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INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 - ANALYSIS OF EVIDENCE AND VIEWPOINTS

Part IV. The Issue of Natural Organic Emissions

Environmental Sciences Research Laboratory
Office of Research and Development
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INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 — ANALYSIS OF EVIDENCE AND VIEWPOINTS

Part IV. The Issue of Natural Organic Emissions

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ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a followup review/analysis effort. The followup effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

In Part IV, the issue of natural organic emissions, measuring them and assessing the role they play in air quality, is discussed by Peter E. Coffey of the New York State Department of Environmental Conservation, Albany, N.Y., and Hal Westberg of Washington State University, Pullman, Washington.

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INTRODUCTION

Basil Dimitriades and A. Paul Altshuller

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The one hundred or so presentations and discussions at the Conference revealed the existence of several issues and prompted EPA to sponsor a followup review/analysis effort. Specifically, this followup effort is to review carefully and impartially and analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere) and to attempt to resolve some of the oxidant-related scientific issues. This review/analysis effort has been contracted out by EPA to scientists (who do not work for EPA or industry) with extensive experience and expertise in the area of photochemical pollution occurrence and control. The first part of the overall effort, performed by the EPA Project Officer and reported in a scientific journal (1), was an explanatory analysis of the problem and definition of key issues, as viewed within the research component of EPA. The reports of the contractor expert/reviewer groups offering either resolutions of those issues or recommendations for additional research needed to achieve such resolutions are presented in the volumes composing this series.

This report presents the reviews/analyses prepared by the contractor experts on the issue of natural organic emissions. In the interest of completeness the report will include also an introductory discussion of the issue, taken from Part I. The reviews/analyses prepared by the contractor experts follow, along with the experts' comments on each other's reports.

THE ISSUE OF NATURAL ORGANIC EMISSIONS

Basil Dimitriades and A. Paul Altshuller

This issue was originally raised as a result of an early report that, on a global basis, rates of organic emissions from vegetation are considerably higher than those from man-made sources (2). Although such natural emissions and the anthropogenic emissions are for the most part geographically segregated, it is nevertheless reasonable to suspect that natural organics, either emitted within the urban or nonurban area or brought in through transport, could contribute to the ambient oxidant problem to an important degree. These suspicions became considerably stronger — and for obvious reasons — as a result of two recent findings: The occurrence of a pervasive rural oxidant problem (3), and the high reactivity of terpenes (4,5). In either case, the finding could be interpreted to mean that natural organics may constitute a significant source of oxidant. As in the case of stratospheric ozone, the question regarding the importance of natural emissions as an oxidant source needs to be answered only for the purpose of more accurately estimating the benefits from man-made emission control.

From a first glance examination of the evidence relevant to this issue, it becomes immediately apparent that certain components of the issue have obvious answers or have been resolved based on scientific evidence, whereas other components remain uncertain or unresolved. For example, it is unquestionable that vegetation does emit organic vapors and that some of these vapors (terpenes) play the dual role of oxidant precursor and oxidant destruction agent. What is in question is (a) the nature (other than terpenic) and emission rates of such vapors, and (b) the net effect upon oxidant of the atmospheric reactions of natural organics. Some evidence relevant to these questions does exist but does not necessarily provide answers. Researchers

are, in general, less familiar with the natural organic emissions, and this lack of familiarity naturally casts doubts over all types of evidence available, from data on chemical identity and ambient concentrations to information on atmospheric photochemistry and on emission and sink processes. It is because of this general lack of confidence that the specific questions offered here as the questions at issue include some of relatively basic nature. These questions are:

1. Given the fact that terpenes are emitted by vegetation, does it automatically follow, or is there evidence to show, that terpenes are present in ambient air at levels commensurate with their emission rates? Are such levels significant?

While it is almost certain that these questions can be answered one way or another, based on evidence available, the judgments needed here are not only on the interpretation of such evidence but also on the reliability or overall quality and conclusiveness of the evidence available.

2. Accepting the possibility that terpenes are present in ambient air at significant levels, does the available evidence — from either direct or indirect data or theoretical inferences — support a predominantly ozone-producing or ozone-destruction role or both roles for such terpenes?

In deliberating such a question, the distinction should be made and recognized between urban and rural atmospheres. It should be clarified and stressed here that the fact that the current concern is mainly about the urban problem does not justify overlooking the rural situation. One reason for this is that oxidant formed in rural areas could contribute importantly to the urban problem. It is precisely this possibility that should be explored in deliberating this question. To further explain, it is conceivable that in rural areas, that is, in forested and thinly, but nevertheless significantly, populated areas, the terpene and anthropogenic emissions could yield mixtures with organic composition and organic-to-NO_x ratios conducive to oxidant formation.

This is one theory that could explain the "oxidant/ozone blanket" phenomenon — of uniform variation of oxidant/ozone levels over large areas — observed in parts of the country (6). Since this "blanket oxidant/ozone phenomenon" could be explained by several theories, namely,

(a) photochemistry of terpenes mixed with anthropogenic emissions in rural areas,

(b) photochemistry of anthropogenic emissions (alone) in rural areas,

(c) pollutant transport from large urban centers, and

(d) stratospheric ozone intrusion,

the judgment called for here is for the relative credibilities of the four theories, and specifically, for the credibility of the terpene theory.

The third question is essentially a solicitation of evidence and/or viewpoint — reported or unreported — on the existence and photochemi- [illegible] o lution role of natural organic emissions other than terpenes.

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REVIEW AND ANALYSIS

Peter E. Coffey

OZONE GENERATION FROM NATURAL HYDROCARBONS

This is a review of the role of natural organic emissions in the production or destruction of ozone in the lower troposphere. The papers reviewed here present a fairly comprehensive picture of the present knowledge on this subject. Throughout the papers many areas of general agreement emerge where a few years ago there was controversy. Some rather puzzling results are presented and much controversy or disagreement still exists. This indicates that more research is needed before the role of the natural hydrocarbons in the production of ozone is firmly established.

Those papers reviewed here report on the results of field studies, smog chamber work, source inventories, and model construction. Since ozone is also generated from anthropogenically produced hydrocarbons and transported to the surface from the stratosphere, some papers dealing with these aspects of ozone are included in the review because they clarify the problem.

The first paper to be reviewed is one with which I am somewhat familiar. This paper, "Evidence of Atmospheric Transport of Ozone into Urban Areas" by Coffey and Stasiuk, makes a rather strong case for the advection and mixing of air from a regional blanket of ozone as the source of much of the ozone measured in urban areas. The observed diurnal fluxuations in ozone concentrations is interpreted to be the result of local ozone destruction by nitric oxide during the hours of nocturnal inversion followed by advection and downward mixing of upwind ozone after the breakup of this nocturnal inversion. In

support of this theory, the paper shows that, above the nocturnal inversion layer, high concentrations of ozone regularly persist throughout the nighttime hours. Additional data in support of these observations have been collected at our site near the top of the World Trade Building in New York City. This data supplemented by instrumented aircraft flights further shows that the ozone concentrations in a city as large as New York are dominated by the upwind source (7).

It has been hypothesized that the nitric oxide levels in urban areas act as ozone shields not only at night under the nocturnal inversion but during the day. This implies that upwind ozone is of no consequence in the urban ozone concentration. However, this paper reports on several cases where ozone concentrations in urban areas exceeded the national ambient air quality standard during the nighttime hours. Since ozone is not generated during these hours this ozone must have been transported into the urban sites from upwind sources. Close examination of the meteorological conditions during these occasions reveals that the nocturnal inversion was destroyed by surface level winds. At the same time the regional ozone concentration was sufficiently high to account for the observed nighttime urban maximums.

The mixing of surface air with the air aloft, but still in the mixing layer, is essentially an eddy process. Thus even if sufficient nitric oxide (NO) is produced in the urban area to destroy the incoming ozone (O_3), the mixing process being what it is must surely result in a "perceived" NO, O_3 reaction rate much slower than the chemical reaction rate.

The authors of the paper make no statements concerning the sources of the observed regional ozone blankets. However, in work since completed it appears that much of the ozone seen during ozone episodes downwind of large urban areas is anthropogenically produced. This is especially true along the east coast of the United States. In several ozone concentration isopleths compiled from 95 reporting stations the urban effect along the northeast sea coast has been shown. However, the source, or sources, of the ozone over the rest of the region covered by the isopleths was not clear.

The paper "Important Factors Affecting Rural Ozone Concentrations" by F.L. Ludwig, et al. (8) reinforces the assertions made by the Coffey and Stasiuk paper that violations of the national ambient air quality standard on ozone occur over extended areas.

By using the trajectory analysis of Heffter and Taylor (9), the authors try to find correlations between various meteorological and emission factors in the trajectory of the air mass. Given what is now known about the existing meteorological conditions during ozone episodes, it is not surprising that positive correlations exist for ozone concentration and temperature during the last 12 hours of the trajectory. The absence of correlations between hydrocarbon emissions and ozone is somewhat surprising as one would expect positive correlations between these two components if anthropogenic emissions cause a significant portion of the ozone. The correlations between ozone and NO_x are really not clear unless the nitrogen oxides are "spiking" an air mass already rich in hydrocarbons.

What is also interesting about the paper is that of the eight regions associated with extensive violations of the national ambient air quality standard, two regions are not located in or near areas associated with heavy anthropogenic emissions. If natural sources or conditions are responsible for these occurrences as the authors suspect, the air quality standard is unrealistic. On the other hand, the ozone precursors may be carried longer distances than the authors suspect.

Following up on the first two papers, the paper "Urban-Nonurban Ozone Gradients and Their Significance" by Martinez and Meyer (3) documents the effectiveness of the urban plume as an ozone generator. Sufficient cases are cited to conclusively support the thesis that plumes from the larger urban centers are capable of generating significant amounts of ozone. While it is not stressed in the paper, those days on which ozone generation in urban plumes is greatest tend to be days in which the regional ozone concentrations reach their higher levels.

The directly observable downwind effect of ozone generation, ranging up to 180 miles for the largest urban areas, seems to be in excellent agreement with most of the other papers I have seen on the subject and with the work we have done in New York.

At this point several questions regarding the ozone produced in these plumes arise. Foremost among these questions is the desire to arrive at a measure of the total ozone quantity produced.

Some very valuable information regarding this question is to be obtained from the paper "Ozone Formation in the St. Louis Industrial Plume" by White, Blumenthal, Anderson, Husar, and Wilson (10). This paper, presented at the International Conference on Photochemical Oxidant Pollution and its Control, September 1976, provides some information on the dispersion of the St. Louis urban plume during typical ozone episodes. The relative isolation of this city from other large cities eases the task of data interpretation.

The authors made several cross-sectional and vertical profile flights in the plume during some days on which ozone production would be expected. The plume was monitored well over 200 km for aerosols and over 160 km for ozone. Of interest was the observation of significant ozone generation within the plume. This is in agreement with the findings of the previous paper.

The cross-sectional plume flights made up to 165 km from St. Louis reveal a relatively small amount of cross-sectional size increase in the plume with distance.

If the estimated nonmethane hydrocarbon emissions are correct, then the ozone yield in the plume is close to the theoretical stoichiometric upper limit. This raises the question of both upwind hydrocarbons being advected into the city and hydrocarbons from downwind sources being ingested into the plume. If this is occurring, natural hydrocarbons could be playing a significant role.

After approximately 120 km on a typical day the net generation of ozone seems to be less than the net destruction of ozone in the plume. It would be interesting to attempt more distant cross-sectional flights on the plume extending if possible into the second day. That portion of the plume that does not get trapped under the nocturnal inversion layer should remain intact; ozone observations on the second day coupled with NO_x and hydrocarbon measurements should provide worthwhile information on the long-range transport of anthropogenically produced ozone and the ozone generating capability of the less reactive hydrocarbons.

The report "Natural Emissions of Gaseous Organic Compounds and Oxides of Nitrogen in Ohio and Surrounding States" by the Research Triangle Institute (11) certainly addresses a basic question. To ascertain the effects of natural hydrocarbons the quantity of emitted material must be known. I believe that the paper does a reasonably good job in estimating the emissions and making the reader well aware of the guesswork that went into the estimate. However, the manner in which the data is presented is not very suitable to the subject of photochemical ozone generation. It appears that anthropogenic hydrocarbon emissions occur at a fairly uniform rate over a 12-month period. This is not true for natural emissions. They occur mostly during the growing seasons, which run for less than one half of a year in the states cited in the report. Of equal significance is the fact that regional excursions of the national ambient air quality standard on ozone almost always occur during the meteorological conditions of maximum sunlight, high temperatures, and high humidities. It is precisely under these conditions that natural emissions from plants and trees would occur at a greatly increased rate. Because of the high temperatures, additional hydrocarbons would also be released from the soil where they have been stored. During these periods, anthropogenic emissions do not increase very much. Thus the ratio of natural to anthropogenic hydrocarbon emission during an ozone episode must be many times the yearly ratio given in this report.

The paper "GC-Chemiluminescence Method For the Analysis of Ambient Terpenes" by Robert L. Seila (12) discusses a new method for measuring ambient

terpene concentrations. Qualitatively the method sounds reasonable. We have investigated Quickert's technique of ozone chemiluminescent measurement of olefins and feel that it might have some potential when used as described in this paper. Because of efficiency problems encountered with the Tenax cartridges, it is quite evident that the method described here is not yet a quantitative one. However, the levels of terpenes seen by the authors in the pine forest are in the same "ball park" as measurements we and others have made. I am somewhat surprised that only two terpenes were discovered.

The slide talk on "Recent Field Studies" by R.A. Rasmussen is very interesting and pertinent to this review in that it characterizes the air found at several locations around the country. Several of these areas are in the approximate locations of studies cited in many of the papers reviewed here.

As Rasmussen notes, much of the Midwest and east coast rural areas available for study are in fact intercorridor regions between urban centers. The air at Whiteface, New York, can usually be classified as rural while a rural site in Wooster, Ohio, is intercorridor. It is noteworthy that mention is made of the fact that very sparse data exists on background levels of NO, which probably is the major NO_x emission.

His characterization of the Ohio air as a spent air mass in his study agrees quite well with the findings of the Lonneman paper reviewed here. Rasmussen's statement to the effect that rural air has the potential to produce 20-60 ppb of ozone from the irradiation of natural oxidant precursors is probably in the right range judging from what we observe in New York State.

Rasmussen's statement that urban input into rural areas is by way of direct ozone advection has been demonstrated by many researchers. However, subsequent reaction, especially on the following day, of less reactive anthropogenic hydrocarbons to produce substantial ozone concentrations while possible still has not been demonstrated in field measurements to my satisfaction.

I disagree with Rasmussen's statement regarding the NO shield at the urban boundary. Indeed, we see in New York many instances of rural ozone,

whether it be of natural or anthropongenic origin, entering the urban area in concentrations above the 80 ppb standard. For example, a 2-year study in the New York City area showed that during regional ozone episodes high concentrations of ozone (often exceeding the ambient air quality standard of 0.08 ppm) remain above the nocturnal inversion layer over the city (7). The daytime ground-level buildup of ozone is initially due in the main to the downward mixing of this ozone after the breakup of the inversion.

Both airborne and fixed station measurements indicate that daytime ozone concentrations are greater than those in the early hours measured above the inversion. Ground-level ozone concentrations in the air entering the city often increase throughout the early afternoon. This coupled with the evidence of significant concentrations of hydrocarbons in air entering New York City, presumably from upwind sources, suggests photochemically produced ozone is added to that transported from above the nocturnal inversion. Most probably there are downwind effects resulting from photochemical reactions involving precursors from New York City, and this is suggested from an analysis of regional ozone concentration isopleths; but the levels of ozone measured within New York are generally most reflective of the quality of the air advected into the city.

Regarding long range transport we agree that ozone can be transported above the nocturnal inversion layer with only small losses. Case studies made at Whiteface, New York, reveal transport of ozone in excess of 80 ppb for distances exceeding 200 miles (13).

The paper "Analyses of C_5 to C_{10} Hydrocarbons in Rural Atmospheres" by R.A. Rasmussen and M.W. Holdren (14) is one of a series of papers reporting on actual hydrocarbon levels in remote areas. Of particular interest are the observations concerning both the concentrations of rural hydrocarbons on the basis of specie and the number of species detected. The 10 to 60 compounds generally found in concentrations at the parts per billion level and the range in atmospheric organic burden from several to over 100 ug/m^3 underlines the difficulty in evaluating the effect of natural hydrocarbons on the production or destruction of ozone.

The almost complete absence of terpenic hydrocarbons in the samples taken 100 yards from a forest composed mostly of coniferous trees is puzzling. Apparently the terpenes react rather quickly if they were present in the forest itself. It would have been useful if the authors had also sampled within the confines of the forest.

The most remote area sampled was also the inland site with the lowest concentration of hydrocarbons. However, the time of year (November 6th) would not be the time of the most vigorous organic emissions.

As interesting and informative as the data collected by the authors are their collection techniques. The Cryocondenser technique that they describe seems to be well suited to the detection of trace concentrations of natural C_5 - C_{10} hydrocarbons.

The paper "Ozone and Hydrocarbon Measurements in Recent Oxidant Transport Studies" by William A. Lonneman (15) differs from the remote rural work performed by Rasmussen in that Lonneman did much of his sampling in the urban plume.

It seems quite reasonable to use the ratio of olefin to acetylene as a means to measure olefin reaction. The observation that as much as 70% of the olefins had reacted by late afternoon is not surprising in light of the urban ozone plumes observed by many researchers.

This work was performed in the intercorridor regions between large urban areas. In these regions especially on the east coast, northeast of the New York City/New Jersey area, it is not surprising that the hydrocarbon mix frequently resembles that of a diluted urban hydrocarbon mix with the loss of the more reactive compounds during the transport process. However, the author does not have sufficient data to ascribe all or even most cases of elevated ozone concentrations in rural areas to the transport of urban pollutants.

The results of the author's studies of natural hydrocarbon emissions in a loblolly pine forest appear quite similar to the results we have obtained from

a pine forest in northern New York. In work submitted for publication ("Measurement of Terpenes and Other Organics in an Adirondack Mountain Pine Forest" by R. Whitby and P. Coffey), terpene concentration was found to range from 10-45 $\mu g/m^3$ within the forest and 2-20 $\mu g/m^3$ downwind. Unidentified lower molecular weight species were measured in concentration ranges of 20-80 $\mu g/m^3$ within the forest and 5-25 $\mu g/m^3$ downwind. Significant terpene levels were also observed on the mountain summit (7-27 $\mu g/m^3$). The summit is several hundred feet above the tree line.

No change in ozone concentration was noted upwind or downwind of the forest.

Another paper addressing terpene reactivity is "Atmospheric Reactivity of Monoterpene Hydrocarbons, NO_x Photooxidation and Ozonolysis" by E.P. Grimsrud, H.H. Westberg, and R.A. Rasmussen (16). Of interest in this paper is the high reactivity of all the olefinic compounds. However, the most reactive of the terpenes have RO_3/RNO_x values considerably greater than unity. Again depending upon the NO_x levels and background O_3 concentration, these terpenes may very well first react with ozone in the ambient air. Thus it is quite conceivable that these species may not produce ozone under existing ambient conditions. The next paper seems to address this question more fully.

The paper "The Chemistry of Naturally Emitted Hydrocarbons" by Bruce W. Gay, Jr. and Robert R. Arnts (17) attempts to resolve the basic question of actual ozone generation by isoprene and several terpenoid hydrocarbons.

It is difficult to evaluate individual smog chamber experiments from a distance since so many imponderables are involved.

The authors report, for their experiments, optimum hydrocarbon/nitrogen oxides ratios for ozone formation. These optimum ratios are rather low, being only 1.7 for limonene. This series of observations seems to agree quite well with the letter report of October 8, 1975, from Dr. H. Westberg of Washington State University, to Dr. Basil Dimitriades of the Environmental Protection

Agency. In reviewing these two papers, I wish that the HC/NO_x ratio were not reported as ppm compound/NO_x in one paper and ppm C/NO_x in the other.

One comment that concerns both papers is the generation of an aerosol. With such high concentrations of nitrogen oxides and hydrocarbons one might expect, under the intensity of radiation used, enough aerosol generation to keep the aerosol concentration of submicron particles very high. Does this newly available surface affect the concentration of resultant species?

The statement in the Gay and Arnts paper about the extremely high hydrocarbon/nitrogen oxides ratio in rural areas bothers me somewhat. While enough measurements of natural hydrocarbons have been taken to give us an estimate of their concentration in some areas, the nitrogen oxides levels are not known as well. This is an area that I feel needs more work. Thus I agree with the authors that more experimental field and laboratory work is necessary before final conclusions are made.

Tai Yup Chang and Bernard Weinstock in their paper "Net Ozone Formation in Rural Atmospheres" (18) approach the problem of rural ozone from a different angle than does the previous paper. They examine the ozone-producing ability of the less reactive hydrocarbons, those which might be seen in an urban plume after the depletion of the quickly reacting species. Their acknowledgment of the controlling role played by the hydrocarbon/nitrogen oxides ratio is quite consistent with that of most other workers in the field. The levels of nitrogen oxides in rural areas, however, as pointed out by the authors, are still not accurately known.

The authors' modified model with the HO radical source and heterogeneous wall reactions relies heavily on the existence of the HO radical in the laboratory smog work. Unfortunately, this specie is rather difficult to measure. Here again, because of the imponderables involved in smog chamber work and modeling, more data from field studies would be helpful in settling the issue of nonreactive hydrocarbons as a significant source of ozone.

The authors claim that detailed hydrocarbon compositions measured in rural areas do not show much evidence of accumulated species of less reactive anthropogenic hydrocarbons. Again this claim runs counter to observations made in rural areas that should be classified as intercorridor between urban areas. However, in remote areas such as Whiteface Mountain, New York, there appear to be almost no anthropogenic hydrocarbons present.

The last paper to be reviewed is "The Kinetic Ozone Photochemistry of Natural and Perturbed Nonurban Tropospheres" by T.E. Graedel and D.L. Allara (19). Unfortunately, most of the compounds reacting in the atmosphere are present in quantities that are very poorly known (NH_3) or are estimated on a global basis. This can be expected to lead to large errors in making predictions on a regional basis. The assumption that all compounds are fully mixed within the mixing layer is not supported by measurements, especially with regards to the natural hydrocarbons. For example, all investigators see a rapid concentration drop-off with increasing altitude. I question if, at this point, we are sufficiently knowledgeable about the chemical structure of the rural atmosphere to make meaningful predictions, especially regarding a reactive, nonterminal compound such as ozone. I do not want to sound overly critical of this paper because I believe that this type of model, as more data becomes available, will enable us to understand what we now must guess at.

In attempting to ascertain the contributions of the natural hydrocarbons to the production of ozone, it is useful to consider the contributions of other sources. Much has been said already about the transport of urban ozone and its precursors into rural areas and downwind urban areas. Additional ozone may be descending from the stratosphere in significant amounts. A paper being submitted for publication by Husain, Coffey, Meyer, and Cederwall titled "Ozone Transport From Stratosphere to Troposphere" addresses the stratospheric ozone input in the New York region during several typical summertime ozone episodes. This work reports on simultaneous measurements of ozone and ^7Be (debris from the stratosphere and upper troposphere). Admittedly the fate of ^7Be and ozone are different, the ^7Be residing on aerosol particles and the ozone being a reactive gas. The data indicates increased ^7Be activity during

all but the final day of a typical ozone episode. However, indications are that the amounts of stratospheric ozone reaching the surface are minor compared to tropospheric ozone. More qualitative answers will result from a just completed, similar study in which a radioisotope of phosphorous, from the stratosphere, was also measured.

In summary there are several important aspects of rural ozone concentrations that are agreed upon by most researchers:

- There exist large regional concentrations of ozone in excess of 80 ppb.
- These regional episodes of elevated ozone concentrations are frequently seen during the warmer months in regions under the influence of the backside of a high pressure system.
- During these times the plumes of large urban centers often generate ozone. Such ozone in excess of background, which may itself be greater than 80 ppb, can be distinguished at distances of 180 miles from the plume source.
- Many of the naturally emitted hydrocarbons, especially the terpenes, are very reactive. Whether these compounds produce significant amounts of ozone is still unresolved in my mind. Better measurements of rural NO_x levels coupled with hydrocarbon measurements might completely settle this question.

The concentrations of natural hydrocarbons that have been reported are generally in the same order of magnitude, that is, at most, several parts per billion per specie.

As with most investigators, we have noticed a very rapid decrease in concentration of the most reactive natural species, the terpenes, as we measure concentrations farther away from the source areas. However, at least in the Whiteface area, the drop-off in concentration is not as sharp as seen by some researchers elsewhere. For example, we have measured, at ppb concentrations, terpenes on the summit of Whiteface several hundred feet in elevation above the tree line.

One question that, judging from the papers reviewed, seems to be unresolved is the effectiveness of the urban NO shield in isolating the urban area from the intrusion of rural ozone. Our studies in New York clearly show the ineffectiveness of this shield. Hydrocarbon and NO_x measurements in the New York City area show that much of the ozone seen in the city originates from upwind urban areas. During the same time periods the origins of the high ozone concentrations in the northern New York area are not so clear. The hydrocarbon mix is essentially natural in low ppb per specie concentrations. However, trajectory analysis carried out for several night-long ozone episodes on the summit of Whiteface mountain indicate that ozone can easily be transported, in concentrations above 80 ppb, 200 miles.

During ozone episodes we see clear evidence of increased stratospheric influence as measured by ^{7}Be activity. However, in work soon to be submitted for publication, we do not see clear indications that this stratospheric ozone is the major component of the total ozone. In fact, evidence points toward a tropospheric source as the major contributor.

On the issue of reactivity and the ability of the lesser reactive, anthropogenic hydrocarbons to generate significant concentrations of ozone on second and subsequent days after emission, I would like to see more field evidence.

As I have suspected, the urban plume does not spread out very much over the course of a day's travel. This was clearly shown in the Blumenthal *et al.* paper I noted in the review. With this in mind, I suggest an experiment to pick up a slug of an urban plume, such as the one from Saint Louis, on the second day after generation. Since the ozone concentration in the plume had begun to subside toward background levels by the end of the first day, second day ozone generation, if it is to be of regional significance, should be extremely easy to detect. This type of data would be extremely useful in evaluating the reactivity orientated smog chamber work.

The prime sources and mechanisms producing rural ozone might very well change in different regions of the country. Direct stratospheric transport

could much more frequently be the dominant ozone supplier in those states just to the lee of the Rocky mountains than in the Eastern States.

Certainly, those areas, urban or rural, that are typically under the plume of large urban areas during prime photochemical generation periods are subject to massive influxes of anthropogenically produced ozone. The influence of this ozone has clearly been shown to persist frequently for over 100 miles.

The case is not clear to me for regional ozone concentration excursions in excess of 80 ppb where the influence of urban plumes has not been demonstrated. In these areas, I believe that it is quite plausible that the photochemistry of terpenoid compounds, perhaps with some anthropogenic emissions, is responsible for most of the ozone recorded.

COMMENTS BY HAL WESTBERG

In analyzing Dr. Peter Coffey's review on oxidants, I have picked out several important issues and will comment on each below. In each case a quote from the Coffey review will be listed and my response will follow.

> "This data---------shows that the ozone concentrations in a city as large as New York are dominated by the upwind sources."

I think this is probably true in certain parts of the eastern United States when a high pressure system is situated off the Atlantic coastline, resulting in southerly gradient wind flow. A meteorological condition such as this is conducive to oxidant production and pollutants such as ozone certainly are moved into a region from upwind sources. It should not be forgotten, however, that emissions from a city such as New York contribute greatly to ozone buildup in downwind areas. This has been documented very clearly for the area downwind of New York City (EPA Report 600/3-77-017) (20). In other words, while ozone moving into the city might be the predominant source for oxidant measured in the actual *urban* area, the much higher ozone levels recorded in areas downwind of the city result primarily from urban emissions.

"The absence of correlations between hydrocarbon emissions and ozone is somewhat surprising as one would expect positive correlations between these two components if anthropogenic emissions cause a significant portion of the ozone."

I do not feel this is surprising at all. There is a large amount of guess work involved in estimating hydrocarbon emissions for a region. There is also a great deal of approximation involved in calculating air mass trajectories. When these two elements are combined, the chances of error are compounded even more. I believe there is sufficient *aerometric* data to prove that a good correlation does exist between ozone and hydrocarbon levels. The work conducted by EPA contractors in the Midwest during 1974 clearly showed that periods of high ozone were accompanied by higher hydrocarbon levels. For example, during the month of July, several migratory high pressure systems crossed the State of Ohio from northwest to southeast. These systems provided a relatively clean air situation as they first entered the state; however, the air quality deteriorated rapidly as the high moved to the southeast. Table 1 and Figure 1 show typical hydrocarbon and ozone data collected in the Canton, Ohio, area during the passage of an anticyclone. It is clear from this data that hydrocarbon levels were highest when ozone concentrations exceeded 80 ppb. Many other examples of this type are available in EPA technical reports that include aerometric data tabulations.

"The ratio of natural to anthropogenic hydrocarbon emissions during an ozone episode must be many times the yearly ratio."

I do not know of any evidence to support this contention. From aerometric data collected at rural sites, it is possible to document increases in anthropogenic hydrocarbon concentrations during ozone episodes; but no observations of increased natural hydrocarbon levels have been reported. Emission studies conducted by Zimmerman and Rasmussen at Washington State University (21) indicate that if any maximum occurs in natural hydrocarbon emissions, it takes place in the late fall as a result of decaying vegetation.

"Lonneman does not have sufficient data to ascribe all or even most cases of elevated ozone concentrations in rural areas to the transport of urban pollutants."

It is my impression from reading Lonneman's reports and talking with him that his data strongly implicates significant anthropogenic input whenever ozone levels exceed the Federal Air Quality Standard in rural areas. This has been demonstrated through correlations between acetylene and ozone, fluorocarbon-11 and ozone, as well as general increases in other anthropogenic pollutants (NO, NO_x, CO, etc.) during rural ozone episodes.

> "The case is not clear to me for regional ozone concentration excursions in excess of 80 ppb where influence of urban plumes has not been demonstrated. In these areas, I believe that it is quite plausible that the photochemistry of terpenoid compounds, perhaps with some anthropogenic emissions, is responsible for most of the ozone recorded."

It is my belief that terpene photochemistry contributes very little, if any, to the oxidant burden in rural areas. The reasons for this were discussed in detail in my review on "The Issue of Natural Organic Emissions." It is quite obvious from reading papers published by Dr. Coffey and his coworkers that they have channeled their research efforts into trying to prove that the regional "ozone blanket" results primarily from natural causes. However, at no time has data been presented that supports this contention. Their latest study involving ^{7}Be appears to rule out the stratosphere as a source for most of the ozone observed during episode periods. I feel that anthropogenic precursors must be considered the most important contributor to the ozone problems in the eastern United States.

TABLE 1. AFTERNOON LIGHT HYDROCARBON CONCENTRATIONS AT GROUND LEVEL AND ALOFT UNDER VARIOUS METEOROLOGICAL CONDITIONS

	July 16 Leading Edge of High with Northerly Winds (mixing depth ∿4000')		July 17 Stragnation Period with Light and Variable Winds (mixing depth ∿4500')			July 18 Trailing Edge of High with Southwest Winds (mixing depth ∿3500')				
	Ground	4000'	Ground	3300'	4300'	Ground	1000'	2300'	4000'	6000'
Ethane	7.0	5.0	15.5	17.5	8.0	9.5	8.0	10.5	7.0	5.5
Ethylene	3.5	4.0	3.5	4.5	4.0	3.0	4.5	3.5	2.5	3.0
Acetylene	1.0	*	1.5	1.5	2.0	1.5	1.5	1.5	*	*
Propane	3.5	2.5	7.5	11.0	10.5	5.5	6.0	7.0	4.0	4.0
Propene	1.0	.5	.5	2.0	1.0	.5	3.0	1.5	1.0	1.0
i-Butane	1.5	.5	4.5	8.0	5.5	3.5	4.0	3.5	3.0	2.0
n-Butane	3.0	1.0	8.5	14.5	11.0	7.0	7.0	8.0	6.0	5.0
i-Pentane	3.0	1.0	7.0	11.0	9.0	6.5	6.5	7.5	3.0	2.5
n-Pentane	1.5	*	3.5	6.0	4.5	3.0	2.5	3.0	2.0	1.5
	25.0	14.5	52.0	76.0	55.5	40.0	43.0	46.0	28.5	24.5

* = Less than .5 $\mu g/m^3$.

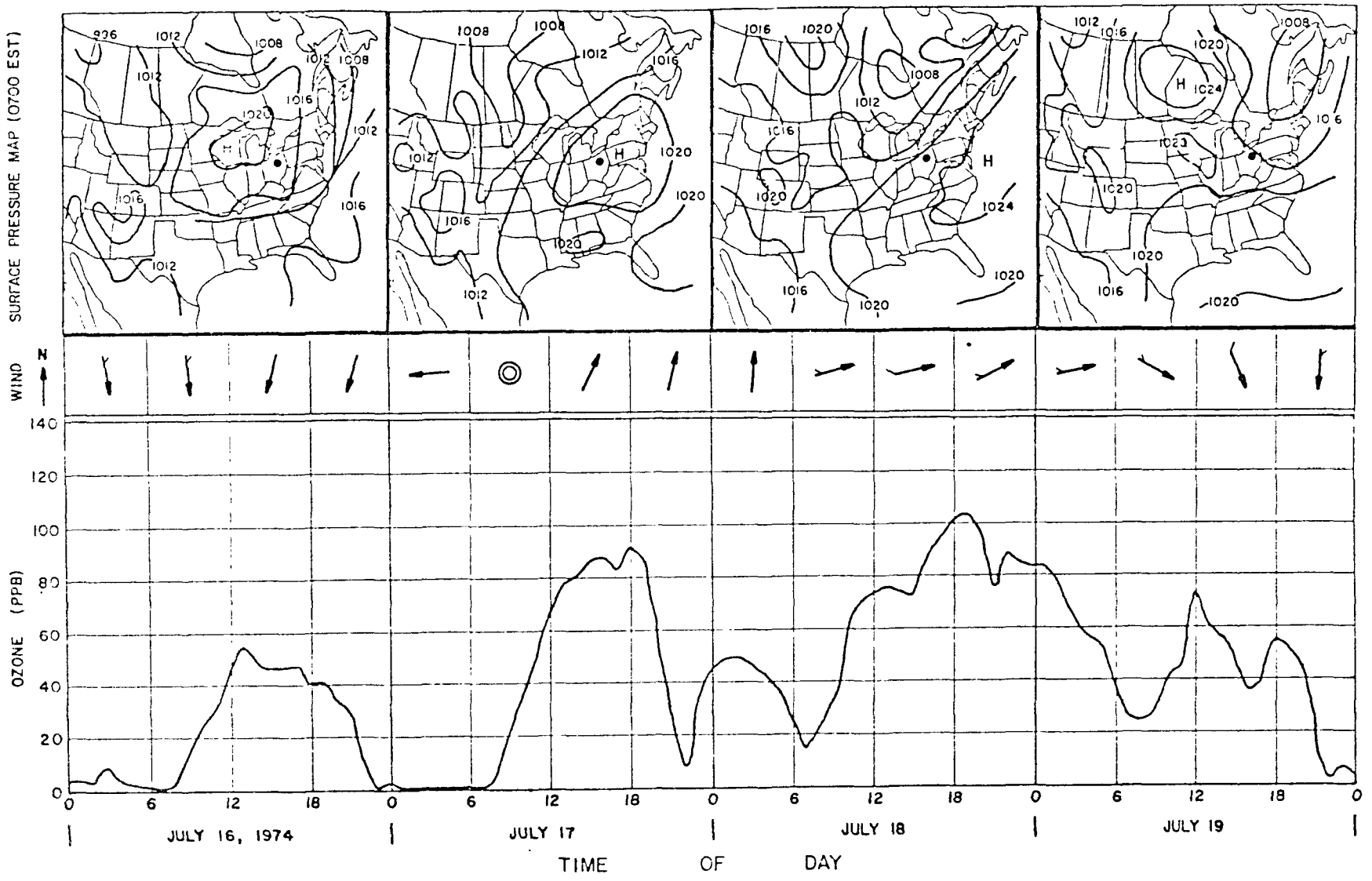

Figure 1. Ozone changes as high pressure system crosses Canton area.

REVIEW AND ANALYSIS

Hal Westberg

INTRODUCTION

The purpose of this paper is to provide an analysis of evidence and viewpoints concerning relationships between natural hydrocarbons and rural oxidant formation. The main topic areas to be addressed include:

- photochemical reactivity and oxidant-forming potential of natural hydrocarbons,
- identification, emission rates, and ambient concentrations of natural hydrocarbons,
- contribution of natural hydrocarbons to oxidant levels in rural atmospheres.

The second category will receive major emphasis in this review because, without a good understanding of ambient natural hydrocarbon levels, no estimate of their contribution to oxidant production in real atmospheres can be made.

PHOTOCHEMICAL REACTIVITY AND OXIDANT-FORMING POTENTIAL OF NATURAL HYDROCARBONS

Most of the studies dealing with terpene reactivity have been conducted by researchers at the University of North Carolina (UNC), Washington State University (WSU), and EPA-Research Triangle Park. The first evidence that natural hydrocarbons can produce ozone in a terpene-air-NO_x-$h\nu$ system was provided by the Ripperton group at UNC. Their studies also showed that large numbers of aerosol particles were produced when natural hydrocarbons were irradiated.

Beginning in 1972, the Washington State University group (5) initiated a gas-phase kinetic study designed to examine the reactivity of a number of monoterpene hydrocarbons that are known or expected to be present in ambient forest air. The study concentrated on two possible pathways by which monoterpenes could be initially altered in the atmosphere. One is represented by the irradiation of air samples containing nitrogen oxides in addition to the hydrocarbon of interest and using artificial light of wavelengths characteristic of natural sunlight. The other pathway examined was the reaction of ozone with the olefinic natural hydrocarbons.

The experimental procedure for the photolysis studies was patterned after that employed for the determination of hydrocarbon reactivity in urban areas. The ozone-hydrocarbon reactions were studied in a flowing kinetic system at reactant concentrations from about 0.1 to 5 ppm. Table 1 lists all the compounds examined and their NO_x photooxidation and ozonolysis rate constants. Since the relative reactivity of isobutene compared to many other hydrocarbons has been established, inclusion of it provided a means of placing monoterpenes on the overall hydrocarbon reactivity scale. It is evident from the WSU experiments that reactivity patterns for monoterpenes parallel in many respects those reported for simple olefins. Reactivity increases in the order saturated < aromatic < olefinic, and within the latter group, increased substitution on the double bond facilitated the reaction.

From the ozonolysis rates listed for all the hydrocarbons in Table 1, it is apparent that the order of reactivities is nearly identical to that of the NO_x photooxidation series. This suggests at least a rough mechanistic similarity between the two systems, i.e., electrophilic chemical species are most probably responsible for the initial attack of each hydrocarbon in each reaction system.

The laboratory results were extrapolated to occurrences in real rural atmospheres in the following manner. Conservatively, assuming an average rural ozone concentration of 30 ppb, it is possible to convert the second-order ozone rate constants to pseudo first-order constants describing the rate

TABLE 1. NO_x PHOTOOXIDATION AND OZONOLYSIS RATE CONSTANTS OF MONOTERPENE HYDROCARBONS

Hydrocarbon	Photooxidation $k \times 10^4$ [a]	Ozonolysis k [b]	$k \times 30$ ppb [c] $\times 10^4$	R_{O_3}/R_{NO_x} [d]
ρ-Menthane	0.11			
ρ-Cymene	0.25			
Isobutene	0.84	3.6×10^{-4}	0.11	0.13
β-Pinene	1.1	9×10^{-4}	0.27	0.25
Isoprene	1.3			
α-Pinene	1.3	3.6×10^{-3}	1.1	0.85
3-Carene	1.4	3×10^{-3}	0.9	0.64
β-Phellandrene	1.9	4.4×10^{-3}	1.3	0.69
γ-Terpinene		7×10^{-3}	2.1	
Carvomenthene	2.1	1.3×10^{-2}	3.9	2.0
Limonene	2.4	1.6×10^{-2}	4.8	2.0
Dihydromyrcene	3.0	1.7×10^{-2}	5.1	1.7
Myrcene	3.8	3.1×10^{-2}	9.3	2.4
cis-Ocimene	5.3	5×10^{-2}	15	2.8
Terpinolene	11	2.5×10^{-1}	75	6.8
α-Phellandrene	12	2.9×10^{-1}	87	7.2
α-Terpinene	55-110	2.2	630	6-12

[a] sec^{-1}, average first-order HC decay rate in irradiation vessel with added 7 ppb NO and 10 ppb HC

[b] $ppm^{-1}sec^{-1}$, average second-order ozone-HC rate constants plus 9% to correct values to a pressure of one atmosphere (average barometric perssure of Pullman, Washington is about 700 mm Hg)

[c] sec^{-1}, calculated pseudo first-order ozone-HC rate constants in air containing a steady-state 30 ppb ozone concentration

[d] rate ratios of hydrcarbon attack expected for competing ozonolysis and NO_x photooxidation in a simulated rural atmosphere

of each hydrocarbon's decay due to this steady-state ozone supply expected in a real rural air mass. These values, listed in the third numerical column of Table 1, can be compared directly with the NO_x photooxidation rate constants for an indication of the relative importance of these two potential pathways of terpene breakdown. This comparison has been made by listing the ratios of those first-order rate constants in the last column of Table 1. It is obvious that a wide range of values exists. The most reactive monoterpenes have R_{O_3}/R_{NO_x} values considerably greater than unity and therefore, in rural air, might be expected to first react with ozone. The reaction pathways of the monoterpenes having R_{O_3}/R_{NO_x} values closest to unity would, of course, be mixed.

The kinetic studies just described demonstrate that natural hydrocarbons are very reactive both in photochemical processes and ozonolysis reactions. The most reactive monoterpenes, such as terpinolene, α-phellandrene and α-terpinene, would likely react with ozone very quickly after entering the atmosphere, while the less reactive species, such as α-pinene, β-pinene, and Δ-carene, would exist long enough to participate in photochemical processes.

Since the natural hydrocarbons were shown to be reactive, it was of interest to study their oxidant-producing potential. The WSU and EPA groups have conducted laboratory studies to define the amount of ozone produced in the terpene-NO_x-hν system. Several terpenes were photolyzed at varying hydrocarbon/NO_x ratios. Upon irradiation, all the terpenes produced ozone with the amount depending on the initial HC/NO_x ratio. Very little oxidant was formed when the ratio was less than 5 or more than 40 (ppbC to ppb NO_x). Both research groups found the optimum ratio to be about 20. However, the absolute yield of ozone at this optimum HC/NO_x ratio was low when compared with other classes of hydrocarbons.

Typically, it required from 10 to 30 ppb of carbon to produce 1 ppb of ozone. This means that from 10 to 30 ppb α-pinene would have to be present to produce 10 ppb ozone. It is generally felt that the majority of the carbon present in terpenes is tied up in aerosol production.

Even though oxidant yields appear to be low in terpene-NO_x-$h\nu$ reaction, significant ozone levels could be produced if the natural hydrocarbons were present in high concentrations in rural areas. In the next section a detailed discussion of ambient terpene measurements will be presented.

IDENTIFICATION, EMISSION RATES, AND AMBIENT CONCENTRATION OF NATURAL HYDROCARBONS

As indicated previously, laboratory studies have shown that naturally emitted hydrocarbons, terpenes specifically, have the potential to produce ozone through photochemical processes. These findings have encouraged speculation on the contribution of biogenic hydrocarbons to high ambient air ozone concentrations measured in several rural areas of the Eastern United States. Although little information is available on the role of natural organic emissions in ambient air photooxidation processes, it is important to make a judgment on the basis of existing data as to the significance of this source and its implications for revising and/or modifying current control strategies.

To assess the contribution of naturally produced organic vapors to the overall hydrocarbon burden, a valid estimate of natural hydrocarbon emissions is essential. Unfortunately, a review of the pertinent literature reveals that only a modicum of data is available to make these estimates. Very little study has been devoted to organic gases from natural sources so that information in several areas critical to the development of a realistic assessment of natural hydrocarbon emissions is wholly or partially lacking. In particular, more work is needed on quantification of the various pathways through which organic compounds enter the atmosphere, as well as the emission rates for specific chemical compounds from given classes of vegetation.

Additional study is also needed on identification of compounds released to the atmosphere by natural sources and the effects on emission rates of such variables as soil, precipitation, solar radiation, wind, and temperature.

This scarcity of information, coupled with the sources of error inherent in any attempt to predict emissions from biological systems, raises serious

doubts about the reliability of published emission rates. Yet, it is precisely because of this lack of data that we must rely on crude approximations to provide information on the magnitude of biogenic hydrocarbon emissions.

In 1960, Went estimated that 1.75×10^8 tons of terpenoid vapors per year were emitted from the earth's land surface (22). Rasmussen and Went increased this estimate to 4.32×10^8 tons per year 5 years later (23). Ripperton et al. concluded a need for a twofold to tenfold increase in this figure by assuming that terpene-like materials (α-pinene as the representative type) are the major natural atmospheric gases that consume ozone in the troposphere and thus keep the ozone contribution from the stratosphere in balance (24). In the late 1960s, Robinson and Robbins based their estimate of 4.80×10^8 tons of organic emissions emitted per year largely on Rasmussen and Went's figure (25).

A serious shortcoming of these approximations in terms of providing a rate of organic emissions is that they deal only with terpenes and their derivatives. Since many other compounds have been identified as biogenic emission products, it is obvious that terpenes and related compounds are only one fraction of the total volatile organics emitted to the air. Therefore, even if Rasmussen and Went's often quoted figure of 4.32×10^8 tons per year is correct, it refers only to terpene and terpenoid vapors.

Research Triangle Institute, in a report published during 1974 (11), sought to establish a realistic range of values for natural organic emissions. They believe the figure for organic emissions on a worldwide basis should be greater than 4.32×10^8, Rasmussen and Went's estimate, and less than 1.217×10^{11} tons per year, the total primary production (carbon fixation by green plants) on the land surface of the world as estimated by Leith (26). By assuming that total emissions are 0.10 of the latter figure and 10 times the former, they obtained a range of approximately 0.4×10^{10} to 1.2×10^{10} with an average of 8.0×10^9 tons per year.

A problem exists in evaluating the validity of the RTI method, since their estimate is based on two other estimates. It seems probable that their

figure is closer to the actual amount of total organic emissions than Rasmussen and Went's value, yet the provided no documentation for assuming that Rasmussen and Went's figure was 1/10 of the lower limit. In addition, no statement was made about the validity of Leith's estimate for worldwide primary production, nor was any basis described for assuming that the upper limit was 1/10 of Leith's estimate.

The various assessments for worldwide emissions of natural hydrocarbons and total organic compounds are summarized in Table 2. The wide range of values provides a measure of the uncertainties hampering any attempt to estimate these types of emissions. Regrettably, lack of information at the present time makes any effort to quantify terpene and/or organic emissions on a worldwide basis an extremely difficult task resulting in values useful only as guidelines.

Perhaps more important than determining worldwide natural organic emissions is the quantification of biogenic emissions for a particular region. All too often, this is accomplished by choosing the particular worldwide estimate that seems appropriate and multiplying by the ratio of regional land area to world land area. This method ignores regional variation in vegetation type, growing season, biomass, solar radiation, etc.; and as already mentioned, the initial estimate is open to serious question. The lack of data on emissions of organic gases from various plants and the concentrations of organics in the atmosphere, while inadequate for determining the annual rate of such emissions for the world, are even less adequate for determining biogenic emissions from a particular region.

Determining regional emission rates for natural hydrocarbons is especially critical, since many recent studies have shown the possibility that air pollution, and particularly oxidant formation, can affect a much wider area than previously thought. If it is indeed the case that air pollution control regions should include larger geographic areas, possibly covering several states, then emission inventories must include not only anthropogenic but biogenic sources as well. It is precisely for this reason that more

TABLE 2. ESTIMATES OF WORLDWIDE EMISSIONS OF NATURAL HYDROCARBONS

Investigator	Method	Emission Rate (tons/yr)
Went (1960)	Sum of sagebrush emission and terpenes as percentage of plant tissues	1.75×10^{8} [a]
Rasmussen & Went (1964)	Direct *in situ* ambient conc.	4.32×10^{8} [a]
Ripperton, White & Jeffries (1967)	Reaction Rate O_3/pinene	2 to 10 x previous estimates [a]
Robinson & Robbins (1968)	Based largely on Rasmussen and Went's data	4.80×10^{8} [a]
RTI (1974)	Lower limit = 10 x Rasmussen and Went's figure Upper limit = .10 x total carbon fixed by green plants	$0.4 - 1.2 \times 10^{10}$ [b] (avg: 8.0×10^{9})

[a] natural hydrocarbon emissions, i.e. terpenoid vapors

[b] natural organic emissions

exact information is required on biogenic emissions so that their contribution to the overall hydrocarbon burden of an area can be more reliably determined.

RTI undertook to estimate the natural organic emissions for Ohio and surrounding states (11). Using Rasmussen and Went's worldwide figure multiplied by the ratio of surface areas state/world, the estimates of terpene-type emissions varied between 0.9 to 5.4 times the anthropogenic contribution. Taking 0.10 times the primary production rates based on data for North Carolina, Tennessee, and Wisconsin, the total natural organics varied from 4 to 24 times the anthropogenic.

Recent studies at Washington State University have attempted to improve the reliability of natural emission estimates. The approach taken by Zimmerman and Rasmussen (21) has been to establish emission rates for a specific land area, time of year, and/or vegetation type. They have completed a sample emission inventory to estimate biogenic total nonmethane hydrocarbons based on a relatively small number of samples collected in one area of the U.S.

According to Zimmerman and Rasmussen, after a specific area and time period have been designated for an emission-study program, there are four major steps in developing an emission inventory.

1. Identify the major vegetation types and predominant plant species.
2. Select the representative species to be sampled.
3. Quantify the biomass for each species selected.
4. Conduct a field testing program to collect and analyze emission samples from each of the representative species.

They have developed a simple, practical method for collecting samples to complete the field sampling program. Their system, combining the advantages of a static enclosure system and dynamic flow system, involves enclosing a portion of the vegetation in a Teflon bag. The bag is quickly filled with hydrocarbon-free air and then allowed to remain over the vegetation for about

10 minutes. A sample of the bag air is collected and returned to the laboratory for GC analysis. The branch is clipped, dried, and weighed to determine the quantity of biomass. The emission rate is equal to the total number of micrograms of hydrocarbons released per gram of vegetation sampled per unit time (μg/g x minute).

The success of this method is based upon the short enclosure time (15 minutes or less) and the large amount of dilute "zero air." Both of these factors mitigate static chamber difficulties such as high chamber temperature and the long-term accumulation of metabolic CO_2 and/or water vapor. The sampling occurs under the most natural possible conditions so that sampling induced perturbations are kept to a minimum. At the same time, the hydrocarbons present are concentrated enough to allow good quantitation.

To calculate a yearly emission rate for the continental United States, an emission inventory was constructed based on collected data. Seasonal variations were taken into account by correcting emission rates for temperature. To calculate an annual emission rate, the season was considered to consist of 5 months of summer (temp. 23°C) and 7 months of winter (temp. 7.5°C). Deciduous species, leaf litter, and low-lying grass were estimated to have a negligible emission rate during the winter. A ponderosa pine litter sample was used as an estimate of summertime litter emissions. The results are shown in Table 3. The total yearly emission rate for vegetation and leaf litter in the United States is estimated to be 8.73×10^7 tons/year, approximately four times the total attributed to anthropogenic sources. The average summer emission rate is 5.24×10^7 tons, while average winter emissions are 3.49×10^7 tons.

From the foregoing discussion, it is clear that all emission estimates completed to this time predict that natural sources contribute significantly to the atmospheric hydrocarbon burden. However, this does not necessarily mean than ambient concentrations of natural hydrocarbons will be high. The concentrations of natural species will be low if the volume of dilution air is large relative to their emission rate. Because all of the various attempts to assess natural hydrocarbon emissions suffer from a lack of pertinent data, it

is important to examine the information available to determine the reasonableness of the estimates being proposed. In short, is there evidence to show that terpenes are present in ambient air at concentrations commensurate with suggested emission rates?

TABLE 3. TOTAL YEARLY EMISSION RATE FOR CONTINENTAL U.S. BASED ON LEAF BIOMASS

Summer Emissions:	
Average Vegetation Emission Rate	
1.36×10^4T/hr x 708.7 hrs/mo x 5 mo =	4.82×10^7T
Litter Emission Rate	
132 $\mu g/m^2$-hr x 1 x $10^6 m^2/km^2$ x 9.06 x 10^6 km^2/U.S. = 1.2 x 10^3T/hr	
1.2 x 10^3T/hr x 708.7 hrs/mo x 5 mo =	4.20×10^6T
Total Summer Emission	5.24×10^7T
Winter Emissions:	
Average Winter Emission Rate	
7.04 x 10^3T/hr x 708.7 hrs x 7 mo =	3.49×10^7T
Total Yearly Emission Rate for Vegetation and Leaf-Litter	8.73×10^7T/yr
Total Yearly Emission Rate from Anthropogenic Sources	2.12×10^7T/yr

Natural Emissions as the Percent of the Total Emissions from all Sources

$$\frac{8.73 \times 10^7 \text{T/yr}}{2.12 \times 10^7 \text{T/yr} + 8.73 \times 10^7 \text{T/yr}} = 80\%$$

Although some information is at hand, few studies have successfully measured ambient air concentrations of naturally emitted hydrocarbons. Westberg and Holdren reported on an analysis of monoterpenes from a rural forested site in northern Idaho by a gas chromatograph linked directly to a mass spectrometer (27). Their data show substantial variation in the concentration of the trace hydrocarbons with values for total monoterpene concentrations

varying from well over 1 ppb to less than 100 ppt. This contrast is attributed primarily to changes in wind speed which, other meteorological conditions being equal, will affect the exchange time per unit volume of air within the forest canopy. Benzene and toluene were also monitored at the forest site. Very little difference in their levels was noted, leading the authors to conclude that these two compounds originated from anthropogenic sources rather than biogenic production.

Besides benzene and toluene, four monoterpene compounds were observed in this rural atmosphere: α-pinene, β-pinene, Δ-carene, and limonene. Limonene was usually present in much smaller concentrations than the other three, often by an order of magnitude. α- and β-pinene were most often present in highest concentrations, frequently twice that of Δ-carene. Values ranged from a few ppt for limonene to 730 ppt for α-pinene.

To better define the concentration pattern within the forest canopy, samples were collected at varying elevations above the ground with the same general area. The results indicate that: (a) ground surface samples are always higher than the corresponding 3-foot level samples; (b) samples collected 3 feet above the ground surface vary considerably within the forest canopy; (c) sampling in tree branches does not significantly differ from the 3-foot level sampling; and (d) samples taken outside the forest canopy show no measurable terpenes. Differing localized emission strengths yielding concentration gradients are seen as the reason for this significant variability.

During this investigation, emission rates were determined using techniques developed by Zimmerman and Rasmussen as described earlier. This method provides higher concentrations of biogenic hydrocarbons and makes more precise measurements possible by allowing total ion analysis through gas chromatograph-mass spectrometer linkage. In this way, increased sensitivity and specificity allows detection of as little as 10 ppt compound in 400 cc air samples and provides positive identification even at these low concentrations.

The emission rates determined in this manner were then used to calculate expected ambient air terpene concentrations within the forest canopy. Assuming an average terpene emission rate of 3120 $\mu g/m^2$-hr (obtained for a coniferous forest in this region) and a typical canopy height of 20 meters, 3120 μg of terpene compounds are emitted into a volume unit 1 meter x 1 meter x 20 meters (20 m^3) in 1 hour. The time (t) for the forest canopy to vertically exchange its volume can be calculated utilizing the "random walk assumption," which states that $t \simeq Z/2D$, where Z is the mixing distance (20 m) and D is the vertical diffusion coefficient in the forest canopy (assumed to be $10^4 cm^2/sec$). Using these values the time for vertical exchange was calculated to be 200 seconds. It is now possible to calculate the expected ambient air concentration within the canopy.

$$\frac{3120\ \mu g}{20\ m^3\ hr} \times 200\ sec \times \frac{1\ hr}{3600\ sec} \times \frac{1\ ppb}{5.56\ \mu g/m^3} = 1.6\ ppb\ total\ terpene\ concentration$$

The calculated value of 1.6 ppb agrees relatively well with the highest concentration measured during the course of this study. This calculation indicates that normal dilution processes can account for the low ambient terpene concentrations measured in rural atmospheres.

Recently, Lonneman reported a study of natural hydrocarbon emissions at a forested area west of Durham, North Carolina (15). Vegetation at the site consisted primarily of loblolly pine. Measurements showed a maximum of 87 ppbC α-pinene, 19 ppbC β-pinene, 3.3 ppbC myrcene, and 4.8 ppbC Δ-carene observed at ground level, suggesting pine needle litter as the principal source. Concentrations basically agree with Westberg and Holdren's findings, although Lonneman's value for α-pinene is significantly higher and trace amounts of terpenes were observed in downwind samples at the North Carolina site. The components of the total hydrocarbon burden for both sites were essentially the same, with the exception of myrcene and limonene. The former appeared only in the North Carolina measurements and the latter only at the north Idaho site.

Studies in the same North Carolina area have shown total nonmethane hydrocarbon (TNMHC) concentrations in the forest canopy were 15-50 percent

higher than concentrations 20 feet above the forest canopy. Within the canopy, TNMHC reached a maximum of 170 ppbC with corresponding values of 37 ppbC α-pinene and 10 ppbC β-pinene. Ozone both in and above the trees was about 50 ppb. When ozone reached a maximum of 65 ppb, TNMHC decreased to 80 ppbC and the combined α- and β-pinene concentration was approximately 5 ppbC. In a second study, acetylene (assumed to be from anthropogenic sources) varied from 2 to 48 ppbC, TNMHC from 95-200 ppbC, α-pinene from 5-40 ppbC, and β-pinene from 1-10 ppbC.

An earlier study by Rasmussen and Holdren (14) described a portable cryogenic collection system (cryocondenser) that made it possible to study C_5 to C_{10} components in ambient air at remote sites. Gas chromatography analysis indicated that 10 to 60 hydrocarbon compounds were normally present in rural and remote areas with concentrations of individual compounds usually below 1 ppb. The total C_5 to C_{10} organic burden ranged from a few to over 100 $\mu g/m^3$. Although this study indicated that the composition of natural organic gases was more complex than previously thought, sensitivity and specificity possible with this technique were not sufficient to identify or quantify all hydrocarbon compounds at the trace levels found in rural atmospheres.

Hydrocarbon concentrations in rural areas have also been reported by Whitby and co-workers (28) and Whithead and Severs (29). Individual hydrocarbons were not identified in either of these studies; therefore, it is impossible to establish a concentration range for terpenes. It is this reviewer's feeling that it is improper to assume that unidentified peaks in a gas chromatogram are natural hydrocarbons just because the sample was collected in a rural area. As indicated earlier, the Washington State University and EPA research teams commonly find acetylene, benzene, and toluene in rural environments. The presence of these species implies that hydrocarbons from anthropogenic sources are definitely present in these areas.

Prior to 1964, the hemiterpene isoprene was not believed to be a major component of volatile organic emissions. However, Rasmussen (30) and Rasmussen and Went (23) observed a hemiterpene tentatively identified as isoprene emanating from oak leaves, aspen, and sweetgum foliages during *in situ* studies

using a gas chromatograph in remote natural areas of the U.S. Rasmussen (31) presented gas chromatographic, infrared, and mass spectrometric analyses showing that isoprene was indeed involved in these leaf emissions and occurred under natural conditions from intact, living foliage of numerous plant species. Preliminary data on the dominant tree species for the forest of North America indicated that isoprene occurred approximately as frequently as α-pinene, although species variations existed. Tables 4 and 5 show the emissions of major forest trees.

In an article published during 1972, Rasmussen stated that the major components of volatile organic emissions consisted of monoterpenes (C_{10}) like α-pinene, β-pinene, and limonene, and the hemiterpene (C_5) isoprene (2). He found the emission rate of isoprene to be light-dependent and range between 0.04 to 2.4 ppb/cm^3/min/l. An inventory of North American forest regions revealed that an average of 70% of the trees in U.S. forested regions emitted terpenes to the atmosphere (values ranged from 15% to 100%). Table 6 relates the composition of the five North American forest regions to the type of foliage emission.

Up to the present time, monoterpene compounds have been exclusively associated with forested areas, and there is no evidence available to suggest that they are transported downwind in appreciable quantities. Isoprene, on the other hand, has been shown to occur under natural conditions from intact, living foliage of numerous plant species, as well as certain types of forest trees. *In situ* measurements by Rasmussen et al. (32) demonstrated significant levels of isoprene (∿10 μg/m^3) in a lightly forested agricultural region of southwestern Missouri. It was also observed that isoprene concentrations exhibited pronounced diurnal variation with maximum in the late afternoon. Evidence accumulated during the summer of 1975 by an EPA-ESRL mobile laboratory at Chickatawbut Hill in Massachusetts, approximately 10 miles south of downtown Boston, also indicated substantial isoprene concentrations, particularly in the afternoon (20). It is believed that these isoprene emissions resulted from the woodlot vegetation in the area surrounding the sampling site.

TABLE 4. EMISSIONS OF MAJOR EASTERN FOREST TREES

Softwoods		Hardwoods	
Emit α-Pinene	Emit Isoprene	Emit Isoprene and α-Pinene	Type of Emission Unidentified
White Pine	Oak	Sweetgum	Hickory
Red Pine	Sweetgum	Yellow Poplar	Blackgum
Jack Pine	Sycamore	Balsam Poplar	Beech
Longleaf Pine	Willow	Spruce (Softwood)	Birch
Slash Pine	Cottonwood		Maple
Shortleaf Pine	Balsam Poplar		Ash
Loblolly Pine	Aspen		Black Walnut
Hemlock			Hackberry
White Cedar			Basswood
Larch			
Spruce			
Fir			
Balsam Fir			
Cypress			

From: "What Do the Hydrocarbons [illegible] to Air Pollution," Rasmussen [1972].

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Slash Pine	Cottonwood		Maple
Shortleaf Pine	Balsam Poplar		Ash
Loblolly Pine	Aspen		Black Walnut
Hemlock			Hackberry
White Cedar			Basswood
Larch			
Spruce			
Fir			
Balsam Fir			
Cypress			

From: "What Do the Hydrocarbons From Trees Contribute to Air Pollution," Rasmussen [1972].

TABLE 5. EMISSIONS OF MAJOR WESTERN FOREST TREES

Softwoods	Hardwoods
Emit α-Pinene	Emit Isoprene
Ponderosa Pine	Aspen
Jeffrey Pine	Buckthorn
Sugar Pine	
Limber Pine	Type of Emission
Western White Pine	Unidentified
Lodgepole Pine	
Grand Fir	Tanoak
White Fir	Red Alder
Alpine Fir	
Western Hemlock	
Western Red Cedar	
Douglas Fir	
Redwood	
Larch	
Sitka Spruce - Also Isoprene	
Englemann Spruce - Also Isoprene	
Colorado Blue Spruce - Also Isoprene	

From: "What Do the Hydrocarbons from Trees Contribute to Air Pollution," Rasmussen [1972].

TABLE 6. COMPOSITION OF NORTH AMERICAN FOREST REGIONS/FOLIAGE TERPENES

Region	No. Major Trees Species	No. α-Pinene	No. Isoprene	% Terpene Emitters
Northern	20	8	6	70
Central Hardwood	16	3	5	50
Southeastern	18	4	4	44
Rocky Mt.	13	10	4	100+
Pacific Coast	24	15	7	92

From: "Isoprene: Identified as a Forest-Type Emission to the Atmosphere," Rasmussen [1970].

In summary, it is apparent that a large number of tree species emit terpenes to the atmosphere and that total natural hydrocarbon emissions probably exceed those from anthropogenic sources. However, it is also clear that ambient terpene concentrations measured in rural atmospheres are very low. Table 7 provides a summary of what this reviewer considers the most reliable ambient natural hydrocarbon data. As can be seen, the total terpene burden varies between about 10 and 50 ppbC (1 to 5 ppb as terpene). If isoprene were included, the total would be slightly higher.

TABLE 7. AVERAGE AMBIENT TERPENE CONCENTRATIONS (ppbC)

	WSU[a]	EPA[b]
α-Pinene	4	23
β-Pinene	3	5
Δ-Carene	<1	5
Limonene	3	--
Myrcene	--	3
TOTAL	∿10	46

[a]Westberg and Holdren [1976]

[b]Lonneman [1976]

CONTRIBUTION OF NATURAL HYDROCARBON TO OXIDANT LEVELS IN RURAL AREAS

In the preceding section, evidence was presented demonstrating that terpenes can be detected in forested regions. The ambient concentrations reported for individual monoterpenes generally fall in the high ppt range with the total terpene burden seldom exceeding a few ppb. It is this reviewer's opinion that these data are of good quality. A detailed evaluation of methods for measuring and estimating emission rates was also provided. The relationship between the estimated emission rate for a specific forested region and ambient terpene concentrations measured in that same area was examined using a

simple meteorological dispersion model. The ambient hydrocarbon concentrations predicted by a physical dilution of the vegetative emissions agree very closely with the natural hydrocarbon levels actually measured. Thus, it appears that in forested areas, ambient levels of terpenes are commensurate with emission rates. Once again it is my feeling that this is not just a coincidence and that the data are truly representative of biogenic and atmospheric processes.

Because of their extremely low concentrations in ambient air, terpenes must have a minimal impact on atmospheric chemistry. Neither an ozone-producing nor an ozone-destruction role seems important. Smog chamber experiments indicate that at an optimum terpene/NO_x ratio, about 20 ppbC would produce 1 ppb ozone. Since 20 ppbC is about that reported for terpenes in rural regions (Table 7), it is obvious that natural photochemical processes involving terpenes alone would have little effect on the normal ozone background level.

From the evidence just presented plus aerometric ozone measurements made at various rural locations, I do not believe that terpene photooxidation contributes to the "blanket ozone phenomenon" observed in the eastern section of the United States. If natural hydrocarbons were important in creating an "ozone blanket" this would be observed in heavily vegetated areas of the west as well. No such problem has been observed in rural regions of the western United States.

From my viewpoint, the role of "other" natural organic emissions in photochemical pollution is impossible to assess. The identity of compounds that make up this "other" category cannot be clearly defined. Irradiation experiments conducted on captured rural air samples indicate little potential for increasing ambient ozone levels. Even if ozone production were observed in this type of experiment, it would be impossible to define which of the trace level organic precursors originated from a natural source and which were transported from a distant anthropogenic source.

COMMENTS BY PETER COFFEY

I believe that it is premature to reach the conclusion that natural organics play a very minor role in the atmospheric chemistry of ozone. Westberg seems to isolate the natural production of ozone from other sources of ozone, and I wonder if this can be done. For example, several years ago Rasmussen "spiked" with NO several Teflon bags of remote rural Idaho air. These bags were allowed to sit in the sun along with unspiked bags of air. The result was a significant increase in ozone production in the bags spiked with NO in contrast to the unspiked bags. Thus, it would seen that under the right conditions, possibly involving interaction with anthropogenic precursors, air containing mostly natural hydrocarbons does have the potential to produce significant quantities of ozone. Perhaps the quantity of ozone generated in the St. Louis plume as seen by White et al. in the paper "Ozone Formation in the St. Louis Plume," presented at the International Conference on Photochemical Oxidant Pollution and its Control, is due in some measure to natural hydrocarbons being forced into reaction by NO in the plume (10).

Westberg's conclusions apparently are arrived at in large measure from the results of smog chamber type of experiments that were performed in the part per million concentration level, in which results must be extrapolated to the ppb levels found in the ambient air.

This of itself can lead to errors; however, in addition, I suspect a very dense aerosol concentration would be generated in these experiments. This aerosol probably with number density greater than 10^7 particles/cm^3 might also affect the ozone concentration by providing active sites for reactions.

Westberg states that it is impossible to assess the role of "other" natural organics. In the face of this statement, I refer to a recent paper by R. Rasmussen, R.B. Chatfield, and M.W. Holdren titled "Hydrocarbon Species in Rural Missouri Air" (32). In this paper, naturally occurring isoprene is suggested as a significant source of ozone in the Elkton, Missouri, area.

In conclusion, I feel that Westberg is somewhat premature in arriving at the conclusion that natural organics play essentially no role in the atmospheric chemistry of ozone. Published data from field studies indicate some role by the natural organics in the ozone formation process. The significance of this role has yet to be determined.

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16. ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a follow-up review/analysis effort. The follow-up effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

In Part IV, the issue of natural organic emissions, measuring them and assessing the role they play in air quality, is discussed by Peter E. Coffey of the New York State Department of Environmental Conservation, Albany, N.Y., and Hal Westberg of Washington State University, Pullman, Washington.

17. KEY WORDS AND DOCUMENT ANALYSIS

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