

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 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 available 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

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 (depolarization) 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 concentration of the gas being measured. Analyzers are designed to operate unattended for at least one week's time. Field comparisons of measurements from colorimetric and coulometric oxidant analyzers where readings did not exceed 20 pphm and corrections were made for NO₂ 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).

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 NO₂, 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 Å. 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 concentrations 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.

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 ppm was reported (15). In the Antarctic the mean monthly surface ozone values from April 1957 to May 1958 ranged from 1.0 to 3.4 ppm (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 ppm to 4.0 ppm by the former method, and from 1.0 ppm to 3.0 ppm 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 ppm to slightly over 4.0 ppm. Diurnal fluctuations in atmospheric ozone concentrations were recorded with oxidant values at night usually less than 1 ppm, increasing in the morning hours to a peak around noon of 3 ppm 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 ppm 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 ppm; in West Virginia 2.22 ppm; whereas, in central Ontario it was only 1.14 ppm.

The frequency distribution of average 15-minute ozone concentrations 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 ppm while in 1967 the mean for this same period was 2.02 ppm. The highest recorded 4-hour-mean ozone concentration in 1966 varied from 4.0 to 5.0 ppm. The corresponding range in 1967 was 5.0 to 8.0 ppm. 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, i.e. calibration of instrument; appropriate filters; servicing requirements.
- 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 Antarctic 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

between June 9 and September 2, 1967, were in excess of 3.0 ppm. On two occasions the 3.0 ppm concentration was exceeded throughout periods of 48 hours. On four occasions the recorded concentration was at least 7.0 ppm 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 instability 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 Aerometric 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.

TABLE I

FREQUENCY DISTRIBUTION OF MEAN HOURLY OZONE
CONCENTRATIONS, JUNE 9 - SEPTEMBER 2, 1967 ^{a)}

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.

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
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Total for days of record	90	99.8

a)

Recorded with Atlas Analyzers with SO₂-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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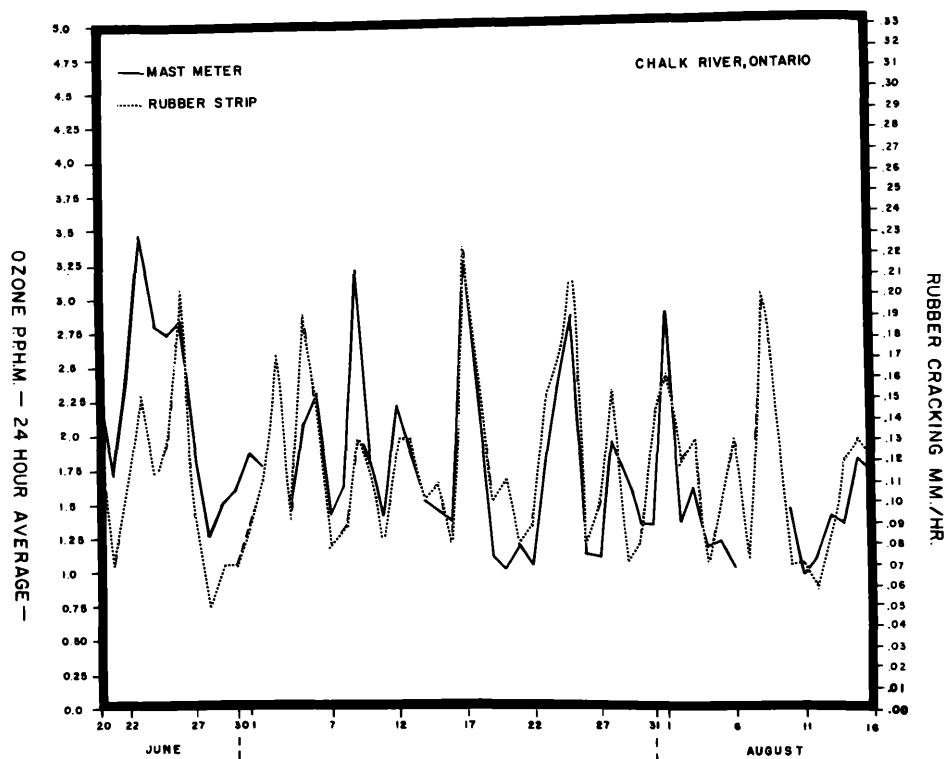


Figure 1 Relationship between coulometric and rubber-cracking methods for the determination of ambient ozone at Chalk River, Ontario from June 20 to August 16, 1966

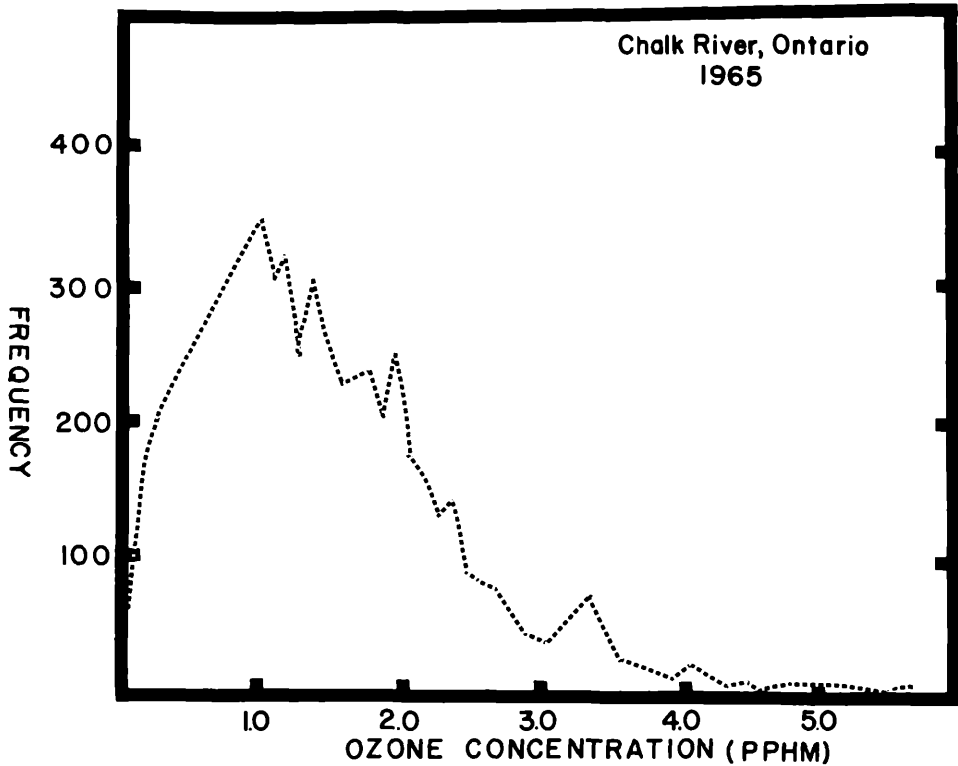


Figure 2 Frequency distribution of average 15 - minute ozone concentrations for 24 hours per day recorded at Chalk River, Ontario from June 1 to August 13, 1965

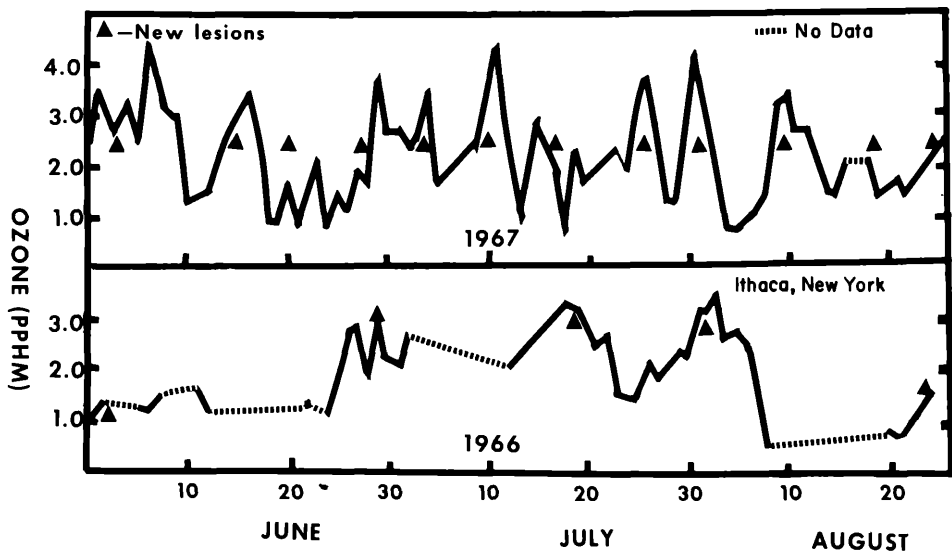


Figure 3 Daily mean ozone concentrations in a stand of *Pinus strobus* L. in New York, U.S.A., and the occurrence of new lesions on current year's foliage of *P. strobus* during the growing seasons of 1966 and 1967