ATMOSPHERIC POLLUTION BY OZONE: ITS EFFECTS AND VARIABILITY

by

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Submitted to the Departments of Aeronautics and Astronautics and of Meteorology on May 1, 1965 in partial fulfillment of the requirements for the degrees of Master of Science.

ABSTRACT

Surface ozone concentrations were measured in the Boston-Cambridge complex for the months of November and December, 1964 and January, 1965. The instrumentation used was a Mast ozone meter and recorder; a chromium trioxide filter was fitted to the air inlet of the meter to remove negatively interfering sulphur dioxide. The effectiveness of this filter was remarkably apparent in that removal of the filter caused ozone reductions of 50-100%.

The overall range of ozone levels for the three months was 0.1 to 6.4 pphmv (part per hundred million by volume), well below toxic limits discussed in detail in this thesis.

The average values for each of the three months indicate a possible correlation with the total ozone trend. Variation of the daily values is discussed with some meteorological factors as well as source strength.

Seven simultaneous measurements of some of the halogens, obtained from a separate study by a colleague, are related to ozone concentrations.

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I INTRODUCTION

In his State of the Union message to the people of the United States of America in January of 1965, President Lyndon Baines Johnson emphasized the need for air pollution studies and control, particularly in the urban areas of the country, as one of the more important matters facing the nation.

Ozone is one of the major contaminants that exist in polluted urban atmospheres and is very harmful to people, plants, and animals if the concentration is allowed to reach certain levels. On the other hand, the presence of ozone in the lower stratosphere shields the earth from the deadly ultra-violet light of the sun.

Since ozone was discovered in Germany by Schönbein over one-hundred years ago, much has been studied and reported about this gas; however, the majority of the meteorological work done has been with the use of ozone as a trace substance in the upper atmosphere where it is produced by photochemical reactions. With the discovery of the toxic properties of ozone in the last few years, a fact that is still reported incorrectly in some recent literature accounts, a new impetus in the field of ozone pollution has arisen in measurements and measurement techniques in all levels of the atmosphere particularly in major urban areas known for pollution problems.

The concentration of ozone in the upper atmosphere between 20 and 30 kilometers reaches values as high as 10 parts per million by volume (ppmv) which is a lethal dosage for humans if exposed to it for a specified length of time. With the advent of supersonic commercial aircraft flying at levels close to the maximum values of ozone, these potential toxic effects will present a tremendous problem to the builders and designers of these planes, a dilemma probably even more critical than effects of cosmic radiation. Elimination of ozone in these deadly proportions will undoubtedly be done by the use of filter techniques in the compressor system, possibly of a catalytic nature, as are used in some high altitude military planes, or of the activated carbon type used in the space field. However, the duration of flight in commercial air travel is in most cases greater than the length of military or space flights; thus greater dangers are presented due to longer exposure times. The effect of ozone in high-altitude cabins is discussed in greater detail by Jaffe and Estes (1964).

In the lower levels of the atmosphere, more specifically in polluted urban areas, it is important that the levels of ozone concentration be determined and monitored. Much of this work has been and is being done in noted smog areas such as Los Angeles and London where pollution is an immediate problem. But what about other cities and areas of this nation and the world where population, industry, and motor vehicles are increasing at a rapid and somewhat alarming pace? In this day and age, there seems to be a trend toward moving everything and everybody into the large city complexes, particularly in the United States.

The measurements of ozone in the past have been concerned in large extent with the total amount of ozone in a vertical column of the atmosphere. But what about surface concentration measurements or measurements at a particular level of the atmosphere? This type of measurement could be extremely important to the meteorologist or toxicologist. Recent work by Kawamura (1964) on measurement of surface ozone in the Tokyo area showed that the concentration of ozone in the lower troposphere and at the surface varied simultaneously with total ozone amount. However, in some areas, it is possible that pollution by surface sources is a greater factor in surface ozone concentration than the ozone which is brought down from upper levels by diffusion, turbulence, and vertical transport. Kawamura's result could be extremely significant, if valid everywhere, in that former investigations which used total ozone content could be reviewed somewhat critically perhaps in view of present surface measurements.

It is hoped that new results can be gathered with the use of surface ozone measurements such as the variability of ozone in different air masses, the effects of source strength, and many other comparisons with regard to the major meteorological parameters. Also comments about the many reactions, both direct and indirect, on the formation and destruction of ozone would be an interesting study area to be probed with better instrumental techniques. Another question to be raised is "Are the concentrations of surface ozone high enough to create a hazard to the vital human activity in the area concerned, and if so what solutions should be proposed?"

The author measured surface ozone concentration in the Boston-Cambridge complex using a portable Mast ozone meter with a filter that removed the negative interference of sulfur-dioxide. The measurements were recorded at three different sites in the city complex during the months of November and December in 1964 and the month of January of 1965.

II DESCRIPTION OF OZONE

A. Properties

Ozone, O_3, is a colorless to blue gas with a pungent odor and has a gas density of 2.144g/liter at 0°C. (760mm) which is 50% greater than oxygen, O_2. In high concentrations, ozone has a characteristic chlorine or sulfur-dioxide like odor, whereas in lower concentrations, it has a so-called "electrical odor" discernable after a thunderstorm. Ozone boils at -111.9°C (760mm) and melts at -192.7°C. It will condense at low temperatures to a blue black liquid. The chemical properties of ozone are similar to those of oxygen, but ozone is more reactive. Many substances that do not react at all with oxygen, or only slowly, react readily with ozone. Silver, for example, which remains bright and shining for years in ordinary oxygen quickly becomes covered with a brown film of silver oxide when exposed to air containing a trace of ozone. Also a stretched rubber band exposed to the action of ozonized air snaps in a few seconds showing how rapidly it is oxidized.

B. Uses

Ozone is used industrially in the bleaching of colors and dyes in textiles and of oils, fats, flour, starch, and sugar in foodstuffs; it is also used in producing peroxides. The use of ozone has also been mentioned in the controlling of mold both in fruit produce, particularly apples, and also in the dairy industry, namely cheese and cheese products. Most recently, there has been thought of using high-energy liquid ozone to replace liquid oxygen in rocket fuels, thus providing a 20% increase in energy over former conventional liquid fuels, such as hydrogen-oxygen. Recent work done at M. I. T. on the delicate job of controlling and storing the dangerous and unpredicatable liquid ozone has made this a feasable proposition.

The last mentioned use of ozone would be a boon in the present space age; however, there exists the possibility of ozonospheric contamination because the exhaust gases of the rockets. The disruption of the upper atmosphere could have serious implications on our environment and would be a very important factor in considering ozone as a fuel for rockets. This problem of contamination by exotic rocket exhaust gases on the atmosphere, particularly the upper portions, is getting more and more acute because of the augmentation in the size of rocket boosters. The total mass of constituents in the upper atmosphere is so small, it is conceivable that the exhaust gases will be approaching these magnitudes. With a possible fuel like fluorine which is a scavenger of electrons, there is a chance of upsetting the ionosphere, thus causing severe communication problems as well as other major disorders. The subject of atmospheric modification by rocket exhausts is not discussed in detail here, but the author refers interested persons to the work being done by the Geophysics Corporation of America (Millman et al, 1962).

A few years ago, ozone was frequently advocated as a means for removing deadly carbon monoxide gas from garages. The ozone was to be produced by ozone generators. Fortunately,this scheme was found to be too slow to convert carbon monoxide to carbon dioxide. Of course if the toxic properties of ozone were well known at that time, the above proposal would have been absurd. The important topic, ozone toxicity, is discussed in the next section.

III TOXICITY

A. Effect on plants

In a 1962 report to the Congress of the United States, the Surgeon General related that plant damage by air pollution cost the nation between one hundred and fifty and five hundred million dollars annually. One of the major air pollutants mentioned as a cause of this damage was ozone.

Many observers and investigators in the nineteen forties noticed smog effects on leafy vegetables and other crops in the Southern California area. A constituent of photochemical smog, ozone was studied with regard to the plant problem by Haagen-Smit et al, (1952). They showed that the combination of ozone at 28 parts per hundred million by volume (pphmv) and gasoline vapors at 340 pphmv produced the same plant damage as observed in the area mentioned above.

Richards et al, (1958) reported that ozone might be the cause of stipple disease on grapes in California. Later Heggestad and Middleton (1959) showed that "weather fleck" disease on tobacco plants could be produced by exposure to ozone, and that high ozone levels were correlated with observed fleck reports. In a Connecticut study, Sand (1959) found that experimental concentrations of ozone greater than 10-20 pphmv produced this leaf tissue injury called fleck in susceptible varieties of tobacco. This susceptibility to fleck is partly genetic as was demonstrated by hybridization experiments in the New Haven, Connecticut station. Sand also mentioned that physical or chemical measures to close the leaf Stomata, or antioxidant sprays to diminish the local concentration of ozone reduced fleck injury.

A suggestion by Daines et al, (1960) in a preliminary study was that a disease of spinach may be related to atmospheric ozone concentration.

The effects of ozone are probably produced by its action on the cell enzymes of the plants discussed. Freebairn (1959) demonstrated that certain reducing agents such as glutathione and ascorbic acid tended to hinder the effects of ozone upon certain reducing groups in vital protein molecules. Further field tests indicated that the damaging effects of smog-associated ozone upon plants were reduced by the use of vitamin C (ascorbic acid) sprays.

B. Effect on animals

Ozone effects on animals have been described by many researchers in papers for a little over a century. From this work, physiologists and toxicologists have obtained much needed data in hopes of studying man's adaptations to ozone.

In an experiment by Diggle and Gage (1955), they found that the LD_{50} (lethal dosage in fifty per cent of cases observed) for rodents exposed for a period of four hours was 12 ppm (vol). This is a rather high concentration of ozone, and it is very unlikely that a concentration of this magnitude would be found in polluted air near the ground. Stokinger (1957) observed that the LD_{50} for rats and mice also exposed for 4 hours was 4.8 - 3.8 ppm (vol). Mittler et al (1957) reported using animals (small) exposed to ozone produced by a corona discharge ozonizer that the LD_{50} in a 3 hour exposure period was 12 ppm (vol) for rodents in one study and over 20 ppm (vol) in another (1956).

Thorp (1941) suggested that the presence of nitrogen oxides which could be generated by some ozonizers may enhance the toxicity of ozone. Diggle and Gage in their paper stated that mixtures of ozone and nitrogen dioxide reacted in part to form N_2O_5 (nitrogen pentoxide) which was about three times as toxic as ozone. Stokinger (1957), however, claimed that as a result of many careful studies on test animals that there are no reasonable grounds for these claims that nitrogen oxides contribute significantly to the toxicity of ozone. In fact, he reports that the lethal effects of ozone on mice was reduced slightly by the addition of nitrogen dioxide.

Many conflicting reports of the above nature occur in the literature. These discrepancies are most likely due to the use of crude ozonizers, unreliable methods of analysis and measurement, and the presence of organic materials readily attacked by ozone.

The cause of death in the above mentioned studies was due to acute pulmonary edema and hemorrhage. In other animal studies, it was found that with repeated exposure to ozone of 1 ppmv (only slightly higher than reported in some urban areas) 8 hours a day for periods up to one year, the animals contracted bronchitis, fibrosis, and bronchiolitus.

Stokinger et al (1961) demonstrated that several other substances of oxidative nature including ozone are capable of educing a comparable acutely toxic response and subsequently causing the development of a tolerance toward further intoxication. For example, pre-exposure to lower levels of ozone seemed to protect animals from subsequent otherwise lethal dosages. Also, hydrogen peroxide (H_2O_2) administered to mice in repeated dosages of about 20% of the lethal dose conferred protection on these animals when they were challenged with acute lethal dosages of ozone. When ozone and carbon dioxide were administered to rodents, it was found that the acute toxicity of ozone was slightly enhanced. Another interesting discovery was that oil mists tended to protect small animals from the acute effects of ozone. This protection was only afforded if the animals were exposed to the mist before coming in contact with the ozone. If the exposure to ozone and mist was simultaneous, the toxicity was slightly intensified. White mineral oil gave greater protection than motor oil. Whether this mist protection would work on human beings is not known.

Ascorbic acid (vitamin C) which was used as a spray in plant protection discussed earlier in section A decreased mortality and lessened pulmonary edema when given to mice before exposures to lethal concentrations of ozone. When combined with reducing agents and other vitamins, ascorbic acid conferred almost complete protection against otherwise lethal exposures.

Serotonin although it did not influence mortality gave some protection in that it lessened the amount of pulmonary edema. Serotonin, however, was given after ozone exposure in large dosages, 1 mg, (Matzen, 1959).

C. Effect on humans

While there have been many studies on ozone effects on animals, such experiments on human beings are few, as is to be expected with any toxic gas. The few reports that are available have dealt only with a small number of subjects in questionable environments. This small sample tends to give some conflicting conclusions because of the wide variability in human beings in reacting to any type of toxicological agent.

Kleinfeld and Giel (1956) described the ozone effects on three welders exposed to 9.2 ppm (vol) of ozone in workshop air, while Kleinfeld et al (1957) reported on intermittent exposures of from 0.3 to 8 ppm (vol) of ozone on electric arc welders. Dyspnea and headache developed rapidly in the welders, and after a nine month period, fatigue and dyspnea were still evident although clinical recovery was complete. Griswold et al (1957) exposed a volunteer to 1.5 to 2.0 ppm (vol) for a period of two hours. The subject was studied with the use of a spirograph, an instrument used for recording respiratory movements. The volunteer suffered dryness of mouth and throat, constrictive substernal chest pains, lack of coördinating ability, and difficulty in expression and articulation. He also suffered significant respiratory embarrassment immediately after exposure and this diminished for 22 hours thereafter.

One of the better studies conducted was by Clamann and Bancroft (1959) on a group of 5 subjects. The volunteers were exposed to concentrations of 1.2 to 6.0 ppm (vol) in periods of 1 to 2 1/2 hours in a controlled room over a period of two weeks. The highest concentration of ozone applied was 6.0 ppm (vol) for 1 hour and the longest exposure time was 2 1/2 hours at a concentration of 1.2 ppm (vol). Although there was great individual sensitivity to ozone, the authors noted a definite effect on the respiratory system with a decrease in vital capacity of the lungs. This lung capacity decreased with increasing concentrations of ozone. With the aid of lung function tests, it was observed that edema seems to begin in men at concentrations of 4 to 5 ppm (vol) at exposure times in the range of one hour. A definite impairment of all the subject's sense of smell was found with no effects on blood pressure, pulse rate, and blood itself. Other discomforts such as a burning sensation in the throat, feeling of oppression of the chest and difficulty in breathing were reported by certain individuals, burning of the eyes was not detected.

In comparing inhaled air of 4.8 ppm of ozone to exhaled air which contained no ozone, it was concluded that ozone decomposes completely in the respiratory tissues.

The above reports are of interest because they indicate the levels to which ozone exposure may go before toxicity becomes evident; they do not take into consideration however, the tolerances that man may exhibit when his exposure includes not only ozone in air but other contaminants as well.

The experimental results in this report are fairly consistent with the maximum allowable concentration value of 0.1 ppm (vol) for an eight hour day which was adopted by the American Conference of

Governmental Industrial Hygienists in 1955. The alert stages for toxic air pollutants in ppm (vol) adopted by the Los Angeles County Air Pollution Control District in 1955 are as follows for ozone: first alert 0.5 ppm, second alert 1.0 ppm, third alert 1.5 ppm. The definitions of the stages are:

First Alert: Close approach to maximum allowable concentration for the population at large. Still safe but approaching a point where preventive action is required.

Second Alert: Air contamination level at which a health menace exists in a preliminary stage.

Third Alert: Air contamination level at which a dangerous health exists.

From the discussion in previous three sections, the requirement for precise monitoring of ozone levels in polluted urban centers should be obvious.

IV FORMATION AND DISTRIBUTION OF ATMOSPHERIC OZONE

A. Upper Atmosphere

Most of the ozone in the atmosphere is found between 20 and 50 km. Ozone is formed in the upper atmosphere by a photochemical process. Similarly, photochemical reactions tend to destroy it. An equilibrium between these reactions determines the concentrations of ozone. The reactions thought to be most important are:

$$O_2 + hv \longrightarrow 2O \qquad (\lambda < 2420\ \overset{o}{A}) \qquad (1)$$

$$O_2 + O + M \longrightarrow O_3 + M \qquad (2)$$

$$O_3 + hv \longrightarrow O_2 + O \qquad (\lambda < 11540\ \overset{o}{A}) \qquad (3)$$

$$O_3 + O \longrightarrow 2O_2^{*} \qquad \text{(excited)} \qquad (4)$$

(1) and (2) determine the production of ozone from oxygen. It is seen that in (1) oxygen dissociates into its atomic form with the absorption of a quantum of energy corresponding to wavelengths less than 2420 Angstrom Units. The collision of this unstable atom with an oxygen molecule in the presence of a third body (either an oxygen or nitrogen molecule) produces one molecule of ozone. Concurrent to this pro-

duction mechanism is the destruction of ozone by the absorption of sunlight to give molecular oxygen and a free atom of oxygen. This, by the way, is the reaction which made ozone a "germicide" by the release of the powerful oxidant, O. The reaction was thought to be very useful to human activity until the toxic properties of ozone were brought to bear. A second collision reaction (4) also aids in the equilibrium.

Craig (1950) and Johnson (1954) show the derivation of an expression demonstrating equilibrium concentration of ozone in terms of solar radiation flux, reaction equilibrium constants, and height (density). From the expression, we can calculate the amount of ozone predicted by photochemical equilibrium alone as a function of height. Qualitatively, the distribution would show a maximum total amount at the equator with a decrease towards the poles, and a temporal maxima in the summer. The vertical profile predicted by theory is in fair accord with observation but the horizontal distribution observed has a maxima at about 60°N and the maximum amount occurs in the Spring season.

It is evident from these calculations that the atmospheric ozone on the whole is indeed not in photochemical equilibrium. Wulf and Deming (1936) investigated non-equilibrium effects and found that above 35 km at high sun angle, if all the ozone were removed, equilibrium would be restored almost immediately. Below this, in the 25 to 30 km level, a

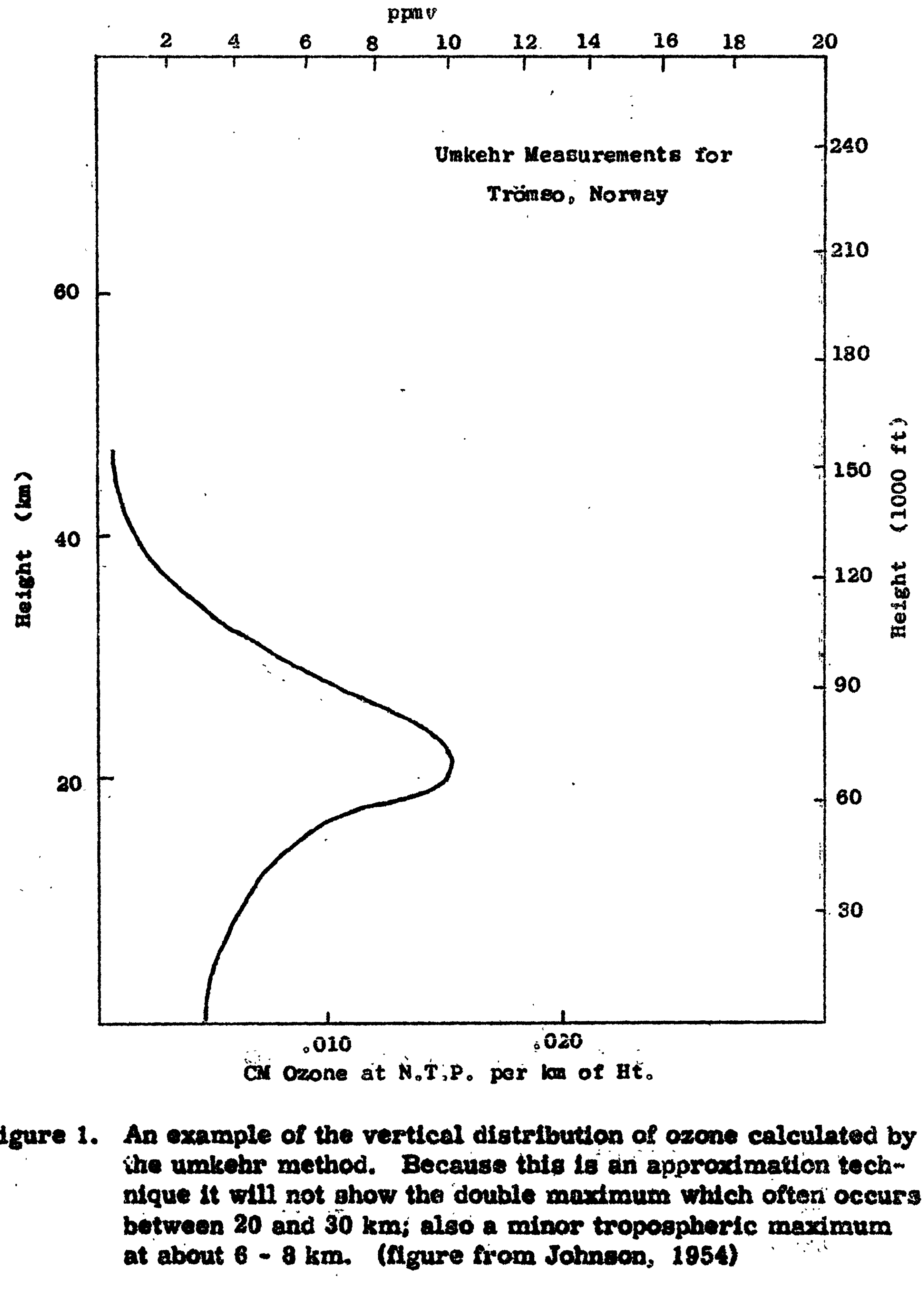

Figure 1. An example of the vertical distribution of ozone calculated by the umkehr method. Because this is an approximation technique it will not show the double maximum which often occurs between 20 and 30 km; also a minor tropospheric maximum at about 6 - 8 km. (figure from Johnson, 1954)

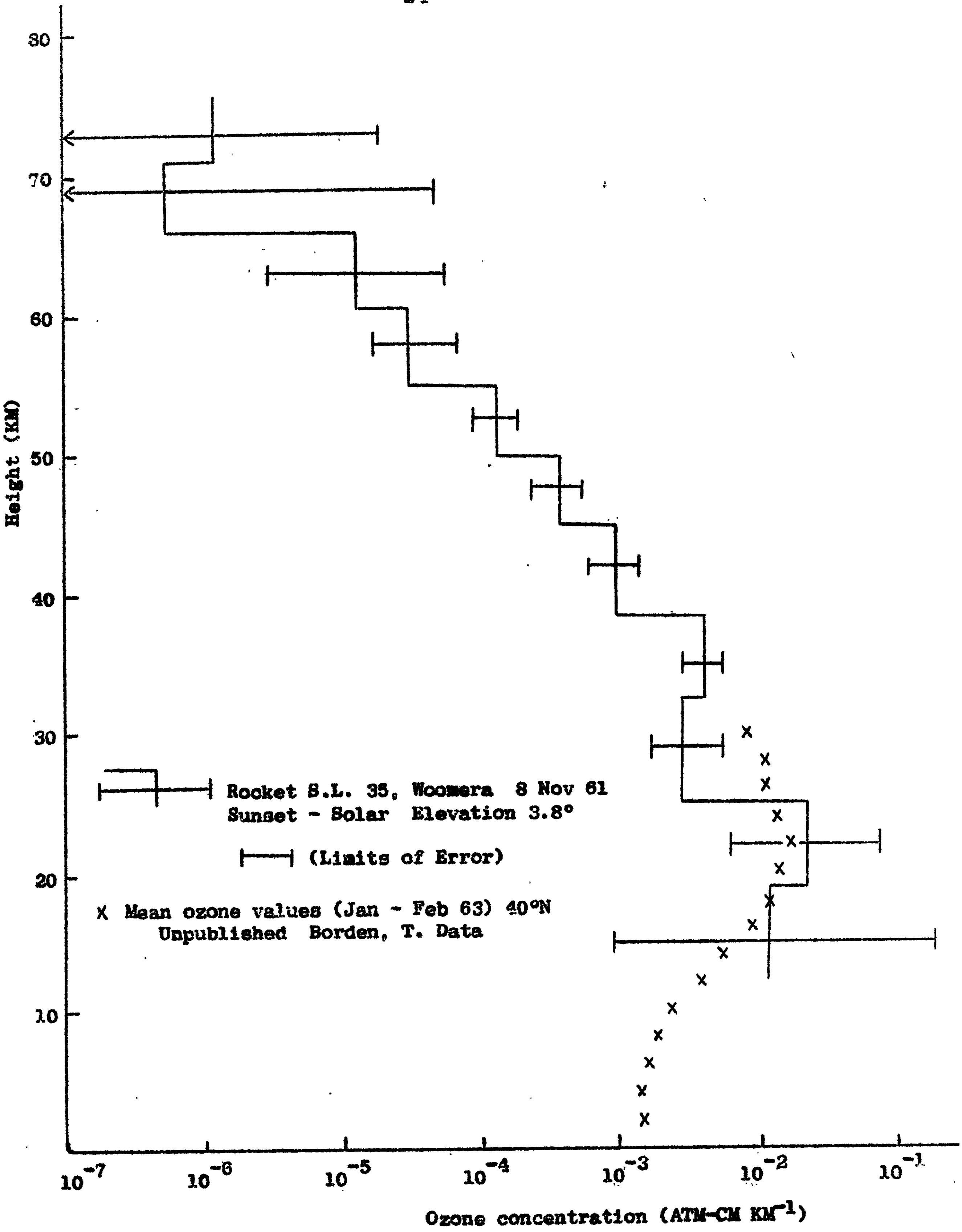

Figure 2. Vertical distribution of ozone.

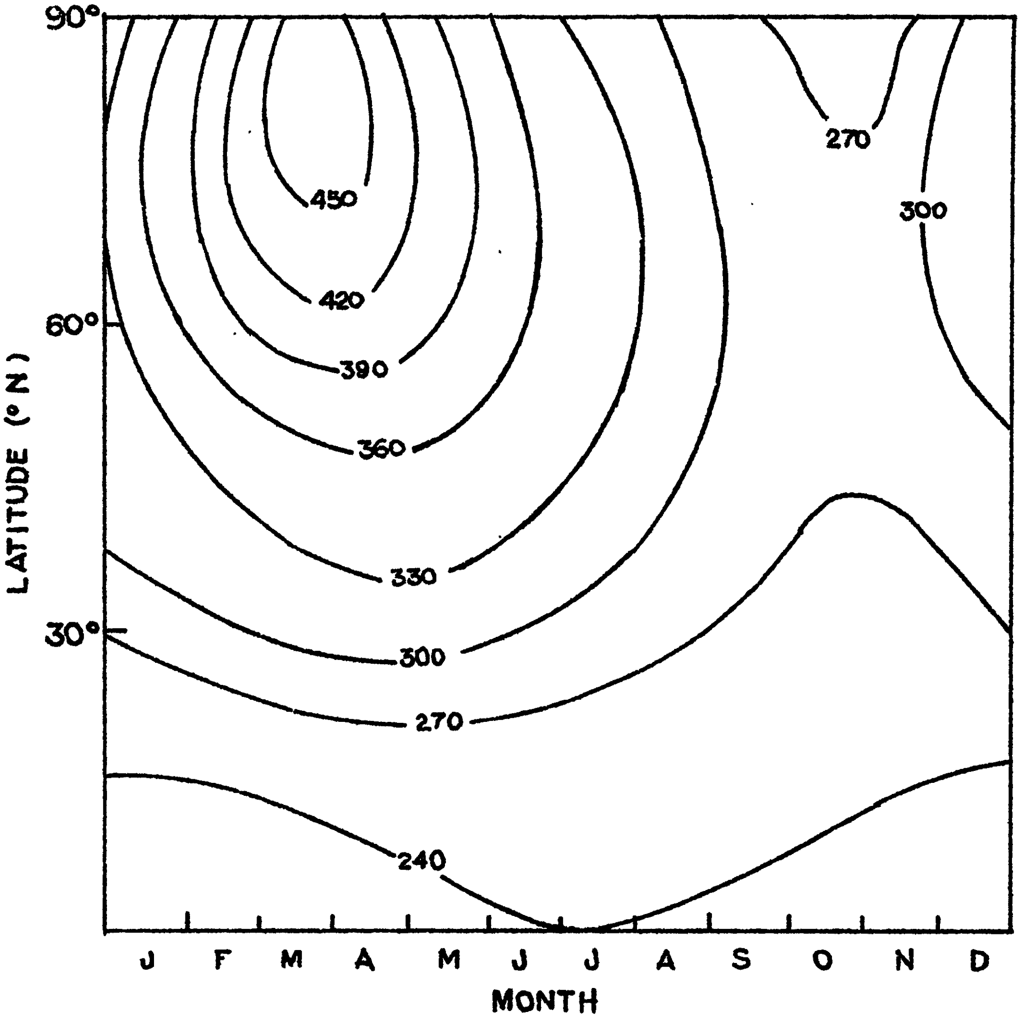

Figure 3. Mean distribution of total ozone as a function of month and latitude. The isopleths give total ozone in 10^{-3} atm-cm (STP cm) on the Vigroux scale. (figure from Godson, 1960)

a similar interruption would take days to months to erase, and still at lower altitudes, equilibrium is almost never restored. The reason for this is that ozone absorbs so strongly in the ultraviolet wavelengths which induce reactions that below the upper few kilometers, the atmosphere is protected from this light. In fact, in the Hartley band (3200-2000 A), as low as 1/145 centimeter layer (STP) can reduce the intensity by 1/10. The entire quantity of atmospheric ozone if reduced to standard temperature and pressure would form a layer only a few millimeters thick. Here, and in most other works on atmospheric ozone, the concentration of ozone is given in terms of thickness. To convert these units into parts per million by volume (ppmv), one needs only the appropriate conversion factors (Appendix A).

B. Transport Properties

A circulation pattern of some type is needed which can create a maximum of total ozone at the latitude and season at which it is found. There are two immediate possibilities, one, a horizontal field of motion which might concentrate it in a certain band, or secondly, a vertical motion which might pull down ozone from the region of photochemical equilibrium. The actual field of motion is probably a combination.

Although we have a fairly good understanding of tropospheric circulations, the fact that ozone is found mainly above 20 km forces us to look to stratospheric motions to describe its behavior. In fact, ozone is one of our better tracers to aid in the investigation of the stratosphere.

It is interesting to note that the early thinking on a stratospheric general circulation followed the same pattern as the development of the tropospheric circulation. Craig (1948) found the ozone measurements to indicate a mean meridional cell. However, a variety of data and m many investigators, Reed (1953), Martin (1956), Dütsch (1959), Newell (1963a, 1963b), have led to a postulated circulation similar to the troposphere, one in which the eddies play a major role in middle latitudes.

The work of Reed (1953) and that of Dütsch (1959) indicates that there is a steady downward flux of ozone into the troposphere where it is destroyed in large quantities by chemical, photochemical, and catalytic reactions. The mechanism by which it is passed through the tropopause region is not thoroughly understood but the transfer apparently occurs in the vicinity of the jet stream, in frontal zones, and perhaps also directly across the tropopause region. These transfer processes have been discussed by Danielson (1959, 1964), Brewer (1960), Staley (1960), Newell (1963a) and Briggs and Roach (1963). The following presentation of four mechanisms is from Brewer's paper (see Figure 4):

1) Here is a continuation across the tropopause of the flow nonadia-

batic descent which is presumed to have brought the ozone down to the tropopause. This process would tend to give a relatively uniform rate of transfer of ozone into regions. The outflow would be greatest in late Spring when the high concentrations are found near the tropopause.

2) Since the tropopause often slopes relatively to the isentropic surfaces, especially in the region just north of the subtropical jet stream, motion along the isentropic surfaces can take ozone out of the stratosphere. This process would give greatest outflow just north of the subtropical jet and requires relatively high concentrations of ozone just above the tropopause in these regions.

3) Exchange can occur along the isentropic surfaces which lie in the lower stratosphere of temperate regions and pass through the subtropical jet into the upper, tropical troposphere. Ozone-free air can enter the stratosphere and conversely the ozone-rich air can pass out of the stratosphere. This mechanism will concentrate outflow at the region of the subtropical jet and will be greatest in Spring when the temperate stratosphere contains most ozone.

4) There is also the possibility of this circulation pattern through the lower stratosphere. Any contribution which such a circulation makes to the transfer of ozone to the troposphere will give outflow in the region of the subtropical jet with a strong maximum in late Spring

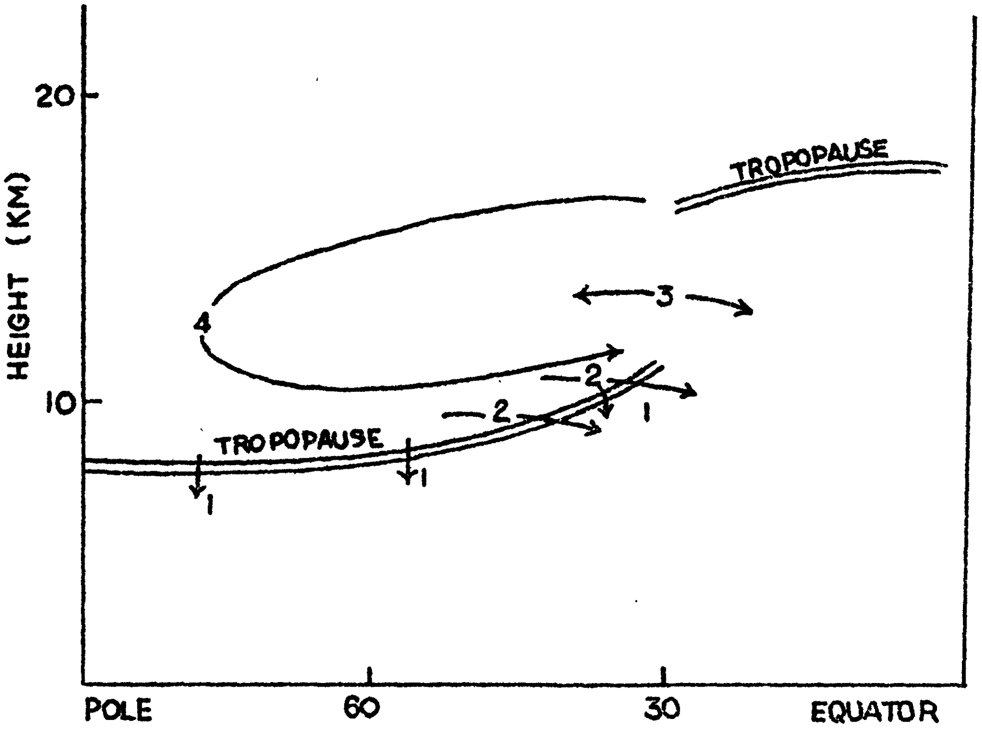

Figure 4. Possible Mechanisms for the transfer of ozone from the Temperate Stratosphere into the Troposphere (Brewer, 1960).

and early Summer when the ozone levels near the lower part of the jet is highest.

For a more quantitative estimate of the relative importance of the several transfer mechanisms based upon radioactivity data see a Table by Machta, quoted by Murgatroyd (1964).

In conclusion to this section on ozone in the upper atmosphere, the author feels that with more high-quality measurements, researchers can look forward to a regular grid of reporting stations to aid in making the study of atmospheric ozone a very valuable tool for the purpose of further examination of the behavior of the stratosphere. Persons interested in present upper level ozone measurements are referred to the compilation of data from the work of Mr. Wayne S. Hering (1964) at the Air Force Cambridge Research Laboratories in Bedford, Mass. Hering's data from ozonesondes from different stations over North America give the ozone concentrations at various levels in the atmosphere rather than the total ozone amount in a column for the whole atmosphere that was used in the studies mentioned in this section. These reported and tabulated values make it easier to carry on investigations at particular levels in the atmosphere with reliable and not approximate wind data.

C. Lower Atmosphere (at the surface of the earth and particulary in polluted air)

Most of the ozone present in the atmosphere is produced photochemically in the upper levels above 20 km as mentioned in the previous sections; some of this ozone is transported downward into the troposphere where it is partially destroyed by chemical reactions. The small amount that reaches the surface of the earth is almost completely depleted by the ozone reactions with surface soil, plants, etc. In this section, the ozone production in the polluted surface layers particularly in the vicinity of urban areas will be discussed.

Ozone in polluted air is primarily produced and destroyed by the following reactions according to Leighton and Perkins, 1958.

$$NO_2 + hv \longrightarrow NO + O \quad (3100\mathring{A} < \lambda < 3700\mathring{A}) \qquad (5)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (2)$$

$$O_3 + hv \longrightarrow O_2 + O \qquad (3)$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (6)$$

In (3) ozone absorbs between 2000 and 3200 Å in the ultraviolet Hartley bands and between 4500 and 7000 Å in the Chappius bands; however all solar radiation of wavelength shorter than 2900 Å is absorbed in the upper atmosphere. M in (2) is any particle capable of absorbing excess energy released by the reaction (otherwise O_3 would be unstable and quickly dissociate again). The atomic oxygen formed by (5) will also react with other constituents present in the polluted urban atmosphere, but the above mentioned authors reported that 99.5% of the atomic oxygen reacts with molecular oxygen to form ozone and that less than 0.5% reacts by all other processes. Other reactions have been suggested as possible producers both directly and indirectly of ozone but their validity still remains uncertain.

While not immediately involved in the formation of ozone in polluted air there are some constituents of the local air which enhance or slow down the above main reactions. For example, ozone production is apparently increased in the presence of olefins, whereas the production rate of ozone for most paraffins is small as reported by Schuck and Doyle (1959). Also some types of olefins not only promote rapid rates of formation of ozone, but tend to promote high concentrations of ozone. Reaction (2) is slow and does not substantially decrease the ozone concentration but (3) limits the concentration which can coexist with nitrogen-dioxide.

In view of the above reactions, one can easily see that the presence of nitrogen-oxides is very important in the study of both urban and non urban pollution by ozone. The internal combustion engine and other high temperature combustion processes such as industrial furnaces are the chief sources of nitrogen dioxide, especially if the effluents are rapidly cooled. Dickinson (1961) reports that with the gasoline engine, the nitrogen oxide is almost entirely in the form of nitric oxide when exhausted from the engine; however, once in the atmosphere, nitric oxide converts rapidly to nitrogen dioxide. According to Leighton and Perkins, it appears that the conversion of nitric oxide to nitrogen dioxide is assisted by many organic substances such as olefins, aromatic hydrocarbons, aldehydes, and paraffins.

In a most recent work by Kawamura (1964), it is suggested that a part of surface nitrogen-dioxide may originate from the surface soil as a result of bacterial reaction. Kawamura also found from measurements in Tokyo that nitrogen-dioxide in the surface air had a marked duirnal variation with two maxima in the day which occurred respectively in the morning three hours after sunrise and in the evening two hours after sunset. This duirnal variation of nitrogen-dioxide in polluted air could be explained as a result of meteorological conditions, photochemical effects, and traffic density. A similar result was found by Dickinson (1961) in the Los Angeles area.

To show the importance of nitrogen-dioxide in the formation of surface ozone, Vassy (1963) reported that the ozone concentration in Paris was but a fraction (on the order of 1/10) of the concentration measured in Los Angeles during comparable conditions. Most of this difference was attributed to the smaller number of automobiles in the French city; in a similar comparison between London and Los Angeles, the ozone concentration ratios were in the same proportion as the engine cylinder ratios. Other possible reactions of ozone with constituents of polluted air are those with members of the halogen family, most important of which could be chloride. These particular chemical reactions will be discussed more completely in a later section of this thesis; this evaluation is a direct result of this author's work in sampling ozone in the Boston-Cambridge complex.

D. Other mechanisms in the production of ozone

In addition to the reactions mentioned in the previous three sections, ozone is formed in other ways; one of these is the dissociation of molecular oxygen into atomic oxygen by an electrical discharge and the subsequent reaction of the oxygen atom with molecular oxygen to form ozone. In the atmosphere, this is a common occurrence during lightning in thunderstorms, discharge from airplanes, and even in silent discharges that happen in snowstorms. Vassy (1954) showed while measuring surface ozone in Paris that there is a definite increase in concentration during thunderstorms; however, the abrupt increase of this concentration occured three and one-half hours before the first discharge on the average. It is the opinion of Kroening and Ney (1962) that ozone produced by lightning is on the same order as that produced by solar ultra-violet light.

Another ozone production method discussed by Kroening and Ney is of nuclear origin; they calculated that the amount of ozone produced by a fifty megaton nuclear device is approximately 0.1% of the ozone in the entire atmosphere.

There is also a production related to the presence of aerosols as reported by Reshetov (1961). Here, the reaction of water and oxygen (in air) due to selective adsorption on the surface of the aerosol particle forms hydrogen-peroxide; the reactions that follow are discussed in full by the author and will not be repeated here. Reshetov's proposal stems from many so-called unexplained facts on ozone; one of which was the report of high ozone content near waterfalls and in the vicinity of sea sprays as measured by Leybinzon (1936). All of the facts except the one above can be explained by conventional means; however, the present author feels that measurement techniques at that time were questionable. Regener (1954) considered atmospheric aerosols to be a scavenger but not generator of ozone and conceded that the photochemical dissociation methods are probably the most important.

V INSTRUMENTATION

A. Ozone measuring devices

Ozone can be measured by two techniques, spectrophotometric or chemical; the former has been used mostly for total ozone (Appendix A) as well as vertical distribution, and this "umkehr effect" is discussed in detail by Mitra (1952) or Johnson (1954). Mateer (1964) concluded that there is no possibility of determining from umkehr observations whether or not there exists a distinct secondary maximum in the lower stratosphere. He also states that the vertical distributions of ozone obtained from umkehr observations are to be compared with each other <u>only</u> when determined by the same objective technique. Great care must be taken when making inferences about atmospheric motions from vertical distributions of ozone obtained from umkehr observations since the evaluator sometimes uses subjective methods on what the vertical distribution "should" look like.

Chemical methods of ozone determination go back 100 years when measurements were made in the layer of the atmosphere closest to the earth in Germany with the use of Schönbein's potassium iodide starched paper. Dauvillier in 1933-35, used a reaction of the oxidation by ozone with a titration solution of sodium arsenite to measure the ozone. The ozone amount was determined by the portion of the solution which remains unoxidized. This portion was titrated with an iodine solution. Also at this time, a rubber cracking method was used, but this was an emperical scheme in that it was not specific to ozone and had to be interpreted with caution; the technique was a cumulative test for total substances in the atmosphere effecting rubber (Jacobs, 1960).

In the last two decades, great improvements have been made on the potassium iodide method for ozone determination, and also a new method, oxyluminescence, was discovered. At one time, a colorimetric analysis was used, whereby the products of the reaction were usually determined by comparison of the color of the indicators at a certain stage of the reaction. For example, oxidation by ozone of solutions of potassium iodide and other iodides are accompanied by an increase in the solution of the effective concentration of hydrogen ions (an increase of the pH). This kind of reaction leads to the use of color indicators such as phenol, bromothymol, nirtophenol, phenolphthalein, and others for the qualitative determination of high ozone concentrations in the air. Here, absolute values of the ozone concentration can be obtained by comparing the action of each indicator in a specific schedule of measurements with one of the absolute methods of measurements of the ozone. Another example of the colorimetric method is the reaction of the oxidation by ozone of indigo carmine, a substance used by Britayev

(1959) in a number of cases for a qualitative evaluation of comparatively high ozone concentrations in the atmosphere. The ozone concentration is calculated by the equation of the chemical reaction and by the amount of air passed through the solution. In spite of the simplicity of the colorimetric analysis, it still involves the subjectivity of the estimation of the color alteration, and this is its most important fault.

Ozone causes luminescence in contact with several chemical elements (iodine, sulphur, sodium, thallium), mineral compounds (the sulphides, the chlorides, and also an oxide of nitrogen), sea water, milk, and also chlorophyll. Very strong luminescence can be observed when ozone acts on luminol in an alkaline solution. Bernanose and Rene (1959) determined the ozone concentration by the intensity of oxyluminescence. However, a small amount of moisture is essential for this chemiluminescent reaction to take place in luminol. Regener (1964) used the chemiluminescent reaction between ozone and rhodamine B which does not show this type of moisture effect. His instrument in balloon-borne sonde equipment is used widely in investigations in the upper atmosphere over North America.

The basis for the majority of present-day electrochemical methods of ozonometry is the reaction by ozone of potassium iodide in aqueous solution.

$$O_3 + 2KI + H_2O \longrightarrow I_2 + O_2 + 2KOH \tag{7}$$

The reaction with potassium iodide is characterized by great selectivity with regard to ozone. Exact quantitative measurements of ozone are effected by electrochemical methods, where the reaction of the destruction of the ozone is checked by the alteration of the electrical properties of the solution being oxidized by the ozone. The instrument chosen by this author for study of the air in the Boston area was the Mast ozone meter (Mast and Saunders, 1962). This particular instrument was chosen for its simplicity of operation, ease of handling, cost, and most important the quickness in obtaining the instrument for immediate use. In this instrument, the above chemical reaction takes place on the cathode portion of an electrical support. At this cathode, a thin layer of hydrogen gas is produced by a polarization current:

$$2e + 2H^+ \longrightarrow H_2 \tag{8}$$

When the voltage is applied to the electrodes (0.24 volts), the hydrogen layer builds to its maximum, and the polarization current ceases to flow. When free iodine is produced by the reaction with ozone, it reacts immediately with the H_2 as follows:

$$H_2 + I_2 \longrightarrow 2HI \tag{9}$$

The removal of hydrogen from the cathode causes a re-polarization current of two electrons to flow in an external circuit, re-establishing equilibrium. Thus, for every ozone molecule reacting in the sensor, two electrons flow through the external circuit. Hence, the rate of electron flow, or current, is directly proportional to mass per unit time of ozone entering the sensor. The instrument was connected to a recorder which was calibrated in pphmv (part per hundred million by volume) and could be read directly when the air flow rate was 140 ml/min at STP. To correct for ambient conditions and thus get a more accurate reading, the instrument values should be multiplied by a factor of $\frac{\text{p (ambient)}\ \ \text{T (standard)}}{\text{p (standard)}\ \ \text{T (ambient)}}$. The uncertainty or accuracy of the instrument is reported to be 1 ppbv (parts per billion by volume) which is approximately the limit to which the graph on the recorder can be read. Further information desired about the Mast ozone meter and recorder can be obtained from the Mast Development Company, Davenport, Iowa.

B. Disturbing agents in the electrochemical (KI) method of ozone analysis (use of filter)

When considering the measurement of ozone by the electrochemical method with a potassium iodide solution, one should be aware of possible interference from oxidizing or reducing agents or erroneous readings from other means. Possible interfering agents, mostly found in polluted air are sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and nitrate ion (NO_3^-). There is also possible destruction of ozone from the wall-effect of glass tubing (Kawamura, 1964) which is used as an air inlet by many authors and researchers; however, in this study of Boston air, a polyethelene and teflon tubing was used for inlet air intakes.

Of the above mentioned contiminants, sulfur dioxide is the most important. Saltzman and Wartburg (1964), Ripperton (1964), and Kawamura (1964) all reported on the negative interference of this gaseous substance common in polluted or urban atmospheres; but only the first two authors suggested a means for removal of SO_2 from the air inlet so as to improve the accuracy of iodometric measuring devices such as the Mast instrument. Their method is as follows: Prepare a 10 ml solution containing .83 - 1.66 grams of chromium troixide and .46 - .93 cc concentrated sulphuric acid. Drop solution (with eyedropper) onto 6 sq. in. of glass fiber filter paper; dry paper in oven at 80°C for one hour or until paper turns pink (in my case, this happened in approximately one half hour). Now, cut dried filter paper into 1/4 by 1/2 inch pieces and fold the pieces into V shapes. Place the folded paper into 100 mm Schwarz U tube (glass). (I used a 100 mm straight polyethalene tube). The paper (pie shaped because I used circular filter paper, 1 in. diameter) was folded to prevent nesting together when packed in the tube. The final product resembled a large cigarette type filter and acted in essentially the same manner. Conditioning of the filter and also ensuring against any blocking of the air intake flow was accomplished by drawing laboratory air through the filter with the aid of a small vacuum pump. The theory of this filter technique is based on the fact that the chromium trioxide is an excellent oxidizing agent; thus the sulfur dioxide is oxidized to SO_3 (highly hygroscopic) which then clings to the glass fiber filter paper. Saltzman and Wartburg (1964) report that the filter is good for thirty days and are still in the testing phase for longer periods of time.

Nitrogen dioxide (NO_2) interfers positively on the instrument to the order of from one to ten percent of the amount of NO_2 present depending on whether one uses Kawamura's or Ripperton's figures. Junge (1963) gives typical values of NO_2 of approximately 15 $\mu g/m^3$ (.7pphm) for large urban areas whereas for Tokyo, Kawamura reports maximum readings of 75 $\mu g/m^3$ (3 pphm). If maximum error is used, one gets only values of .07 pphm or 0.3 pphm which are very small compared to actual readings of ozone; in fact, these figures are the same magnitude as the reported accuracy of the instrument. Also, the use of a buffered potassium iodide solution (this is used in Mast instrument) tends to reduce the effect of NO_2 even more; so no problems were to be encountered in this aspect of the study.

The disturbing effect due to the presence of the nitrate ion (NO_3^-) in the atmosphere is negligible as reported by Kawamura (1964) in his research report of pollution in the Tokyo area.

VI SELECTION OF THE SAMPLING SITES

The ozone concentration data reported in this study represent measurements with a portable Mast ozone meter taken at three types of sampling sites. It was decided to choose one location near a major traffic thoroughfare and another a short distance away elevated above the street level; these locations should be in the heart of a city complex. A third site should be away from the city, i.e., in the suburbs, so as to have a sample of non-urban classification. In addition to the above restrictions, several other practical considerations were met in the final selection of the three sampling sites. The first two sites mentioned should be close enough together to represent the same conditions of industry and traffic density. All the sites should be near an outlet for electrical power to drive the ozone meter. During the curb-side period of the test, the operator must remain on site to take and record various readings of meteorological and traffic conditions and to safeguard the equipment against possible interference by over-curious passers-by. Therefore, the curb-side site should allow legal parking to permit the operator to employ his vehicle as a base of operations and a place of temporary storage for the equipment directly and indirectly involved in the test.

The sites actually chosen for this test meet the above criteria quite well and are described below. The curb-side site is located along the campus (north) side of Memorial Drive in Cambridge, Mass., about two hundred and fifty yards from the intersection of Memorial Drive and Massachusetts Avenue. The ozone meter was located on the side of the west-bound traffic flow, composed of two lanes plus an additional parking lane. Approximately twenty-five yards across a divider are two more traffic lanes for flow in the opposite direction, plus another parking lane. The nearer lanes represent traffic outbound from Boston, while the farther lanes represent inbound traffic. Thus, the ratio of near-lanes traffic to far lanes traffic changes from roughly one-to-two during the morning rush hours to about one-to-one around noon and to approximately two-to-one during the afternoon and evening rush hours. The distance from the center of the near lanes to the instrument site is about thirty-five feet, which is the minimum possible without requiring the electrical cord to extend across a wide side walk which is used continuously by the students of the Institute. The speed of the traffic on both sides of the divided thoroughfare is relatively constant at about thirty-five to forty miles per hour. Vehicles operating at idle are infrequent to nil, with the exception of an occasional vehicle entering or leaning the parking lanes.

The elevated site is on the roof of the new Cecil and Ida Green

Center for Earth Sciences, on campus approximately two hundred yards from the curb-side site. The exact location of the meter on the roof depends on the wind. That is, it is almost always positioned upwind of the laboratory hood exhaust and the air conditioning cooling water spray, either of which might act as a contaminant source without suitable precautions.

The third and final site is the author's home in Roslindale, approximately ten miles southwest of the Cambridge-Boston complex. The instrument was placed in an upstairs (2nd floor) room about 25 feet above the ground with the inlet tube sticking out of the window. The author intended to alternate the meter equally between the urban and suburban, sites but the severe weather (specifically strong winds) necessitated the sheltering of the instrument.

VII DISCUSSION OF RESULTS

A. Ozone Measurements in the Boston-Cambridge Complex

The following results were recorded and computed from the ozone measurements at the three sampling locations; specifically, the November data was obtained from the roof-top locality with fifteen hours of curb-site measurements interfused, while the December and January values were taken from the third sampling site mentioned (less than ten miles from the other two) with approximately three days of roof-top site recordings intermingled. While it is difficult to make any defendable conclusions on the effects of the change of location, because there are no samples taken an all locations simultaneously or under completely equivalent weather conditions, it is felt that since the measured substance is gaseous, a thorough mixing at low levels near the surface is a reasonable assumption. This postulate was borne out somewhat; for in the several instances when the instrument and recorder were transferred between sites (transfer time less than one hour), the recorder values of ozone concentration did not change in this site to site transferrence.

The monthly means were computed by averaging one hour means for the entire month concerned. This was a tedious operation because one inch of the trace on the recorder paper corresponded to one hour.

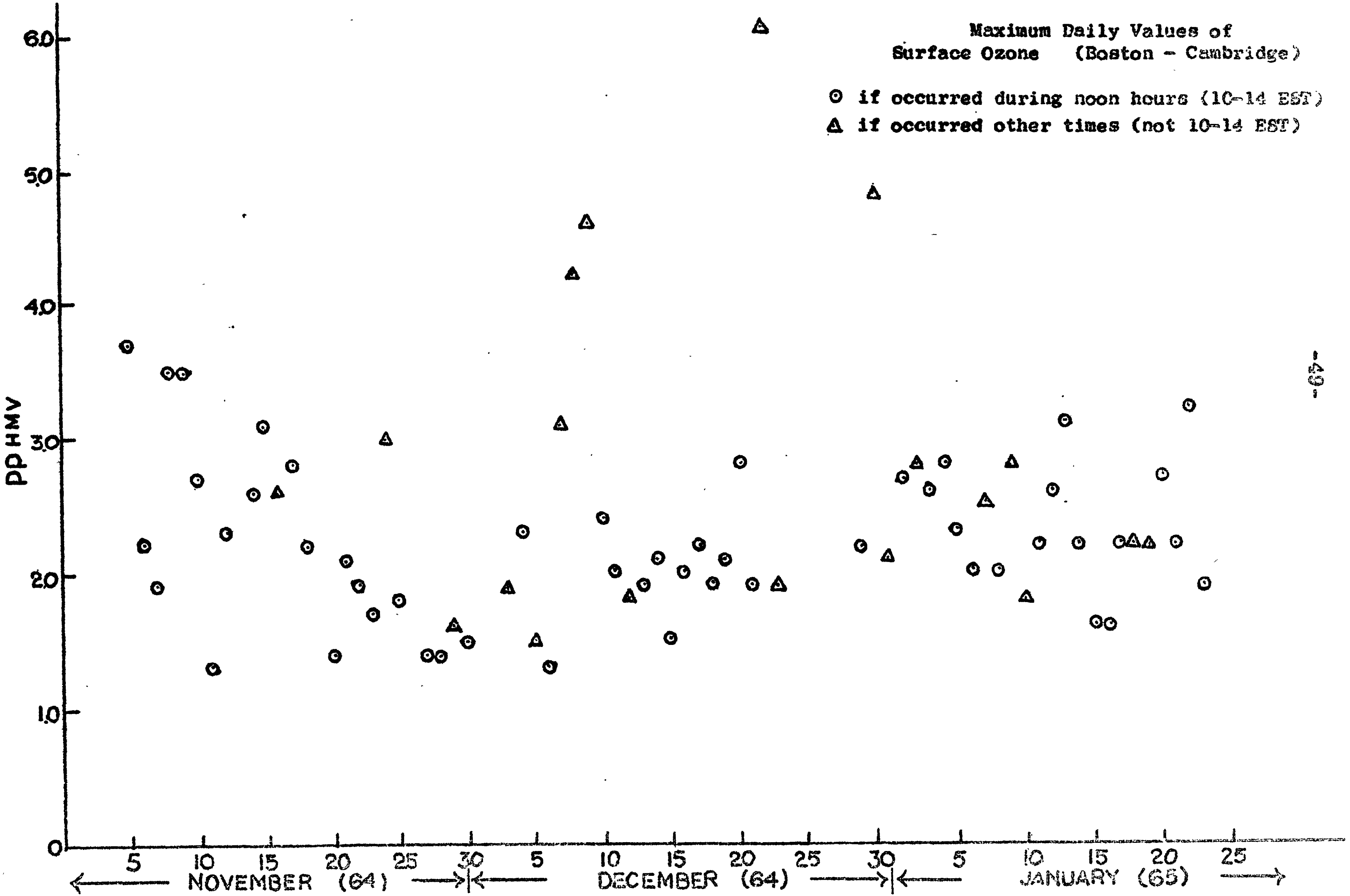

Figure 5 Maximum daily ozone values

There were approximately 700 hourly averages to include for each month.

Table 1. Surface ozone in Boston-Cambridge Complex

Month	Range (pphmv)	Average (pphmv)
November 1964	0.3 - 3.5 (4.3*)	1.1
December 1964	0.4 - 6.4	1.3
January 1965	0.1 - 3.1	1.3

*The 4.3 pphmv was measured inside a dome (fiberglass) on the roof of the Green Building at M.I.T. where a strobe light used by the Department of Electrical Engineering was operating. Although shielded by glass, this ultraviolet light did produce small amounts of ozone as detected by the Mast instrument. As it turned out, this reading was the maximum for the month of November; none of the readings in the dome (less than 2 days) were used in computing the monthly averages. The strobe light was not operating during the remainder of the work.

The above values (see Figure 5) demonstrate the important result that the ozone levels for the Boston-Cambridge complex are a great deal lower for the three month period sampled than the toxic levels for humans, animals, and plants as discussed in an earlier section of this thesis (section III). Since the months of the measurements include the time of year when insolation and total ozone in the atmosphere are at a minimum, it would be worthwhile to measure surface ozone during the time of maximum insolation (Summer) and the time of maximum total ozone (Spring). Such a complementary study is being carried out by a colleague in the Meteorology Department. However, it just might be that though the amounts of ozone in this future report will probably contain higher concentration levels, the values could still be much lower than potentially hazardous ones. This does not mean that measurements of surface ozone should then be discontinued with regard to this aspect of the results. On the contrary, measurements of low level ozone along with other pollutants in the urban air should be taken periodically over the years to insure that the concentrations reached remain at these same low levels.

B. Past Measurements

As is the case with any study in which measurements, particularly of very small quantities, of a substance are reported, it is almost always necessary, if possible, to include past measurements of the same substance if only for a comparison of the relative magnitudes. In the measurement of surface or low level ozone, there are slight problems however; first of all, not too many reports of measurements of surface ozone exist in the literature, and secondly, in the majority of measurements that were reported, the researchers did not use techniques which were specific to ozone. In the discussion presented here, the author considers only studies in the last 15 years, for it is only since then that fairly reliable methods for surface ozone analysis have appeared. If the instrumentation had failings or shortcomings in this period, the researchers were essentially aware of them.

Measurements at the surface in the Los Angeles Basin reported as total oxidant by Renzeth (1954) were as follows. At night, the values averaged between 2 and 4 pphmv. The average maximum concentrations for the entire area during the month of November, 1954 were from 7 to 15 pphm(v).

Measurements of surface ozone reported by Cauer (1951) for locales throughout Europe during the years 1949 to 1951 had a range from 0 to 9.5 pphm(v). Most of these measurements were obtained with an Ehmert electrochemical (potassium iodide) technique.

Kawamura's measurements for the Tokyo area were obtained by the same method as reported by Cauer with only minor modifications. The values reported for Tokyo during 1958 and 1959 showed a range from 1 to 3 pphm(v).

Of all the measurements reviewed by this author, the three mentioned below used the Regener Rhodamin B chemiluminescent technique which is specific to ozone.

Kroening and Ney (1961) measured surface ozone in Minneapolis, Minnesota during the month of May and reported daytime values of approximately 2 pphm(v) with minor fluctuations; nighttime values were generally 1/30 of the daytime values.

Ripperton (1964) in analyzing seventeen 24-hour samples taken over a period of one year in Chapel Hill, North Carolina, reported ranges from 0.0 to 13 pphm(v). The nighttime range was 0.0 to 0.1 pphm and the daytime range was 6.4 to 13.0 pphm(v).

Finally values computed from Hering's data for the month of December, 1962 taken in mid-afternoon showed a range of .8 to 2.7 pphm. These values were for approximately a height of three-hundred feet, the same height as the Green Building at M.I.T., and represented the first level of the measurement of the ozonesonde run for Bedford, Massachusetts.

Of course, the measurements discussed in the preceding paragraphs are not going to be exactly the same as this author's measurements in the Boston-Cambridge complex because of variation due to geographical location, time of year, year, and pollutant sources, etc. But it is most gratifying in an investigation of a small concentration substance like ozone in surface air to find that one's results are not drastically different from others reported.

C. Effectiveness of the chromium trioxide filter

During the first month of operation (November, 1964), while the ozone meter was outside on the roof of the Green Building at M. I. T., the filter was periodically removed for the purpose of refilling the solution in the Mast instrument which was enclosed in a weatherproof case. While the filter was removed (only a couple of minutes), the ozone readings were noted on the recorder; thus with ozone values with filter on and off, the effectiveness of the filter could be obtained. It took only a second or two for the instrument through the recorder to respond to this change (i. e., filter removal). The following table presents the results of this operation along with a calculated reduction.

Table 2. Effectiveness of Chromium Trioxide Filter

FILTER ON (pphmv)	FILTER OFF	% REDUCTION
1.4	0.4	73
1.2	0.3	75
2.8	0.9	68
0.8	0.0	100
1.4	0.6	57
2.0	0.5	75

Table 2 cont.

1.7	0.7	59
1.8	0.4	78
1.5	0.7	54

The above table clearly shows the necessity of a filtering scheme to remove sulphur dioxide (in the Boston-Cambridge complex) from negatively interfering with the instrument used and all other potassium iodide methods of ozone analysis. Wartburg and Saltzman (1964) have tested the reliability of the filter for a period of thirty days and are still in the testing phase for longer periods. In my case, the filter was used for the entire month of November, 1964 but the new filter was left on for the full two months of December, 1964 and January, 1965 with no apparent errors or unusual recordings observed. It is important that the tubing and the filter have a snug fit so that no leakage can occur.

One other important fact in regard to the filter is that the above mentioned authors do not recommend use in areas like Los Angeles because there the ratio NO/SO_2 is large compared to the inverse for other locales. The apparent reason for this is the chromium trioxide will oxidize NO to NO_2 which would thus give positive interference to the potassium iodide method of ozone analysis.

D. Discussion of results with respect to

1. Past Measurements

In comparing my surface ozone measurements with past measurements (section B), a few interesting comparisons were noted. First of all, the closeness of Hering's values taken in Bedford during the same months as in this study although a different year was particularly important to this researcher. Secondly, the Los Angeles values, also for the same months, but different year, were approximately 6 times the Boston-Cambridge values, both for daytime and nighttime levels. This was to be expected because of the intensity of the well-known ozone enriched smog so prevalent in the California city. A third slightly unusual comparison was noticed between the Minneapolis values reported by Kroening and Ney and the Boston-Cambridge measurements. The size and human activity of both cities are nearly the same, but the month and year of ozone comparison are different. Even though the daytime concentrations of both locales were almost the same, a striking difference in the nighttime values was present. The nighttime concentrations of ozone in Minneapolis were approximately 1/30 of their daytime values; in Boston, the nighttime levels were generally 1/6 of the concentrations reached in the daytime. Could it be that the destruction of surface ozone at night in the Minnesota city is greater due to time of year, temperature, or other local mechanisms? The Los Angeles ratio of nighttime to daytime values was nearly the same as Boston.

2. Meteorological factors

Cholak et al (1956) measured surface ozone using a Beckman potassium iodide method in ten eastern U.S. cities. They concluded that the levels of ozone concentration were too low and too dependent on sulphur dioxide to be reliably correlated with meteorological variables. This was not the case in the presented study where sulphur dioxide was filtered from the instrument, and the ozone variation was significantly discernible.

In an examination of wind direction dependence, there were only a few days whereby completely satisfying requirements existed for this relationship; that is nearly the same weather conditions (cloud cover, air mass, etc) with a strong wind directional change. In this period (November 7-8), it was noted that with a northwest wind, the ozone levels were less than those which occurred with a west or southwest flow. This difference (a factor of approximately two) can probably be explained in that many pollution sources (cities, industrial areas) are located in these directions whereas to the northwest few sources exist.

It was also decided to examine the possible ozone pollution content with air masses since air masses are roughly internally homogeneous with respect to temperature, moisture content, etc. In analyzing the ozone variation across fronts, no apparent recognized variability was noticed between the air masses. However, in the frontal zones, where considerable overturning of the air is present, considerable fluctuations of ozone levels occured; sometimes the levels came close to daytime values, when fronts passed during the night. These fluctuations also happened with strong surface winds and rapidly changing wind directions; all these conditions are conducive to low level turbulence and will be discussed in the next section, source strength.

Most often, in a study of air pollution, researchers use rawindsonde data to make estimates of the degree of dynamic stability or instability present in the atmosphere. (See Willet and Sanders (1959) for complete discussion). The data is obtained from a nearby Weather Bureau station that participates in the atmospheric sounding network. Robinson (1961), however, advises caution in assuming that data from soundings taken outside the area of an urban pollutant sampling location can adequately represent the temperature structure over a city, in view of the thermal modifications imposed upon the atmosphere by the presence of the city itself. With no vertical temperature difference measurements available, a different parameter must be used. My colleague R. L. Lininger, (Appendix B) used the following technique; and since a small part of my study was done in conjunction with his work, it was decided to discuss this method here as a guideline for future researchers. While the values for this relationship will be presented, no conclusions are to be expected because it was such a small sample. Turner (1961) used this index which he attributed to the work of Dr. F. Pasquill. The method of computation is described briefly below, omitting some of the details.

First, one obtains the solar elevation angle a, which is given by the following equation for daytime observations:

$$a = \sin^{-1}\left[\sin L \sin D + \cos L \cos D \cos H\right]$$

where L = the latitude of the sampling location

H = the hour angle, computed from local noon at the rate of 15° per hour

D = the declination angle of the sun, available in tables, as a function of time of year. See List (1951).

From the solar elevation angle, one obtains an insolation class number which is modified semi-objectively for sky conditions. This modification gives what is termed the net radiation index. (Special rules apply at night, but no night observations are included in this report). Then, entering a table with the net radiation index and the wind speed in knots, one gets an integer which expresses the degree of stability. The integers, which range from 1 to 7 are related to verbal description of the stability by the following: (Turner, 1961)

Stability Class Number	Class
1	extremely unstable
2	unstable
3	slightly unstable
4	neutral
5	slightly stable
6	stable
7	extremely stable

In the study, it has been decided to use the wind at the nearest Weather Bureau station at Logan International Airport; the sky condition likewise. The site winds suffered from excessive interference by the buildings on the campus. The reader will note that three numbers are given, representing the values calculated at the midpoint of each of the three 60-minute periods comprising a sampling interval. This is thought preferable to an arithmetic average, because the original calculation method described above does not deal with non integral values.

Table 3. Stability versus ozone concentration

Date (1964)	Time (EST)	Mid-Hourly Stability Class Numbers	Ozone values avg for each hr (pphmv)
11/06	1133-1433	3, 4, 4	1.8, 1.8, 1.3
11/11	0800-1049	4, 4, 4	1.8, 2.4, 2.0
11/12	0902-1202	4, 4, 4	0.7, 0.7, 0.9
11/12	1307-1607	3, 3, 4	2.1, 1.9, 1.2
11/13	0830-1130	4, 4, 4	0.9, 1.1, 1.3
11/14	0704-1004	4, 4, 4	0.9, 1.2, 1.3
11/14	1100-1400	4, 4, 4	1.8, 1.8, 1.9

As was expected, no relationship is seen from the small sampling presented above. The time periods were those used in Lininger's study. A large sampling, including diurnal and seasonal variations, so as to allow a full scale range of the stability parameter which strongly depends on the strength of incoming solar radiation, is probably necessary to make valid conclusions. The stability classification system has been made completely objective so that a computer could be used to compile the class numbers.

3. Source Strength

A strong diurnal variation was observed in the surface ozone measurements with a broad maximum around local noon and minimum values during the night. At sunrise, the ozone generally increased and then decreased at sunset. This diurnal variation was more pronounced during days of excellent weather conditions (clear with no visibility restrictions). This observation agrees somewhat with the study by McKee (1961) in Greenland where he reported measurable quantities of surface ozone disappeared when the sun was obscured by high level clouds. With low level clouds present, stability as well as photochemical dependence would be an important factor. However these results are not entirely analogous to high ozone concentrations as found with smog conditions in Los Angeles. This is probably due to the difference of pollutants present in the California city compared with our area where the smoke, haze, etc. does not contain much ozone or precursors of ozone.

From Table 1, the monthly means show an increase, a trend that is similar to total ozone amounts which are a minimum in the Fall increasing to a maximum the following Spring. However, a longer period of measurement of surface ozone would be necessary to show absolutely the strong dependence on total ozone rather than local pollution.

During the nighttime hours, when surface winds were strong (> 10kts) and gusting, sudden increases in the surface ozone concentrations were recorded. These levels occasionally approached the higher daytime values. These are called turbulent interludes discussed by

Blackadar et al (1961) where the vertical gradient of wind velocity suddenly becomes disturbed by the creation of turbulence which produces a connection between the surface and higher velocity winds hundreds of feet above the ground. This phenomena also occurred during strong wind shifts, in frontal zones and when an upper level trough was located east of the sampling site (subsidence effect). During these turbulent interludes, one could then assume that the ozone aloft (above the inversion) is brought to the surface by the increased eddy diffusion and subsidence. The above comments are discussed in a qualitative nature because of the difficulty in expressing these factors in a quantitative way and correlating them with the many other variables that come into play on surface ozone values.

Peak surface ozone values versus the concentration of radioactive substances in surface air (β activity) are presented in Figure 6 since both have the lower stratosphere as an ultimate source region. Notice the similar trend particularly in the early weeks of the study.

Finally, a brief table of ozone versus traffic density is offered here. The results were obtained from joint work with R. L. Lininger (Appendix B). The measurements were taken at the curb-site.

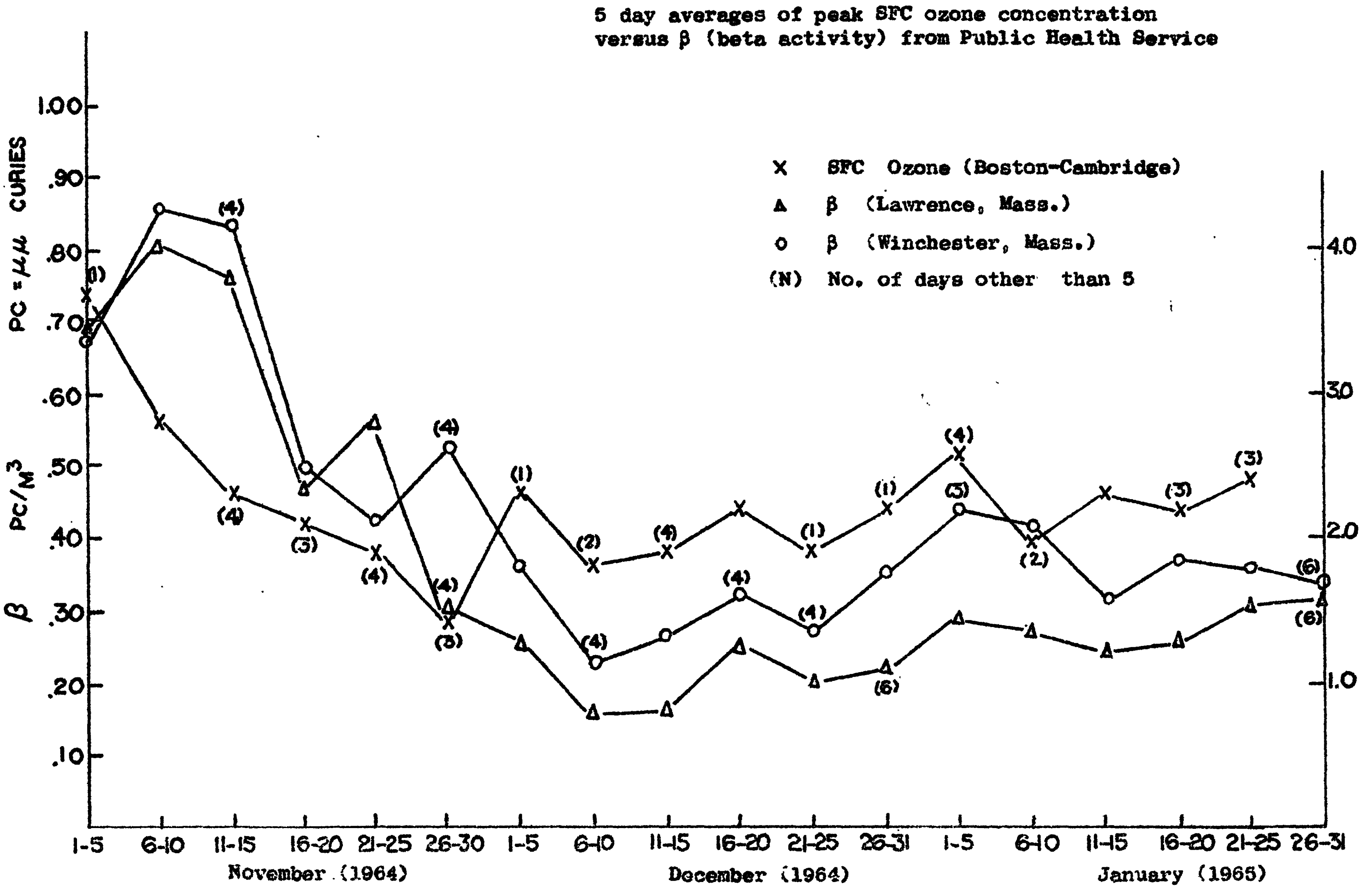

Figure 6. Peak ozone versus beta activity in surface air

Table 4. Traffic density versus ozone concentration

Date (1964)	Time (EST)	Traffic (cars in 5 min)	Average ozone (pphmv)
11/12	0902-1202	145	0.7
11/12	1307-1607	177	1.8
11/13	0830-1130	176	1.1
11/14	0704-1004	108	1.2
11/14	1100-1400	172	1.8

No correlation is noted here. This is probably due to dependence of ozone on insolation, pollution input, etc., and to the fact that the traffic count is not a sensitive enough measure of area-wide exhaust gas.

E. Relationship between ozone and members of the halogen family

1. Relation of ozone to chlorine

Lininger (Appendix B) and I have computed a simple linear correlation coefficient between the simultaneously-measured concentrations of O_3 and Cl^- and found a value of -.55. We fully realize the dangers of ascribing too much significance to a correlation coefficient based on only seven samples. Further, it can be argued that the number of samples which are truly independent in the statistical sense is only five, because two of the samples were taken with a one hour intermission. Having a correlation coefficient based on only five independent samples would be even worse, from the standpoint of the confidence ascribable to the statistic computed.

The joint effort of attempting an explanation of the correlation by possible chemical reactions along with an examination of measurements of chloride and ozone taken by other investigators to see if any indication of a chloride-ozone relationship can be inferred in locales other than the Boston-Cambridge complex is reported by Lininger (1965).

Since chloride increases with an off the ocean wind, and this fact was corroborated by Lininger's study, careful examination of ozone concentrations under these meteorological circumstances should show a decrease (if one accepts the above correlation). However, in the three months of the ozone study, November 1964 to January 1965, and for that matter in all winter months, an easterly wind almost always brings considerable cloudiness and precipitation to the Boston and coastal New England area; it was no exception during the study outlined here. As discussed in an earlier section, this "weather" alone would tend to give low ozone readings. The ideal time to concentrate on this type of investigation of the ozone-chloride correlation would be in the Summer before and after the onset of a sea breeze which is a very common occurrence to the New England coastal areas during the early afternoon of the Summer months.

It is further suggested that more simultaneous measurements of ozone and chlorine be taken, together with measurements of parameters representing insolation and turbulence. Then the ozone values can be adjusted to equal conditions of insolation and turbulence to remove the effects of these processes, and a more statistically reliable correlation can be obtained with chloride content to test the above theories. Perhaps lag correlations should also be studied. If it can indeed be shown that chloride salts can control ozone to some extent even at concentration ratios as low as those observed in this study (Cl/O_3 approximately 0.05 - 0.2), then an inexpensive method of controlling the undesirable effects of atmospheric ozone is suggested; for example, one might spray an ozone-contaminated area with droplets of saturated salt solution, providing of course the corrosive effects of the chloride could be tolerated.

2. Relation of Bromine and Iodine to Ozone

There appears to be essentially no correlation between the ozone amounts and either the bromine or iodine simultaneous concentrations. This lack of correlation would be expected in our data even if there could be any direct reactions (not catalytic) between ozone and either bromine or iodine, because there is a vast overabundance of ozone compared to either bromine or iodine on a molar basis. That is, from

Lininger (1965) $Cl/O_3 \sim 10^{-1}$ moles/mole, and $Br/Cl \sim 10^{-2} - 10^{-3}$ moles/mole; therefore $Br/O_3 \sim 10^{-3} - 10^{-4}$ moles/mole. Consequently, a direct reaction would hardly be noticeable in the total ozone amount. Similarly for iodine, $I/Cl \sim 10^{-4} - 10^{-5}$ moles/mole; therefore $I/O_3 \sim 10^{-5} - 10^{-6}$ moles/mole, and the conclusion is even more valid. A reaction suggested by Millman et al (1962) which would occur more effectively in photochemical smog because of I_2 quenching the free radical chain reactions that generate O_3 is:

$$2I_2 + 9O_3 \rightarrow I(IO_3)_3 + 9O_2 \qquad (10)$$

VIII. RECOMMENDATIONS

As mentioned in this thesis, further surface ozone measurements should be taken in the same location to obtain concentrations during the Spring (total ozone maximum) and Summer (insolation maximum), to confirm or deny if possible the surface ozone dependence on total ozone, and to corroborate the ozone-chloride correlation by ozone readings before and after the onset of a sea breeze. Also further measurements might resolve the problem of local source versus stratospheric source.

Further work should be done, preferably by a graduate student in the chemistry department, to investigate the feasability of sulphur dioxide determination, either empiracally or analytically, by the filter technique; specifically, use the ozone values before and after filter is removed.

Other areas for further examination are with the stability index as well as wind direction versus surface ozone. This should be done with values for an entire year.

Also for the toxicologist, more research should be done on the toxicity of ozone; the literature still contains some conflicting arguments.

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Appendix A. (useful ozone conversions)

ppm(v) = parts per million by volume

pphm(v) = parts per hundred million by volume

ppm(m) = parts per million by mass.

$$1 \text{ ppm(m)} = 1.66 \text{ ppm(v)}$$

$$\frac{1 \text{ ugm } (O_3)}{m^3 \text{ (air)(STP)}} = .468\ (10^{-3}) \text{ ppm(v)}$$

$$\text{ppm(v)} = \frac{P(\mu \text{mb})\ (O_3)}{P(\text{mb})\ (\text{air})}$$

$$1 \frac{\text{gm}}{\text{liter}} = 10^{-9} \frac{\mu \text{gm}}{m^3}$$

Total ozone -- Usually measured in length unit at STP (atmospheric-centimeters), and it is the integrated ozone in a column of air extending from the bottom to the top of the atmosphere. Conventionally, the units have been 10^{-3} cm. A logical choice is milli-atmosphere-centimeters (m atm - cm).

$$\Omega \text{ (m atm - cm)} = .46697\ \Omega \left(\frac{\mu \text{gm}}{\text{cm}^2}\right)$$

Appendix B.

The measurements of the halogens in this study have been supplied to this author by his friend and colleague, Captian Ronald L. Lininger, a fellow graduate student in the Department of Meteorology. They represent a large part of his graduate thesis. His measurements have been collected in the Cambridge-Boston complex using a Casella four stage cascade impactor. The analysis for the halogens were conducted by pile neutron activation. Since Captain Lininger's project began slightly earlier than this study, there were no ozone measurements for the first theree periods or aerosol collection that totaled ten in all. The ozone meter operated within a few yards of the cascade impactor intake orifice during the periods of the remaining seven aerosol collections.

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