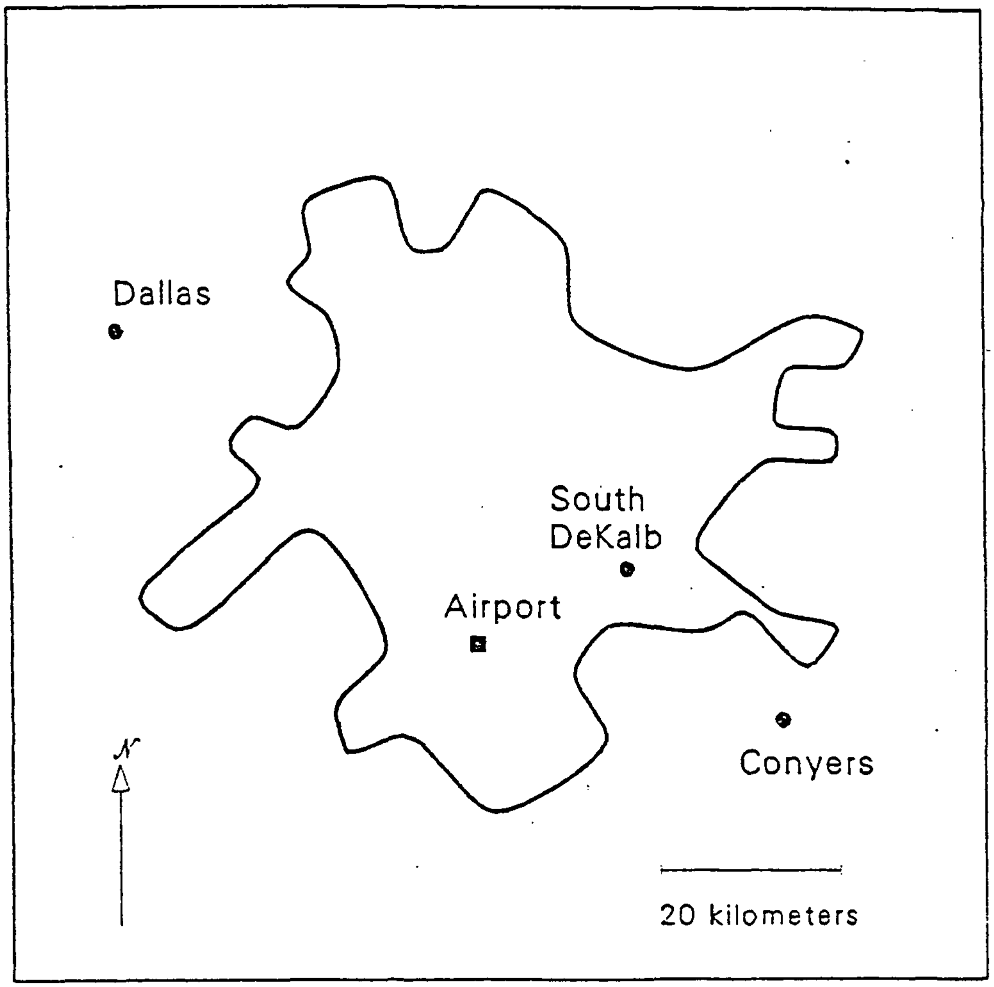

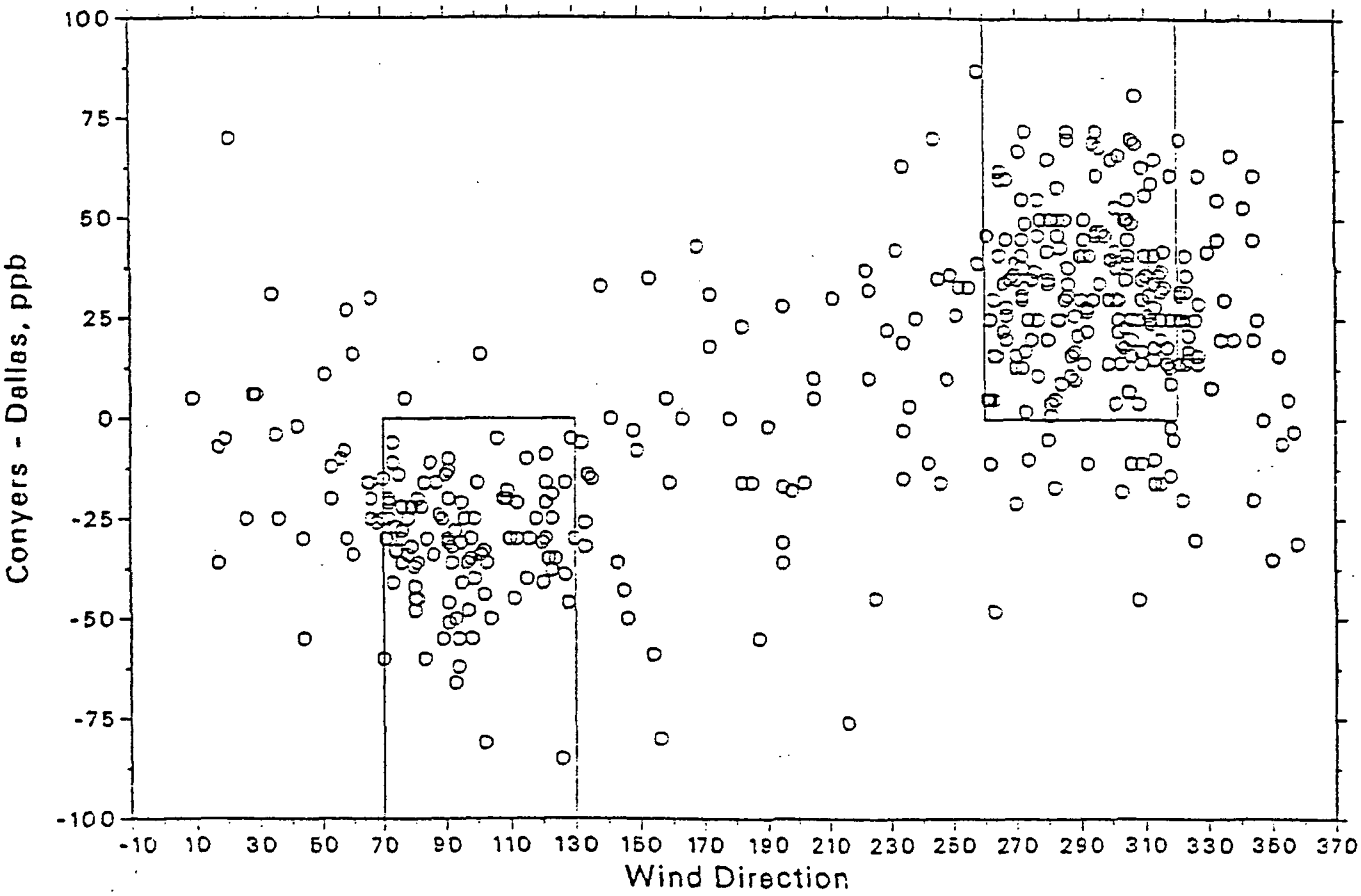
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Conyers - Dallas, ppb
Wind Direction

APPENDIX C

The Biochemistry of Ozone Deposition to Plant Leaves: The Role of Ascorbic Acid

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Abstract

A mathematical formulation is derived which describes the transport and chemistry of atmospheric gases as they diffuse through the open stomata, inner air spaces, and cell walls of plant leaves before depositing on the mesophyllic plasmalemma. The formulation is applied to the problem of ozone deposition on plant leaves to determine if reactions in the mesophyllic cell-wall water can prevent ozone from reaching the plasmalemma and initiating harmful oxidation reactions. Calculations indicate that a major portion of the ozone diffusing through the leaf can react with ascorbic acid in the cell wall. Other mechanisms such as ozone reactions with biogenic olefins and ozone decomposition in the cell-wall water are found to be unimportant. These calculations suggest that plants may protect themselves from the harmful effects of ozone by concentrating ascorbic acid in their cell walls; by reacting with ozone in the cell wall, the ascorbic acid limits the amount of ozone that can penetrate through the cell wall and reach the more vulnerable material inside the wall.

Introduction

Approximately 1 billion metric tons of ozone (O_3) are removed from the atmosphere annually by dry deposition to vegetative surfaces. Much of this deposition occurs when O_3 diffuses into plant leaves through open stomata and reacts with the internal cell material of the leaf[1,2]. Because O_3 is phytotoxic[3,4,5] its deposition can have harmful biological effects; it has been suggested that in regions affected by air pollutants, enhanced O_3 levels may be a contributing factor in forest diebacks and crop loss[6,7]. Experimental studies have shown that the sensitivity of a plant to O_3 can vary widely from species to species and even from individual to individual within a given species[8]. While the factor or factors which determine a plant's sensitivity remain uncertain, ascorbic acid appears to often play a role. A number of investigators have found a strong inverse relationship between plant sensitivity and ascorbic acid levels within the plant leaf[9,10,11,12]. In this work a mechanism is proposed by which ascorbic acid protects a plant from O_3 damage.

To study the chemistry of ozone dry deposition, a mathematical formulation is adopted which treats the process of gaseous diffusion through a leaf as a one-dimensional, molecular diffusion problem involving a series of diffusive layers. While this formulation represents a gross simplification of a very complex mass transfer problem, it has been found to adequately describe the transfer of carbon dioxide and water vapor between the leaf and atmosphere and should therefore also provide a reasonably quantitative framework from which to study the transfer of atmospheric O_3 to leaves.

Ozone Transfer Across The Mesophyllic Cell Wall

Similar to the uptake of atmospheric CO_2 by plants during photosynthesis, O_3 deposition onto the internal mesophyllic cells of a plant leaf must be preceded by O_3 transfer through a series of diffusive layers[13]. These layers are: 1. the thin laminar layer of air in contact with the leaf surface; 2. the stomatal openings on the leaf surface; 3. the inner air space inside of the leaf; and 4. the cell walls surrounding the mesophyllic plasmalemma. Once an O_3 molecule has penetrated through the cell wall to the plasmalemma, it can react rapidly with the polyunsaturated fatty acids (PUFA) in the lipid membrane and initiate destructive oxidation reactions[14,15]. In this section we focus on the processes which control the transfer of O_3 across the cell wall.

The cell wall in a leaf typically has two major components: a complex matrix of cellulose microfibrils, lignens, and other polymers, which give the cells their rigidity, and an aqueous solution surrounding the microfibrils which facilitates the transfer of CO_2 from the leaf's inner air spaces to the photosynthetically active cells[16]. To cross the cell wall and reach the plasmalemma, O_3, like CO_2, must diffuse through this aqueous solution. If O_3 was unreactive in this solution, then the one-dimensional diffusion equation describing the time rate of change of ozone within the cell wall would be given by

$$\frac{\partial[O_3]}{\partial t} = D_w \frac{\partial^2[O_3]}{\partial z^2} \qquad (1)$$

where $[O_3]$ is the aqueous-phase O_3 concentration within the cell-wall water in moles/liter (M), D_w is the aqueous phase molecular diffusion coefficient (2×10^{-5} cm^2/s), t is time, and z is distance within the cell wall. At steady state, the flux of O_3 in the cell wall is conserved and solution to Eqn. (1) yields

$$\Phi_{cw} = \Phi_p = \frac{H\ Av}{10^3\ r_{cw}} \left\{ X_{cw} - \frac{[O_3]_p}{H} \right\} \qquad (2)$$

where Φ_{cw} and Φ_p are the O_3 fluxes (in molecules/cm^2/s) crossing the inner-air-space/cell-wall boundary and cell-wall/plasmalemma boundary, respectively, Av is Avogrado's Number, X_{cw} is the O_3 partial pressure at the inner-air-space/cell-wall boundary, $[O_3]_p$ is the aqueous-phase O_3 concentration in moles/liter (M) at the cell-wall/plasmalemma boundary, H is the O_3 solubility constant (0.01 M/atm [17]), and r_{cw}, the transfer resistance of the cell wall, follows the standard form for an aqueous diffusive layer, e.g.,

$$r_{cw} = \frac{L}{D_w} \qquad (3)$$

In (3), L is the effective thickness of the cell wall.

If, on the other hand, O_3 reacts in the cell-wall water, the one-dimensional diffusion equation takes the form of

$$\frac{\partial[O_3]}{\partial t} = D_w \frac{\partial^2[O_3]}{\partial z^2} - k[O_3] \qquad (4)$$

where k is the first-order loss coefficient (in s^{-1}) for O_3 in the cell-wall solution and is assumed for simplicity to be a constant. In this case the O_3 flux is not conserved and the steady state solution to (4) yields

$$\Phi_{cw} = \frac{H\ Av}{10^3\ r'_{cw}} \left\{X_{cw} - \frac{[O_3]}{H\ \cosh(q)}\right\} \qquad (5)$$

and

$$\Phi_p = \frac{H\ Av}{10^3\ r'_{cw}} \left\{\frac{X_{cw}}{\cosh(q)} - \frac{[O_3]_p}{H}\right\} \qquad (6)$$

where

$$q = \left(\frac{k}{D_w}\right)^{1/2} L \qquad (7)$$

and r'_{cw}, the reactive transfer resistance of the cell wall, is given by

$$r'_{cw} = \tanh(q)/(kD_w)^{1/2} \qquad (8)$$

The fraction, FR, of the total O_3 flux entering the cell wall that reacts before reaching the plasmalemma is, by mass conservation, given by

$$FR = (\Phi_{cw} - \Phi_p)/\Phi_{cw} \qquad (9)$$

and from (5) and (6) we find that

$$FR = 1 - \coth(q) \qquad (10)$$

Values for FR as a function of k are plotted in Figure 1 for L = 1, 3, and 30 μm; this should represent a reasonable range for L given the thickness of cell walls (a few tenths to about 10 μm) and the fact that O_3 molecules diffusing through the wall must take a circuitous path around the microfibrils[16]. Figure 1 indicates that for intermediate values of k ranging from 0.1 to 10^4 s^{-1}, FR increases as both k and L are increased. Since an increase in k shortens the chemical lifetime of O_3 in the cell wall, FR is found to increase with increasing k. Since an increase in L lengthens the time an O_3 molecule requires to diffuse through the wall, an increase in L also causes an increase in FR. However for k-values outside this intermediate range, FR is essentially independent of both k and L. In the unreactive regime when $k \leq 0.1$ s^{-1}, FR is $\simeq 0$ and a negligibly small fraction of the O_3 reacts in the cell wall; in this case virtually all of the O_3 which enters the cell wall reaches the plasmalemma. In the reactive regime when $k \geq 10^4$ s^{-1}, FR $\simeq 1$ and virtually all of the O_3 reacts in the cell wall and never reaches the plasmalemma.

The results suggest that the impact of any given reaction on the flux of O_3 diffusing through the cell wall can be determined by evaluating that reaction's k-value. A reaction with a k in cell-wall water of 0.1 s^{-1} or less is in the unreactive regime and will not be important. A reaction with a k of 10^4 s^{-1} or more is in the reactive regime and can therefore represent a major sink for O_3 in the cell wall. Since the major organic components of cell walls (e.g., cellulose, lignens, and pectins, and other uronic acids) do not fall into the classes of compounds that are reactive with O_3 [8], it is likely that reactions with these compounds would be in the unreactive regime. In the discussion below three other mechanisms are considered.

O_3 Decomposition and Peroxidation

It has been speculated that damage to plants by O_3 may be caused by peroxidation[18] where dissolved O_3 first decomposes into free radicals which then either react directly with the cell or form peroxides which react with the cell. Since O_3 must decompose for this process to be of importance, it is interesting to determine the extent to which O_3 can decompose to form free radicals as it diffuses through the cell-wall solution. In the bulk aqueous phase O_3 decomposition proceeds via reaction with hydroxyl ions with a bimolecular rate constant of about 50 M^{-1} s^{-1} [19,20]. Assuming that this rate constant can be applied to the aqueous-phase solution of the cell wall and using the fact that under physiological conditions $[OH^-]$ is at most 10^{-7} M [16], a first order loss coefficient, k_{decomp}, for O_3 decomposition in the cell wall of only 5×10^{-6} s^{-1} or less can be inferred. This value is well within the unreactive regime (see Figure 1) indicating that O_3 decomposition in the cell wall is far too slow to be of significance. A negligibly small fraction of the O_3 diffusing through the cell wall will decompose before reaching the plasmalemma.

O_3 Reaction with Biogenic Hydrocarbons

Plants emit a wide range of olefinic compounds[21,22]. In a deciduous forest the primary olefin emitted is typically isoprene while terpenes are generally the major species produced by a coniferous forest[23]. In addition plants generally emit small amounts of ethylene, often in response to environmental stress[24]. During a typical summer day within a deciduous forest as much as 6000 μg-C cm^{-2} hr^{-1} can be emitted as olefins by the trees of a deciduous forest; ambient isoprene concentrations within the canopy of such a forest are typically a few ppbv (parts-per-billion by volume)[23].

Because O_3 is reactive with olefinic compounds[25], the possibility exists that O_3 reacts with these compounds as it diffuses through the inner air spaces and cell walls of leaves and that these reactions play an important role in the process of O_3 dry deposition to the leaves. In fact, in a recent series of experiments involving O_3 fumigation of pea seedlings, Mehlhorn and Wellburn[26] found a close correlation between O_3 damage and the amount of stress ethylene emitted by the plant. These investigators proposed that the release of stress ethylene determines the sensitivity of a plant to O_3 and that the reaction of O_3 with ethylene within the leaves may in fact initiate a series of reactions that ultimately leads to leaf necrosis.

In light of these observations it is interesting to determine if a significant fraction of the O_3 diffusing through the cell walls can react with olefinic compounds produced by the leaf before reaching the plasmalemma. Using a resistance model for mass transfer of olefinic compounds from the plasmalemma to the atmosphere (similar to the one described later in this work for O_3 transfer to the plasmalemma), the total concentration of olefinic compounds in the cell-wall water of leaves in a deciduous forest canopy can be estimated as a function of the abundance of olefins in the canopy and the rate at which olefins are produced by the leaves. Assuming a leaf area index of 5, a biogenic-olefin production rate of 1.6 x 10^{12} molecules cm^{-2} s^{-1} (equivalent to 6000 μg-C m^{-2} hr^{-1} for a five C-atom molecule such as isoprene), an olefin abundance in the canopy of 4 ppbv, and an olefin solubility of 0.01 M atm^{-1}, a cell-wall water concentration of about 10^{-7} M was obtained. Given that the bimolecular, rate constants for aqueous-phase O_3-olefin reactions range from 10^5 to 10^6 M^{-1} s^{-1} [27,28], these calculations imply a first order loss coefficient, k_{ole}, for the reaction of O_3 with olefins in cell-wall water of only 0.01 to 0.1 s^{-1}. This loss coefficient falls within the unreactive regime indicating that, as in the case of O_3 decomposition, an insignificantly small fraction of the total O_3 flux diffusing through the cell wall reacts with olefins before reaching the plasmalemma. An equivalent analysis for the fraction of the O_3 flux which reacts with olefins in the laminar layer outside the leaf and in the inner air spaces of the leaf yields similar results.

Given the very small fraction of O_3 that can react with olefins before O_3 reaches the PUFA-rich plasmalemma and the fact that ethylene comprises a very small fraction of the total olefinic emission rate, it seems unlikely that a causal relationship exists between ethylene production and O_3 damage as proposed by Mehlhorn and Wellburn[26]. It seems far more likely on the basis of this analysis that enhanced ethylene release during O_3 fumigation is a result of O_3 damage rather than a cause of the damage. (In this regard it should be noted that Mehlhorn and Wellburn found that plants which would be otherwise damaged by O_3 fumigation showed no damage from O_3 if they were first sprayed with a 1 mM solution of aminoethoxyvinylglycine (AVG), an inhibitor of ethylene biosynthesis. While this finding was interpreted by the investigators to mean that O_3 damage was prevented by blocking ethylene production, it should be noted that AVG has a double C-bond and therefore should be reactive to O_3[25]. It is possible that the application of a 1 mM solution of AVG to the leaf surfaces rendered these surfaces highly reactive to O_3 and thereby prevented O_3 penetration to the plasmalemma.)

O_3 *Reaction with Ascorbate*

A number of investigators have found an anti-correlation between the ascorbic acid (AA) levels in a plant leaf and its sensitivity to O_3 [9,10,11,12]. However the mechanism by which AA protects leaves from O_3 damage remains unclear. A number of complex mechanisms have been proposed; these include AA scavenging of O_3-generated peroxides and AA repair of O_3-damaged PUFA in the lipid membrane. However little attention has been paid to the fact that AA, because it has a double C-bond, is reactive with O_3 and could therefore protect a plant from O_3 damage by simply scavenging the O_3 before it can react with the vulnerable components of the cell. We explore this possibility below.

AA levels in plant leaves generally range from about 0.1 to 1.0 μg/g leaf fresh weight (LFW)[29,30]. However to determine AA's effectiveness as an O_3 scavenger in the cell wall, the AA concentration in the cell-wall water is needed. Only a very little data exists on this parameter. Castillo et al.[31] measured about 2-3 μg/g LFW of AA in the intracellular fluid of Norway spruce needles; assuming that the cell wall comprises about 50% of the fresh weight of a cell and that the cell wall is about 60% water[32,16], this measurement implies an AA concentration in the cell-wall water of about 5×10^{-5} M. On the other hand, Castillo and Greppin[33] report an observation of AA in the cell-wall water of S. Album leaves exposed to O_3 of 10^{-3} M.

Under physiological conditions AA is essentially completely dissociated into ascorbate (the AA pKa is 4.19 M [34]); thus in order to determine AA's effectiveness as an O_3-scavenger in cell-wall water, the rate constant for the reaction between O_3 and ascorbate is needed. Giamalva et al.[15] measured a biomolecular rate constant for the aqueous-phase reaction between O_3 and ascorbate of 6×10^7 M^{-1} s^{-1}; J. Hoigne (private communication, 1987) reports a lower limit of 10^7 M^{-1} s^{-1} for this reaction. Combining the kinetic data of Giamalva et al. with the AA concentration range noted above, a first order loss coefficient, k_{AA}, for the reaction of O_3 with ascorbate in the cell-wall water of 3,000 to 60,000 s^{-1} is inferred. These k-values are in the reactive regime (see Figure 1) and thus it appears that AA in the cell-wall solution can act as an effective chemical barrier to O_3. For the range of AA levels observed in the cell walls of two species, the calculations indicate that a very large fraction of the O_3 molecules diffusing through mesophyllic cell-walls will be scavenged by ascorbate before they reach the plasmalemma.

O_3 Deposition Model Calculations

The ability of cell-wall AA to limit the flux of O_3 reaching the plasmalemma can be further illustrated through simple model calculations simulating the transfer of O_3 from the atmosphere to the mesophyllic cells of a plant within a forest canopy. Using the standard resistance formulation for mass transfer, the flux, Φ_L of O_3 from the atmosphere to a single leaf can be represented by[16]

$$\Phi_L = \frac{x_a - X_{cw}}{r_a + r_s + r_i} \tag{11}$$

where X_a is the ambient O_3 partial pressure, r_a is the transfer resistance across the laminar air layer in contact with the leaf surface, r_s is the stomatal resistance, and r_i is the resistance of the inner air spaces of the leaf. By conservation of mass it follows that

$$\Phi_L = A_{cw}\ \Phi_{cw} \tag{12}$$

where A_{cw} is the ratio of the surface area of the mesophyllic cell walls in contact with the inner air spaces of the leaf to the outside surface area of the leaf.

Equations (5), (6), (11), and (12) form a closed set in which Φ_L and Φ_p can be calculated in terms of X_a, $[O_3]_p$, r_a, r_a, r_i, A_{cw}, L, and k. For the illustrative calculations presented here, $[O_3]_p$, as before, is assumed to be small, $L = 3 \times 10^{-4}$ cm, $X_a = 20$ ppbv, $r_a = 1$ s/cm, $r_i = 0.4$ s/cm, $A_{cw} = 10$, and r_s is varied from 3 to 12 s/cm to allow for changes in the size of the stomatal openings. These values roughly correspond to those typical of a leaf in a deciduous forest during the summer.[16] The first order loss coefficient, k, is assumed to arise solely from the reaction of O_3 with ascorbate; thus

$$k = k_{AA} = (5 \times 10^7\ M^{-1}\ s^{-1})[AA]_{cw} \tag{13}$$

where $[AA]_{cw}$, the cell-wall asorbic acid concentration, is varied from 0 to 10^{-3}M.

The calculated fluxes, Φ_L and Φ_p, as a function of r_s and $[AA]_{cw}$ are illustrated in Figures 2 and 3. We find that while the gross rate of O_3 deposition to the leaves, Φ_L, is dependent upon r_s but only weakly influenced by $[AA]_{cw}$, the flux to the plasmalemma, Φ_p, is largely controlled by $[AA]_{cw}$ rather than by r_s. Note in the figures that, for $[AA]_{cw} > 5 \times 10^{-5}$ M, a factor of three increase in r_s causes a factor of 2 to 3 decrease in Φ_L but a factor of 10 increase in $[AA]_{cw}$ causes less than a 20% increase in Φ_L. On the other hand, a factor of 3 increase in r_s causes a relatively small decrease in Φ_p while a similar increase in $[AA]_{cw}$ causes a decrease in Φ_p of almost 3 orders of magnitude. Figure 3 suggests how the AA level in the cell-wall water of a plant leaf can help to determine the plant's sensitivity to O_3. Two plants with the same external as well as stomatal properties, can experience orders of magnitude different O_3 fluxes to the mesophyllic plasmalemma of their leaves simply because of a difference of a factor of 2 or 3 in the amount of AA maintained in their cell walls.

It is useful to note that the results of the calculations have a number of characteristics that are consistent with observations. Φ_L is found to vary from about 2 to 10 x 10^{10} molecules cm^{-2} s^{-1} for X_a = 20 ppbv; for a forest canopy with a leaf area index of 5, this result implies an O_3 deposition velocity of 0.2 to 1.0 cm/s, which is within the range of O_3 deposition velocities that have been measured over forested areas[2]. The fact that Φ_L is found to be a strong function of the stomatal resistance, r_s, but only weakly dependent on the AA level is also consistent with field studies which have indicated that the gross rate of O_3 deposition to vegetation is generally dependent upon the stomatal characteristics of the leaves but largely independent of the internal properties of the leaves[2]. Finally the strong dependence of Φ_p upon AA and its independence upon r_s is consistent with observations which have indicated that a plant's sensitivity to O_3 is typically determined by the internal biochemical properties of the plant but independent of the plant's stomatal resistance[35,36,37].

Conclusion

Calculations indicate that the reaction of O_3 with AA in the cell-wall solution may often represent the major sink of atmospheric O_3 as it penetrates into the internal regions of a plant leaf. The calculations suggest that plants may act to protect themselves from the harmful effects of O_3 dry deposition by placing AA in their mesophyllic cell walls, thereby limiting the amount of O_3 that can penetrate to their more vulnerable cell material.

In comparison to the O_3-ascorbate interaction, other reactions that have been proposed to take place in the cell wall, such as the reaction of O_3 with ethylene and O_3 decomposition followed by peroxide formation, appear to be unimportant. Furthermore it seems unlikely that these reactions would be important in the plasmalemma either; given the high levels of PUFA in the plasmalemma and the relatively high reactivity of O_3 with these compounds[15], direct ozonolysis of the PUFA seem a more likely reactive pathway for the O_3 molecules which reach the membrane.

In light of the conclusion that peroxidation reactions are unimportant it is interesting to take note of the observations of Castillo and Greppin[33]. These investigators found that S. Album leaves exposed to O_3 tended to release enhanced quantities of AA as well as an ascorbate-specific peroxidase into their intercellular fluid suggesting that the cells were attempting to defend themselves against attack from peroxidation rather than ozonolysis. However it should be noted that O_3 is not the only oxidant in the atmosphere and, in fact, regions of high O_3 levels often have high levels of peroxide, which is photochemically coupled to O_3. Thus it is conceivable that Castillo and Greppin, by exposing the S. Album leaves to O_3, were stimulating a generalized response of the plant to atmospheric oxidants rather than a specific response to O_3. Under this scenario a mesophyllic cell under stress from atmospheric oxidants would release AA as a protectant against ozonolysis and AA along with an ascorbate-peroxidase as a protectant against peroxidation.

While the O_3/AA mechanism proposed in this work appears to capture many of the key characteristics observed for O_3 dry deposition to plant leaves, many more observations are needed. Measurements of the intercellular levels of AA in a diverse variety of plants having a wide range of O_3 sensitivities are needed to establish the general validity of the mechanism proposed here. In addition a more detailed understanding of the processes which control the production and release of AA to the cell wall are needed so that we may more accurately predict how plants might respond to the growing levels of atmospheric O_3 in large regions of the North American and European continents[38].

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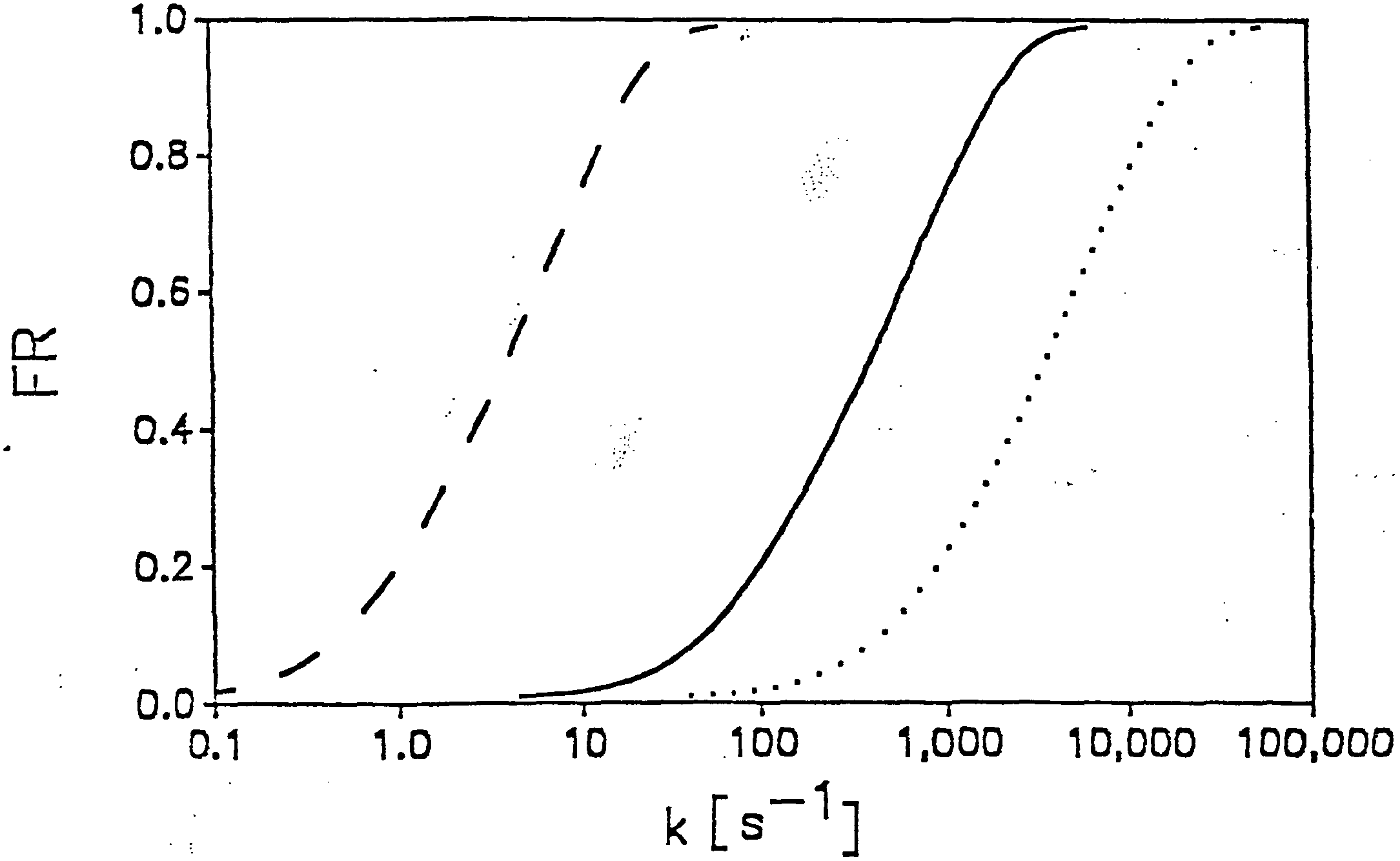
FIGURE CAPTIONS

Figure 1. The calculated fraction, FR, of O_3 molecules diffusing through the cell wall that react before reaching the plasmalemma as a function of k, the first-order loss coefficient for O_3 in the cell-wall solution. The dotted line is for L = 1 μm, the solid line is for L = 3 μm, and the dashed line is for L = 30 μm.

Figure 2. The calculated O_3 flux, Φ_L, to a single leaf as a function of the ascorbic acid concentration, [AA], in the cell-wall water. The dotted line was obtained with a stomatal resistance, r_s, of 12 s/cm, the solid line with an r_s of 6 s/cm, and the dashed line with an r_s of 3 s/cm.

Figure 3. The calculated O_3 flux, Φ_p, to the plasmalemma of a single leaf as a function of the ascorbic acid concentration, [AA], in the cell-wall water. The dotted line was obtained with a stomatal resistance, r_s, of 12 s/cm, the solid line with an r_s of 6 s/cm, and the dashed line with an r_s of 3 s/cm.



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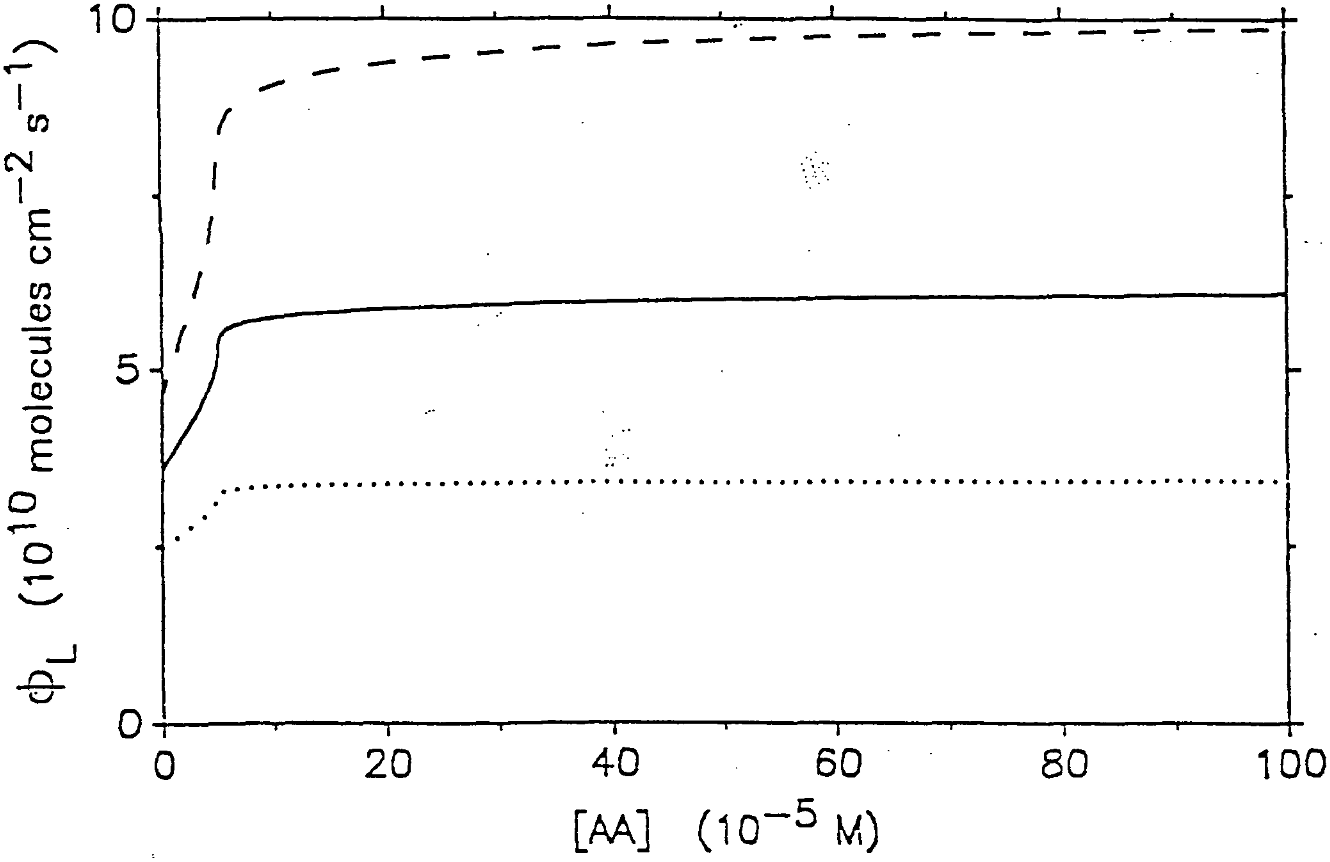

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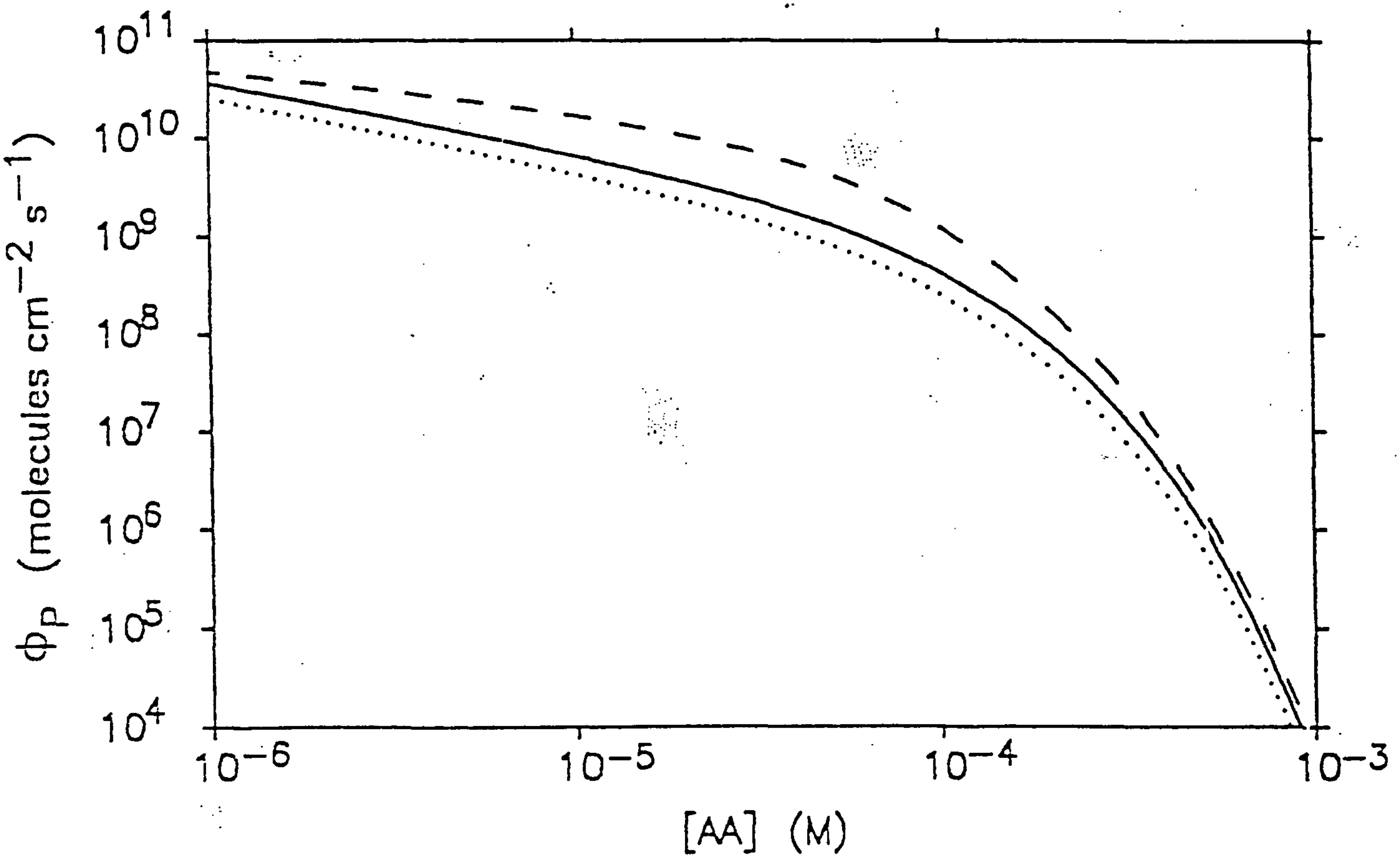

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APPENDIX D

THE ROLE OF BIOGENIC HYDROCARBONS IN URBAN PHOTOCHEMICAL SMOG: ATLANTA AS A CASE STUDY

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ABSTRACT: The effects of natural hydrocarbons need to be accounted for in order to develop a reliable plan for reducing ozone in the urban atmosphere. Trees can emit significant quantities of hydrocarbons to metropolitan areas such as Atlanta and model calculations indicate that these natural emissions can significantly affect urban ozone levels. By neglecting these compounds previous investigators may have over-estimated the effectiveness of an O_3-abatement strategy based on reducing anthropogenic hydrocarbons

INTRODUCTION

Haagen-Smit's pioneering work on photochemical smog first established that the photo-oxidation of hydrocarbons in the presence of nitrogen oxides produces ozone (O_3). (1) In urban areas with large emissions of anthropogenic hydrocarbons (AHC) and nitrogen oxides (NO_x), this mechanism often drives summer O_3 levels above the 0.12 ppmv National Ambient Air Quality Standard (NAAQS). In the U.S., a plan for O_3-abatement was implemented in the 1970's through the Clean Air Act. While the law called for emission reductions in either AHC or NO_x, its implementation by the U.S. Environmental Protection Agency (EPA) and the relevant state agencies has, for a variety of social, technological, and economic reasons, focused on AHC reductions. (2) However in spite of large reductions in AHC emissions over the past ten years and the expenditure of billions of dollars, O_3 in many locales has not decreased. (3,4) Sixty-eight cities remain in violation of the NAAQS; almost 40% of these are in the southeastern U.S. The apparent lack of success in the AHC-based O_3-abatement strategy suggests that there may be serious flaws in our understanding of the budget of urban hydrocarbons and/or of their role in photochemical smog. In this work we examine one aspect of the urban hydrocarbon budget that has been neglected in the past: biogenic or natural hydrocarbons (NHC).

For an O_3-abatement strategy based on AHC reductions to be effective, anthropogenic emissions must represent the dominant source of reactive, O_3-producing hydrocarbons. In this work we suggest that AHC emissions may not, in fact, be the only important source of reactive hydrocarbons to the urban atmosphere and that NHC emitted by trees and other vegetation can have a significant effect on urban O_3 levels.

The role of NHC is investigated by focusing on the chemistry of a specific city - Atlanta, Georgia. Atlanta is of interest for a number of reasons: it was the subject of an intense field study sponsored by the EPA in 1981 (5); it is situated in the southeast where summertime NHC emissions are relatively high; (6) and while AHC emissions in the Atlanta area have been reduced by an estimated 50% since 1979, O_3 levels have not decreased.(4)

NATURAL HYDROCARBON EMISSIONS

In the U.S. trees are the principal emitters of biogenic non-methane hydrocarbons and isoprene and α-pinene are the primary species emitted. (6,7,8,9,10) It is estimated that nationwide this source amounts to about 30-60 Tg-C yr^{-1}; the nationwide source of AHC is only about 18 Tg-C yr^{-1}. (6,10) However while the importance of NHC in rural forested areas has been documented, (8,11) it is not widely known that NHC emissions can also be significant in urban areas. The Atlanta metropolitan area provides a useful example.

An analysis of digitized LANDSAT data (provided by Mr. N. Faust of the Georgia Tech Research Institute) and information from the Atlanta Regional Commission indicates that about 57% of the 900 km^2, eleven-county, EPA-designated Atlanta non-attainment area was wooded in 1985; these wooded areas are shrinking at a rate of only about 2% yr^{-1} due to urban growth. (12,13) Of this 57%, 23% was deciduous, 18% was mixed, and 16% was coniferous. Combining this data with Zimmerman's (9) 30°C biogenic emission factors for the three forest types, we estimate an Atlanta area-averaged, daytime emission rate of

2100 μg-C m^{-2} hr^{-1} for isoprene, which compares well with Westberg and Lamb's (5) isoprene estimate for Atlanta of 2500 μg-C m^{-2} hr^{-1}, and 1400 μg-C m^{-2} hr^{-1} for non-isoprene NHC. At night isoprene is not emitted and thus the total nighttime NHC emission rate is also about 1400 μg-C m^{-2} hr^{-1}.

For 15 hours of daylight in the summer, the above results imply integrated daytime sources of about 30 kg km^{-2} for isoprene and 50 kg km^{-2} for all NHC. Over a 24-hour period the integrated NHC source is about 65 kg km^{-2}. While these NHC emission rates are small compared to the maximum AHC emission rate of 600 kg km^{-2} day^{-1} found in a 10 km^2 area of downtown Atlanta, they are equivalent to the eleven-county area-averaged AHC emission rate of about 30 kg km^{-2} day^{-1} (4,5). Furthermore, while biogenic emission rates in general have a large uncertainty (Lamb (6) estimates an uncertainty factor of 3), our estimates do not appear to be unrealistic; as we discuss later, model calculations using our estimates yield NHC concentrations that are reasonably close to observed levels. Finally, note that large NHC emissions are not unique to Atlanta. Independent estimates of the NHC emission rates in two other southeastern cities - Houston, Texas (14), Tampa Bay/St. Petersberg, Florida (8) - are roughly equivalent to our estimate for Atlanta. Thus large sources of NHC may be ubiquitous to cities in the southeast and possibly other regions of the country as well.

In spite of their large source, however, the role of NHC in urban photochemical smog has, for the most part, been discounted. This is especially surprising in light of smog chamber experiments which indicate that, for conditions common to the urban atmosphere, the O_3 forming potential of NHC is roughly equivalent to that of AHC (i.e., about 0.1 ppmv of O_3 for every 1 ppmv-C consumed). (15) Some investigators have concluded that NHC were negligible because their urban concentrations are much smaller than those of AHC. (5,10)

However because NHC are more reactive than AHC, they can have a significant impact in spite of their low concentrations. For instance, in the model calculations described below isoprene has a large effect even though it comprises only a few percent of the total hydrocarbon burden.

Lurmann, et al (16) claimed to show that NHC are unimportant through model simulations of the Tampa Bay/St. Petersberg area. Model simulations were reported with only AHC sources and with both AHC and NHC sources. Since the maximum O_3 level calculated with both sources was only about 10% larger than that calculated with only the AHC source, the authors concluded that NHC were not important. However, as Trainer et al (11) have pointed out, these results can be misleading; if the system is not limited by hydrocarbons then the O_3 production rate will respond non-linearly to the addition of AHC as well as NHC. In fact as the model calculations presented below demonstrate, NHC emissions can have a significant effect on urban O_3 levels.

MODEL SIMULATIONS

To illustrate the importance of NHC emissions to urban photochemical smog, model calculations simulating the formation of O_3 in Atlanta, Georgia were carried out using the city-specific Empirical Kinetics Modeling Approach (EKMA). (17,18,19) The EKMA model was developed by the EPA for state agencies trying to formulate O_3-abatement strategies. It simulates the photochemistry of a well-mixed column of air extending from the surface to the top of the mixed layer as the column advects from its initial, 0800 LST position at the city center to some evening position downwind of the city. During advection, surface emissions add hydrocarbons and NO_x to the column and variations in the mixing height cause air from above to be mixed into the column. The effects of changes in the local hydrocarbon source strength are explored with the model by simultaneously varying the initial, 0800 LST hydrocarbon concentration, and the daytime surface emission rates. Changes in the local NO_x source strength are explored by varying the equivalent NO_x parameters.

The model utilizes a 34-species photochemical mechanism known as CB-4 to simulate the chemistry within the air column. CB-4 is a carbon-bond mechanism in which nine functional groups are used to represent the myriad of volatile organics emitted into the urban atmosphere. (20) One of the interesting aspects of CB-4 is that the chemistry of isoprene is explicitly included in the mechanism. However this portion of the mechanism is not typically used; EPA recommends to EKMA-users that isoprene be set equal to zero, thereby inactivating the NHC portion of the mechanism. (18)

For the calculations reported here, the model was tuned to simulate O_3 in an air column advecting from downtown Atlanta to Conyers, Georgia, located 40 km southwest of Atlanta, on June 4, 1984. This day was also simulated by the Georgia Department of Natural Resources (DNR) for their 1987 State Implementation Plan (Mr. R. Collom, private communication, 1988). June 4, 1984 was a typical ozone-episode day in Atlanta. Temperatures during the daylight hours averaged 28°C and peaked at 32°C. The winds were out of the northwest and by the end of the day O_3 at a DNR monitoring station in Conyers had peaked at 0.147 ppmv. Except for the inclusion of a NHC source, the input data for our simulations was the same as that used by DNR. To simulate present-day AHC and NO_x levels, the initial AHC and NO_x concentrations were set at 0.68 and 0.096 ppmv, respectively, in accordance with early morning observations from downtown Atlanta, and the total AHC and NO_x surface emissions from 0800 to 1900 LST were set at 34 and 28 kg/km^2, respectively. The emissions and their distribution as a function of time were chosen to correspond to the emissions an air column would encounter if it followed a trajectory from downtown to Conyers. The chemical speciation of the initial mix of AHC and NO_x and of the emissions was based on the apportioning factors or 'reactivities' recommended by EPA. (18)

In addition to the AHC and NO_x emissions, a source of NHC was added to the EKMA model. Since vegetative emissions are light and temperature sensitive, the NHC emissions were distributed over the course of the day so that most of the NHC was emitted in the afternoon. The NHC emission rate was initially 0, increased linearly until 1200 LST, remained constant from 1200 to 1500 LST, and then decreased linearly to 0 at 1900 LST. (Slightly higher O_3 levels were obtained when the NHC emissions were held constant with time.) Calculations were carried out with total, integrated, daytime NHC emission rates ranging from 0 to 50 kg km^{-2}. In all cases the initial NHC concentration was set at 0.

For simplicity all NHC emissions were assumed to be isoprene. The chemistry of isoprene was simulated in two ways: 1. Using the isoprene chemistry specifically included in the CB-4 mechanism; and 2. Using the functional group chemistry of the CB-4 mechanism with each isoprene molecule represented as two olefins and one paraffin. (21) While the results described below and illustrated in Figures 1 and 2 were obtained using the first approach, both approaches generally yielded O_3 levels within a few percent of each other.

Figure 1 shows the maximum one-hour averaged O_3 level calculated as a function of AHC and NO_x with no NHC emissions. The dot indicates the result obtained for present-day AHC and NO_x levels. The calculated maximum O_3 at this point of 0.150 ppmv is in excellent agreement (although perhaps fortuitously) with the maximum O_3 measured at Conyers of 0.147 ppmv. On the basis of this figure one would project that a 30% reduction in AHC would be needed to reduce O_3 from 0.15 ppmv to the NAAQS of 0.12 ppmv. However as illustrated in Figure 2, this projection changes considerably if NHC are included.

In Figure 2 the maximum O_3 levels calculated as a function of AHC and NHC with NO_x held at present-day levels are illustrated. The vertical dotted-line indicates the results when AHC are held constant at present-day levels; by following this line upward from the x-axis the effects of adding NHC emissions to the existing NO_x and AHC emissions can be explored. Similar to Lurmann et al, we find that adding NHC to the anthropogenic emissions has a very small effect on O_3; for instance the addition of 30 kg/km^2 of NHC causes only a 10% increase in O_3, from 0.15 ppmv to 0.165 ppmv. However it would not be correct to conclude that NHC can be neglected. For these high emission rates, there is an over-abundance of hydrocarbons and, as a result, O_3 responds non-linearly to any hydrocarbon addition. Thus note in Figure 2 that increasing AHC above present-day levels also has a very small impact on O_3. Furthermore NHC can generate significant O_3 levels by themselves. Note in Figure 2 that with AHC set to 0, maximum O_3 levels of 0.08, 0.11, and 0.12 ppmv were obtained for NHC emission rates of 30, 40, and 50 kg km^{-2}, respectively.

Because of O_3's non-linear response to hydrocarbons, the presence of NHC can have a profound impact on the effectiveness of an O_3-abatement strategy based on AHC reductions. With no NHC emissions, the results in Figure 2, similar to those in Figure 1, imply that a 30% reduction in AHC emissions would be adequate to reduce O_3 to 0.12 ppmv. However for an NHC emission rate of 30 kg/km^2 (our estimate of the Atlanta-area isoprene emission rate), a 70% AHC reduction would be needed. For NHC emissions of 50 kg/km^2 (our estimate of the total NHC emission rate), O_3 remains above the NAAQS even after AHC emissions are completely eliminated. In fact we find that for NHC emissions of 30 kg km^{-2} or greater, the percentage reduction in NO_x emissions needed to bring O_3 down to 0.12 ppmv is smaller than that required of AHC emissions.

While our results should be viewed cautiously because of the large uncertainties in the AHC and NHC emissions, a comparison of our results with the observations of Westberg and Lamb (5) suggests that the emission rates we have used are not unreasonable. From early morning measurements at three Atlanta locations, Westberg and Lamb concluded that NHC constituted 2 to 7% of the city's total non-methane hydrocarbon burden. In the model, using present-day AHC levels and a NHC emission rate of 50 kg km^{-2}, the isoprene concentration never exceeded 2.5% of the total hydrocarbon burden.

CONCLUSION

While the effects of NHC are not currently factored into the nation's urban O_3-abatement strategy, calculations presented in this work suggest that it should. The emissions of NHC can be significant especially in cities in the southeastern U.S. such as Atlanta. Furthermore, EKMA model calculations tuned to simulate an O_3 episode in Atlanta indicate that NHC can have a major effect on O_3. In particular the calculations suggest that NHC can profoundly influence the predicted effectiveness of an O_3-abatement strategy based on AHC reductions. For a relatively modest NHC emission rate, the model indicates that NO_x reductions would more effectively reduce O_3 than would reductions in AHC. For a large but not unrealistic NHC emission rate, the model predicts that even if AHC emissions were completely eliminated, O_3 levels would still remain above the 0.12 ppmv NAAQS.

Because of the large uncertainties associated with our model calculations our results should be viewed with caution. In spite of these uncertainties however, the results demonstrate the potential importance of NHC to urban photochemical smog and the danger of pursuing an O_3-abatement strategy which ignores their effect. We believe that an intense investigation of NHC, focusing on their rates of production and atmospheric chemistry, is needed before a reliable strategy for O_3-abatement can be formulated.

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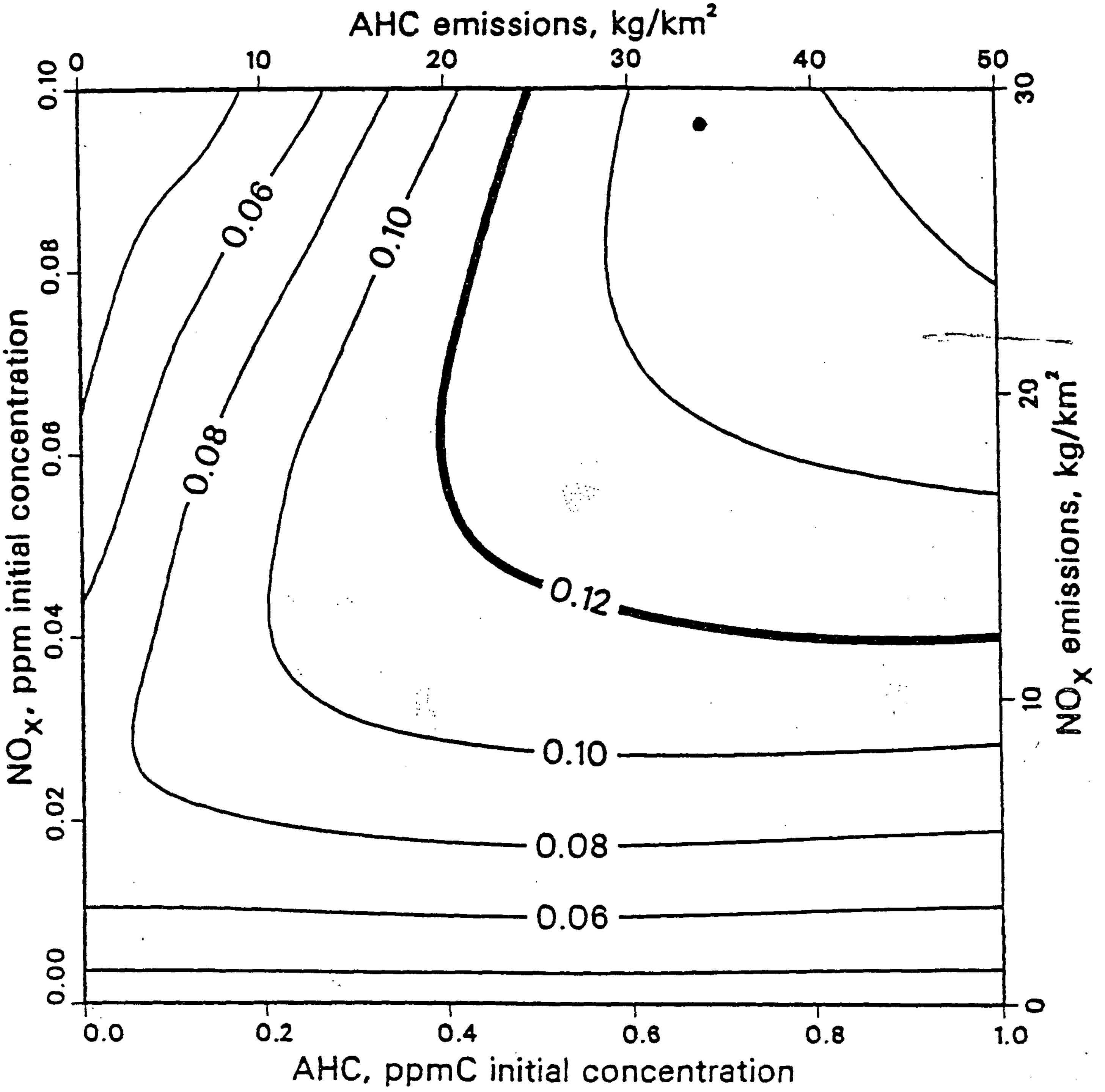
FIGURE CAPTIONS

Figure 1. Isopleths of the maximum, hourly O_3 levels (in ppmv) calculated as a function of NO_x and AHC with NHC emissions set to 0. The solid dot indicates the O_3 levels obtained for present-day conditions (i.e. an initial AHC concentration of 0.68 ppmv, and a total daytime AHC emission rate of 34 kg km^{-2}, an initial NO_x concentration of 0.096 ppmv, a total daytime NO_x emission rate of 10.8 kg km^{-2}). Variations in AHC or NO_x levels are explored in the model by varying the AHC or NO_x initial concentration and emission rate simultaneously. EPA recommends that diagrams like this one be used by state agencies making emission control projections.(18) Since a reduction in AHC emissions from 34 to 24 kg km^{-2} reduces O_3 from 0.15 to the NAAQS of 0.12 ppmv in this figure, we would project, following the EPA procedure, that a 30% reduction in AHC emissions would be needed to bring Atlanta into compliance with the Clean Air Act.

Figure 2. Isopleths of the maximum hourly O_3 levels (in ppmv) calculated as a function of AHC and NHC (as isoprene) with NO_x set at present-day levels. The dotted-line indicates the results obtained with AHC held at present-day levels. Note that even if AHC emissions are 20 or 30% higher than presently estimated, NHC emissions would still affect emission control projections.



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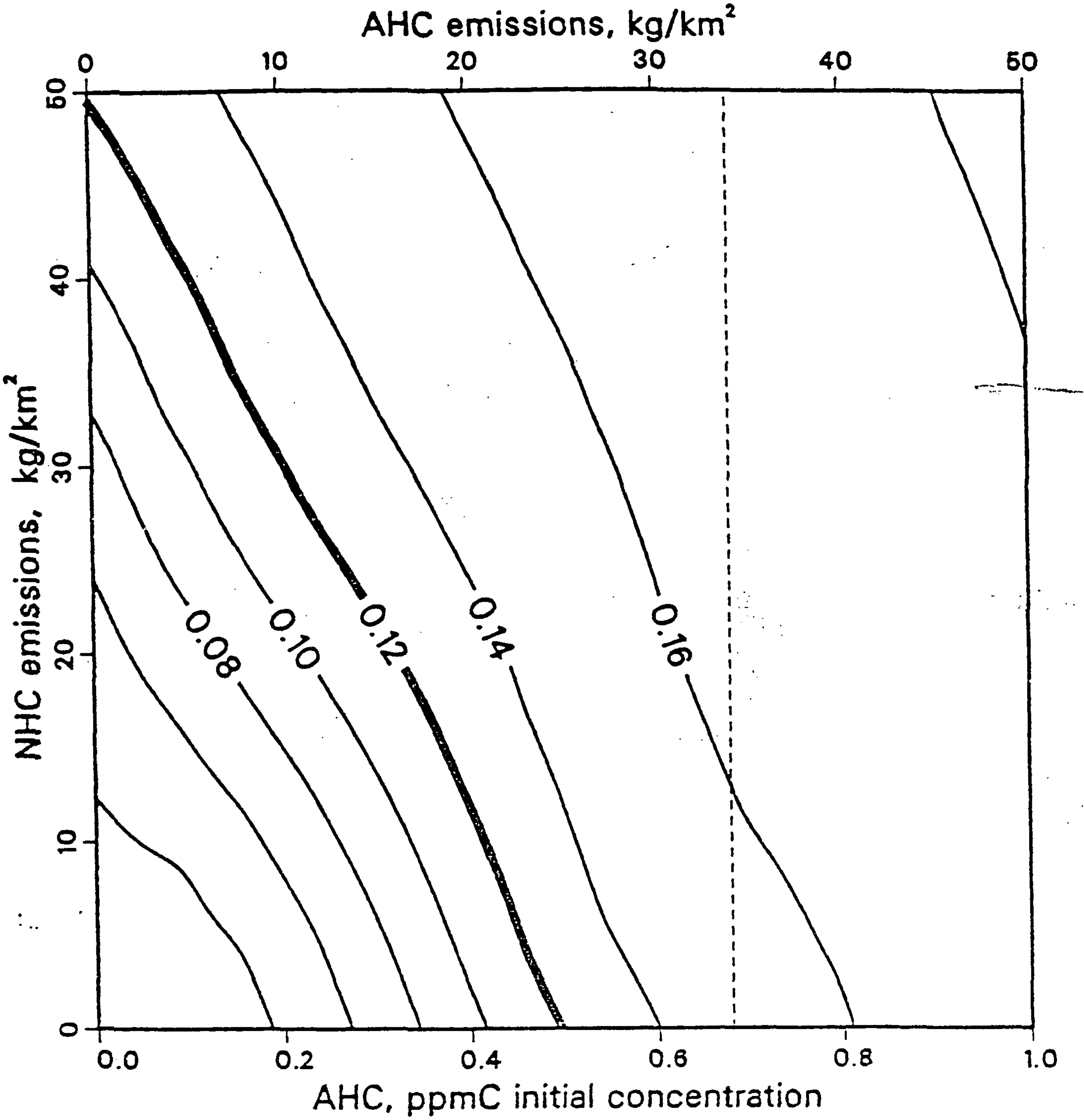

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