METHODS FOR MEASURING PHOTOCHEMICAL AIR POLLUTION IN FOREST AREAS*

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A B S T R A C T

Ambient air contains a mixture of oxidizing and reducing compounds among which are ozone, nitrogen dioxide, peroxyacetyl nitrate, and sulphur dioxide. The concentrations of these compounds can vary within quite wide limits from 0 to over 100 pphm. An accepted general definition for total oxidants in the air would be a compound that will oxidize a reference material which is not capable of being oxidized by atmospheric oxygen. Accordingly methods for measuring atmospheric oxidants consist of exposing an oxidizable substance to a sample of ambient air and determining the degree of oxidation which has occurred. Two of the most widely used methods of determining the degree of oxidation are colorimetric and coulometric analysis of the iodine released from a potassium iodide solution. Since one mole of ozone theoretically liberates one mole of iodine from this solution, the iodine measured is directly related to the concentration of ozone. Reducing compounds in air have an opposite effect on the reference material by causing a decrease in the degree of oxidation observed.

Field equipment to measure atmospheric oxidants consists of continuous automatic instruments and recorders. Sulphur dioxide is scrubbed from the incoming ambient air by suitable chemical compounds. In remote areas specially compounded rubber to which antioxidants have have not been added have proved useful to evaluate atmospheric oxidants.

Field investigations to determine background concentrations of photochemical air pollutants have been carried out in forests in both Canada and the United States, and the monitoring data are provided. The relationship between these air analyses data and effects on forest trees is discussed.

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I.   INTRODUCTION

Ambient air contains a mixture of oxidizing and reducing compounds among which are ozone, nitrogen dioxide, peroxyacetal nitrate, and sulphur dioxide.   The concentrations of these compounds can vary widely from zero to over 100 pphm.

Most of the data on gaseous air pollutants have been derived from measurements conducted in urban areas.   Thus the amount of data avail-able from non-urban areas is small by comparison.   A "non-urban area" as defined for discussion in this paper is a forested area located at a distance from a heavily populated, largely industrialized urban area. An example of the former would be the Pisgah National Forest, in Pisgah, North Carolina; an example of the latter would be a city such as Toronto, Ontario.

The objectives of this paper are to discuss current methods in use for the measurements of oxidants in non-urban areas.   In addition, background concentrations of oxidants recorded in non-urban areas as well as a discussion of the relationship between air analyses data and effects on forest trees are provided.

II. METHODS CURRENTLY IN USE FOR MEASURING OXIDANTS UNDER FIELD CONDITIONS

An accepted general definition for total oxidants in the air would be a compound that will oxidize a reference material which is not capable of being oxidized by atmospheric oxygen.   Accordingly, methods for measuring oxidants consist of exposing an oxidizable substance to a sample of ambient air and determining the degree of oxidation which has occurred.

Comprehensive reviews of methods in use and being developed for atmospheric air sampling for oxidants have been given by Cherniack et al (5), Morgan et al (17), and the U.S. Dept. of Health, Education and Welfare (28, 29).

The most common continuous methods utilize a potassium iodide solution in either a colorimetric or coulometric analyzer (29).   The colorimetric method employs a 10-20% solution of neutral-buffered-potassium iodide as the absorbing medium.   Oxidants in contact with the KI react to free iodine and the tri-iodine ion.   These are then measured colorimetrically in a continuous flow colorimeter at 3,520Å. Sensitivity to oxidizing substances ranges from 0-50 pphm ozone.

The coulometric method is often used.   In this technique, sample air is passed into an electrolytic detector cell containing 2% potassium iodide (14).   Free iodine liberated by the oxidant is redirected at the cathode of the cell causing a current flow through an external

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circuit. The current flow is proportional to the amount of iodine
liberated.   The current is measured with a microammeter calibrated
directly in pphm of ozone.

Another type method employs the iodometric analyses system
which is amperometric-coulometric in principle and is based on the
generation of ozone in a sodium iodide solution (27).   Measurement
of the iodine in the solution, which is stoichiometrically related
to the amount of oxidant is based on depolarization of the electrodes.
When a low potential current is passed between electrodes in an
electrolyte solution there is momentary flow of current, due to
electrolysis, then a stoppage of current flow due to polarization.
Polarization occurs due to an accumulation of a nonconducting film
of hydrogen on the electrode.   Removal of the hydrogen film (depolar-
ization) permits current flow, and the magnitude of current is directly
proportional to the amount of free iodine in the liquid solution. A
second feature of this analyzer is that there is a built in electrical
calibrating system that eliminates the use of time consuming external
methods such as permeation-diffusion tubes.   The instrument will
recalibrate itself automatically from one to four times per 24 hour
period.   The unit provides an uninterrupted recording of the concentra-
tion of the gas being measured.   Analyzers are designed to operate
unattended for at least one week's time.   Field comparisons of measure-
ments from colorimetric and coulometric oxidant analyzers where readings
did not exceed 20 pphm and corrections were made for NO_2 interference
resulted in good correlation between the two methods. (19).

In any discussion of the measurements of ozone in ambient air,
mention should be made of one of the earliest techniques used which
was the rubber-strip-cracking method developed by Bradley and Haagen-
Smit (3).   They developed a rubber formulation which was sensitive to
cracking by ozone.   A strip of this sensitive rubber is put under stress
and then exposed to the air.   Either the time until the rubber begins to
crack or the depth of the crack after a specified time is then related to
the ozone concentration in ambient air.   This method does not provide
a direct quantitative measurement but does have the attributes that it
is inexpensive, is easy to use, and can be of value in survey work.
To date, it has not been automated to obtain continuous data.   Cole and
Katz (6) reported that there was a fair correlation between the rubber-
cracking method and buffered KI methods of measuring oxidants.   Linzon(11)
measured atmospheric ozone at the Petawawa Forest, Chalk River, Ontario
for three summers, 1965 to 1967, utilizing both the rubber strip and
coulometric (Mast)methods.   Good correlation was obtained between the
average daily values of rubber cracking in millimeters per hour and
the average daily ambient ozone values in pphm (Figure 1).   Although
the rubber cracking is presumed to be caused specifically by ozone,
other reactive species such as free radicals may contribute to rubber
cracking over extended periods (30).

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Variations occurring in measurements are usually caused by
reagent flow and interfering compounds. Reducing compounds in air
often give an opposite effect on the reference material by causing
a decrease in the degree of oxidation observed. The result being,
that the net value describes a condition of the air rather than a
specific compound concentration. A filter containing a mixture of
phosphoric acid and chromium trioxide is now often used to remove
sulphur dioxide and other reducing agents (26). However, the filter
will oxidize NO to NO_2, thereby creating a positive interference with
the analysis. The filter is also ineffective if it becomes wet.
As a result of this, concentrated efforts are being made by researchers
to obtain measurements for each specific oxidant present. Most
oxidant data which have been reported are net determinations and
a good correlation between these values and other pollutant levels
has been observed (24).

A widely accepted reference method for comparisons between
techniques is the neutral-buffered KI colorimetric technique
described by Byers and Saltzman (4). In this method, oxidants
are absorbed in a 1% KI aqueous solution and the liberated tri-iodine
ion is measured colorimetrically at 3,500 A. Since one mole of ozone
theoretically liberates one mole of iodine from this solution, the
iodine measurement is directly related to the concentration of ozone
present in the air sample. Results are thus expressed directly as
equivalent volumes of ozone.

III. BACKGROUND CONCENTRATIONS OF OXIDANTS RECORDED IN NON-URBAN AREAS

It is necessary to know the relative concentrations of oxidants
which arise from nontechnological sources. The concentration which
persists if all technological sources are eliminated has often been
termed "background concentration".

There are several possible sources of ground-level ozone.
Regener (21) and Kroening and Ney (10) have shown that there can be
a vertical flux of ozone from the stratosphere and that the concentra-
tions of ozone at ground level usually vary from 0 to 5.0 pphm.
Another interesting possible source of ozone is photochemical reactions
involving terpenes emanating from pine trees (20).

Lightning is another source of ozone. Kroening and Ney (10)
have stated that lightning is "an important source of ozone". They
calculated on a theoretical basis that the production rate of ozone
from lightning could be 10 atoms per square centimeter per second
averaged over the earth. This is the same order of magnitude as that
calculated to be produced by ultraviolet in the high atmosphere. It
should be emphasized that ozone produced by lightning is not uniformly
distributed over the earth and thus it should not be considered as a
consistent source of ground level ozone.

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The following are reported results of a selected number of ozone
determinations in a variety of non-urban areas.   For example, in northern
Greenland in July of 1960, a maximum concentration of 1.3 pphm was report-
ed (15).   In the Antarctic the mean monthly surface ozone values from
April 1957 to May 1958 ranged from 1.0 to 3.4 pphm (18).   At Amundsen-
Scott station, located at the geographical south pole, ozone was measured
using both the chemiluminescent method of Regener (22) from 1961 through
1964, and using the Mast (coulometric) method during 1963 and 1964.   The
monthly mean averages ranged from about 2.0 pphm to 4.0 pphm by the former
method, and from 1.0 pphm to 3.0 pphm by the latter (1).   Linzon (12)
found at the Petawawa Forest, Ontario, using a Mast meter that the daily
average concentration of oxidants varied from slightly under 1.0 pphm to
slightly over 4.0 pphm.   Diurnal fluctuations in atmospheric ozone
concentrations were recorded with oxidant values at night usually less
than 1 pphm, increasing in the morning hours to a peak around noon of
3 pphm and then dropping in the evening hours.   Measurements were made
over a three year period 1965 to 1967, and the highest concentration
encountered was 6.0 pphm ozone for four hours which occurred between
1500 and 1900 hours on two occasions, June 27, 1965 and August 17, 1967.
It is of interest to note that the entire north east seaboard of the
United States experienced a heavy layer of photochemical smog on August 17,
1967 on the same date that the highest oxidant levels were encountered at
Chalk River, Ontario, which is approximately 400 miles northwest of New
York City.

A comparison of background measurements of ozone was made
recently by the U.S.D.H.E.W., National Center for Air Pollution Control
(29).   Data recorded by Linzon (12) using a Mast instrument in the
forests at Chalk River, Ontario, and data collected by Berry (2)
using a Mast meter in the forests of West Virginia and North Carolina
were calculated for frequency distributions.   The arithmetic mean
in North Carolina was found to be 1.69 pphm;   in West Virginia 2.22 pphm;
whereas, in central Ontario it was only 1.14 pphm.

The frequency distribution of average 15-minute ozone concentra-
tions for 24 hours per day for the period of June 1, to August 13, 1965
recorded by Linzon (12) at the Petawawa Forest, Chalk River, Ontario
is shown in Figure 2.

Costonis and Sinclair (7) have reported the frequency distribution
of mean hourly ozone concentrations recorded by Mast equipment equipped
with a CrO_3, SO_2-scrubber in a forest area in New York State.   In 1966,
the mean hourly concentration for the days of record was 1.74 pphm while
in 1967 the mean for this same period was 2.02 pphm.   The highest
recorded 4-hour-mean ozone concentration in 1966 varied from 4.0 to 5.0
pphm.   The corresponding range in 1967 was 5.0 to 8.0 pphm.   The
frequency distribution of mean hourly ozone concentrations during the
1967 growing season reported by Costonis and Sinclair (8) are given in
Table 1.

In 1968, Costonis (9) found that in the Pisgah National Forest,
in Pisgah, North Carolina, the maximum 4-hour ozone concentration was

4.0 pphm which occurred only twice during the growing season, while
on 72.1% of days of record ozone concentrations averaged between 0.0
- 1.9 pphm for the 4-hour-duration from 0900 - 1300 hours (Table 2).

        Miller (16) compared oxidant concentrations at Rim Forest and
San Bernardino, California for a 16 day period in August 1962.   The
city of San Bernardino is approximately 10 air miles south and 4,400
feet lower in elevation than the Rim Forest.   The average daily
maximum oxidant peak was 14 pphm for San Bernardino and 9.0 pphm for
Rim Forest during this period.   Cole and Katz (6) although not working
in a forest situation but what they referred to as the "semi-rural
area" of Port Burwell, Ontario, reported a diurnal variation in ozone
concentrations in which concentrations of ozone increased in the hours
after sunrise to a maximum of about 5.0 pphm in the afternoon and
decreased to low values, or less than 1.0 pphm during the night.   They
reported a maximum ozone concentration of 15.0 pphm.

IV.   CONSIDERATIONS FOR AMBIENT AIR MONITORING IN FORESTED AREAS

        Under field conditions the following factors must be considered
if meaningful data concerning ambient air are to be obtained:

a)   The number and distribution of the oxidant recording instruments.
b)   Type of instrument and shelters.
c)   Power source.
d)   Maintenance features of analyzers, ie. calibration of instrument;
        appropriate filters; servicing requirments.
e)   Properly trained technicians.
f)   Meteorological parameters in the area such as sunlight, rainfall,
        relative humidity, soil moisture, wind movement, temperatures,
        particulate matter.
g)   Frequent field observations over several growing seasons and data
        collection of indigenous vegetation as well as clonal lines of
        trees of known tested sensitivity to a given pollutant to be used
        as biological monitors of pollutants.
h)   Correlation of oxidant buildups with concurrent injury on the
        tree species under study.
i)   A specific definition of the purpose of monitoring and a computer
        system designed to obtain maximum utilization of the data obtained.

V.   DISCUSSION

        It is evident from the preceding sections that oxidants have been
recorded in the atmosphere from Arctic to Antartic regions.   Diurnal
fluctuations in the occurrence of atmospheric ozone have been recorded
in non-urban rural (6) and forested areas (12).   Forest trees are
subject to injury from photochemical oxidants (13) with 3.0 pphm of ozone
for 48 hours considered to be the threshold concentration required to
injure sensitive strains of eastern white pine.   Data reported by
Costonis and Sinclair (8) in Table 1 show that over 26% of mean
hourly ozone concentrations recorded in the New York study area

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between June 9 and September 2, 1967, were in excess of 3.0 pphm. On two occasions the 3.0 pphm concentration was exceeded throughout periods of 48 hours. On four occasions the recorded concentration was at least 7.0 pphm for 4 hours or more. New lesions were detected on ozone-sensitive trees five times in 1966, each occurring 24 to 48 hours after an elevation in ambient ozone concentration (Figure 3). New lesions appeared during 12 of 13 observation periods in 1967, but their appearance could not be related to specific elevation in ambient ozone concentration because these occurred too frequently for loci of injury to be separate on elongating needles (Figure 3).

As more industries move into what were formerly "nonurban areas", and more nitrogen oxides and hydrocarbons are emitted to the nonurban atmosphere from industry and automobile exhausts, it is possible that areas with certain topographical and meteorological conditions could develop phytotoxic concentrations of ozone through photochemical oxidation of these ingredients as described by Renzetti et al (25). An example of the influx of ozone into a forested area is reported in the work by Miller et al (16) in which they have suggested that oxidant which develops in the atmosphere over Los Angeles drifts into the nearby San Bernardino Mountains and is the cause of chlorotic decline of ponderosa pine.

This paper has discussed oxidant analyzers currently in use. These analyzers are mainly dependent on wet chemistry. Those who have worked with such instruments under field conditions recognize the necessity for their improvement. Some of the problems encountered in the field are the frequency with which instruments must be attended, the unstability of reagents, the complex plumbing and accurate solution pumps which result in heavy and bulky instruments. It would seem that future instruments should utilize the physical or physico-chemical properties of pollutants for their identification and quantification.

Morgan et al (17) have recently listed a group of new instruments that are now in their final stages of development and field testing by the staff of the U.S. National Air Pollution Control Administration. These workers (17) are concerned with all types of atmospheric pollutants in their program among which is an improved chemiluminescent method (23) for the specific determination of ozone. A further method that should aid in a better definition of the "oxidants" is a method for determining oxides of nitrogen in which ozone is titrated in the gas phase with a reactive gas and the reaction produces light by chemiluminescence.

A final word should be mentioned concerning the data handling and analysis. The reporting of the data must be in a format that can be used conveniently and rapidly by the researcher. The National Air Pollution Control Administration is developing a very forward looking system termed National Aerometrix Data Information Service (N.A.D.I.S.) which provides an integrated system for the reporting, storing, and analyzing of aerometric data from a wide variety of sources (17). It seems that aerometric data collected in forested areas could apply this same system and the data could be put on a comparable basis and would permit data from various regions of the world to be compared.

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TABLE I

FREQUENCY DISTRIBUTION OF MEAN HOURLY OZONE [a)]
CONCENTRATIONS, JUNE 9 - SEPTEMBER 2, 1967

Concentration (PPHM)	Number of Hours	Percentage of Hours
0.0 - 0.9	619	30.2
1.0 - 1.9	497	24.2
2.0 - 2.9	386	18.9
3.0 - 3.9	291	14.2
4.0 - 4.9	183	8.9
5.0 - 5.9	42	2.0
6.0 - 6.9	22	1.1
7.0 - 7.9	4	.2
8 or more	2	.1
Total	2046	99.8 [b)]

a)
  Recorded by Mast equipment in a rural area in Ithaca, New York, U.S.A.

b)
  0.2% lost in rounding errors.

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TABLE 2

FREQUENCY DISTRIBUTION OF DAILY 4-HOUR-AVERAGES
(0900-1300) OF OZONE CONCENTRATIONS FROM
MAY 22 - SEPTEMBER 7, 1969 [a]

Concentration (PPHM)	Number of Days	Percentage of Days
0.0 - 0.9	22	24.4
1.0 - 1.9	43	47.7
2.0 - 2.9	18	20.0
3.0 - 3.9	6	6.6
3.9 - 4.0	1	1.1
Total for days of record	90	99.8 [b]

[a]

   Recorded with Atlas Analyzers with SO_2-scrubbers in a pure
   stand of *Pinus strobus L.* in Pisgah National Forest, Pisgah,
   North Carolina, U.S.A.

[b]

   0.2% lost in rounding errors.

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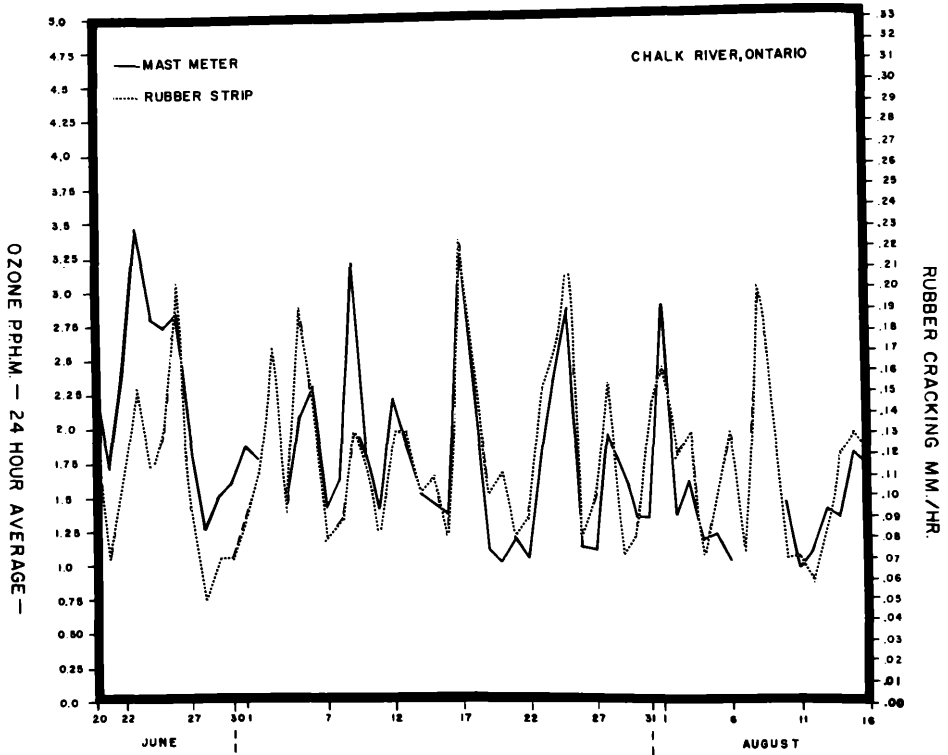
Figure 1   Relationship between coulometric and rubber-cracking methods for the determination of ambient ozone at Chalk River, Ontario from June 20 to August 16, 1966
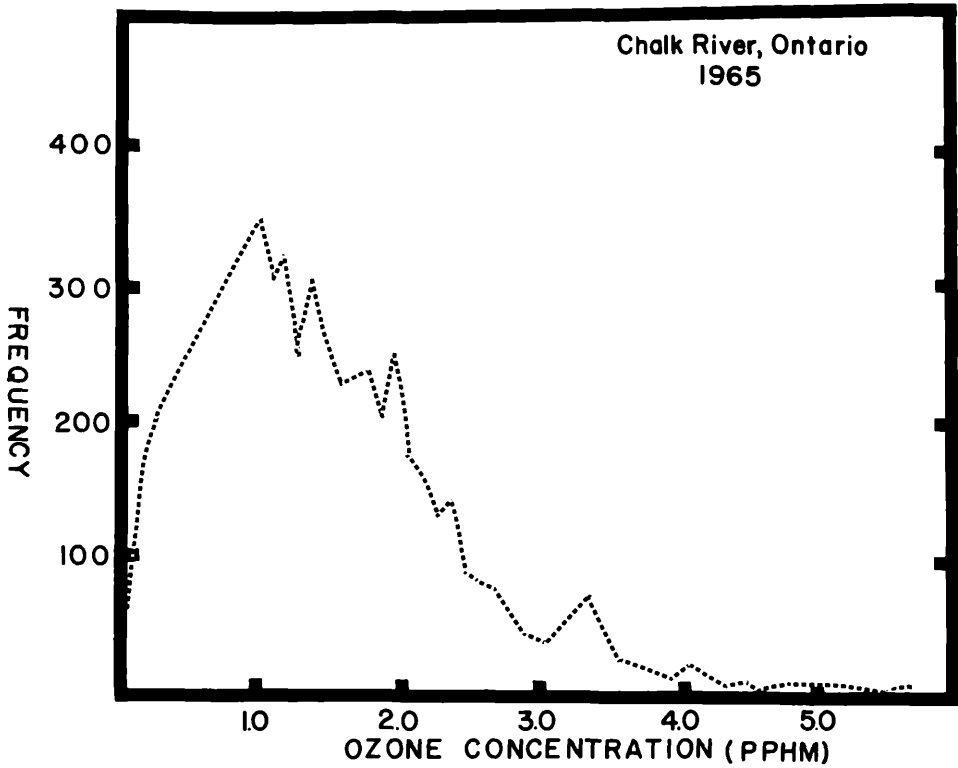
Figure 2   Frequency distribution of average 15 - minute ozone concentrations for 24 hours per day recorded at Chalk River, Ontario from June 1 to August 13, 1965
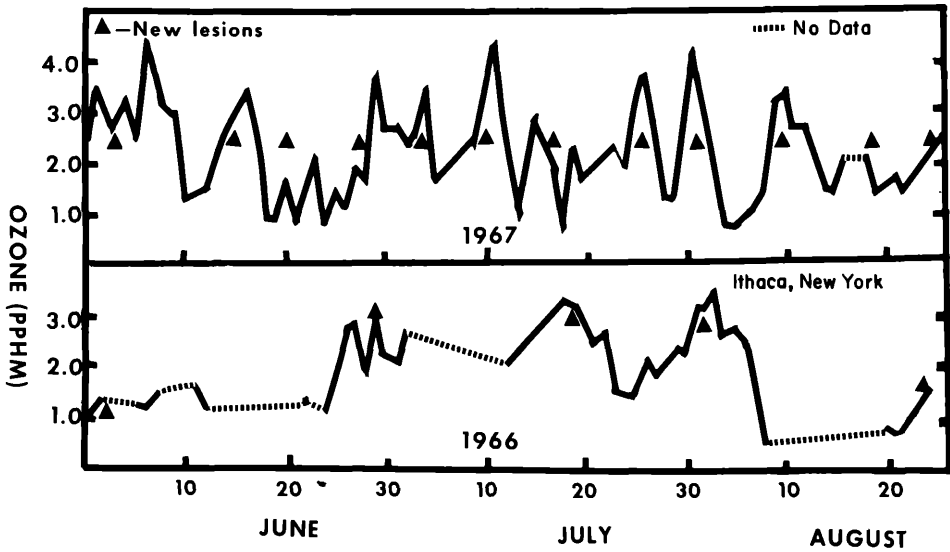
Figure 3   Daily mean ozone concentrations in a stand of Pinus
            strobus L. in New York, U.S.A., and the occurrence
            of new lesions on current year's foliage of P. strobus
            during the growing seasons of 1966 and 1967