# AN INVESTIGATION

# OF

# OZONE AND SULFUR DIOXIDE CONCENTRATIONS

# IN

# THE GREAT SMOKY MOUNTAINS NATIONAL PARK

by

John Michael Rosenquest

Thesis submitted to the Graduate Faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Environmental Sciences and Engineering

APPROVED:

N. T. Stephens, Chairman

J. M. Hughes

J. P. Wightman

December, 1978

Blacksburg, Virginia

ACKNOWLEDGEMENTS

I would like to thank first, , chairman of my advisory committee, whose inventive approaches to research and teaching made this project enjoyable as well as educational. I would also like to thank and for their advice and encouragement while serving on my advisory committee.

Many thanks to F , and especially for providing ground level data.

Special thanks are due my parents, who have encouraged and supported my education. I must also give credit to patient typists , , and my sister who helped my ideas become this report.

Lastly, I must thank for her constructive criticism, patience, and love, during preparation of this thesis.

## TABLE OF CONTENTS

## LIST OF TABLES

LIST OF FIGURES

## INTRODUCTION

The 1970 and 1977 Clean Air Act Amendments to the Federal Clean Air Act clearly indicate that the protection and enhancement of the environment is an important goal nationwide. The commitment to protect public health was apparent in the 1970 Amendments which established the National Ambient Air Quality Standards (NAAQS), but the 1977 Amendments dictate that the air quality in remote and pristine areas must also be preserved.

Specific instructions are given for the protection and enhancement of air quality in areas of national interest. National parks and historical monument areas are given a special designation and only small increases of man-made pollutants are permitted. The regulations governing impact in such areas is the "Prevention of Significant Deterioration" (PSD) section which designates national parks with areas greater than 5,000 acres as "Class I" for maximum protection of the environment. The other class designations II and III apply to areas where "normal growth" and "industrial growth" are permitted; however, the NAAQS are not to be exceeded. The Great Smoky Mountain National Park is a Class I area since it encompasses an area larger than 5,000 acres. Since there were no data on the air quality in the park, there was no method determining if air quality was in compliance with current regulations, or if an increase in pollutant levels would be permitted.

It was deemed desirable in light of the PSD regulations to devise a monitoring system which could supply the necessary data on air quality in remote areas of national parks. The purpose of this study was to develop this method of documenting the pollutant concentrations in the Great Smoky Mountains National Park and other such areas.

In order to accomplish this task, several objectives were formulated which included:

(1) The development of an airborne platform suitable for measuring the distribution of air pollutants in real time

(2) The development of a data storage and retrieval system for use on the airborne platform

(3) The use of the system to gather data in the Great Smoky Mountain National Park

(4) The determination of the air quality in the Park for pollutants included in the PSD regulations

(5) The acquisition of meteorological data to assist in the determination of the origin of pollutants in the Park.

This report contains the results of preliminary observations of sulfur dioxide ($SO_2$) and photochemical oxidant concentrations measured as ozone ($O_3$) in airborne monitoring, and as total oxidant ($O_x$) in ground monitoring. These two pollutants were selected to be studied first because of their potential for causing plant damage, and secondly because of their tendency to form aerosols which cause a deterioration of visibility. Another reason $SO_2$ was studied was that acid sulfates ($SO_4^{=}$), formed from $SO_2$, are suspected to be a major contributor to stream acidification which is taking place in the Park.

The Great Smoky Mountains National Park is located 20 miles southeast of Knoxville, Tennessee and covers about 1,000 square miles of Tennessee and North Carolina (Figure 1). The Park is a heavily forested area with few roads and only a few small communities and campgrounds within its boundaries.

The land use of the north and south sides of the Park are quite different. Knoxville is a metropolitan area with a population of over 300,000. Also on the north boundary is a resort area which attracts over 1,000,000 visitors a month during the summer. The south side of the Park is sparsely populated, and the largest city is Asheville, North Carolina which has a population of about 60,000 and is located 25 miles east of the Park.

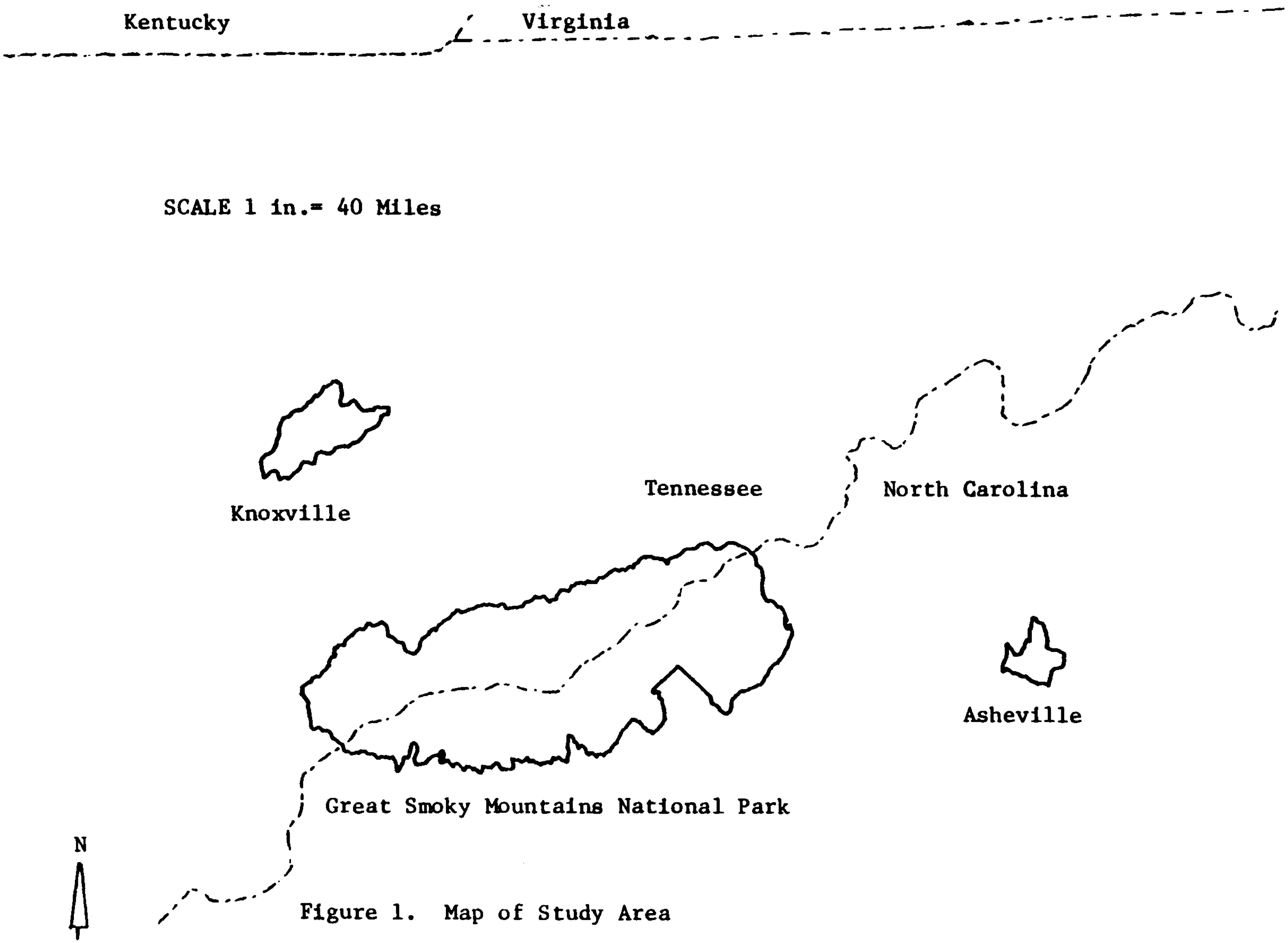



Figure 1. Map of Study Area

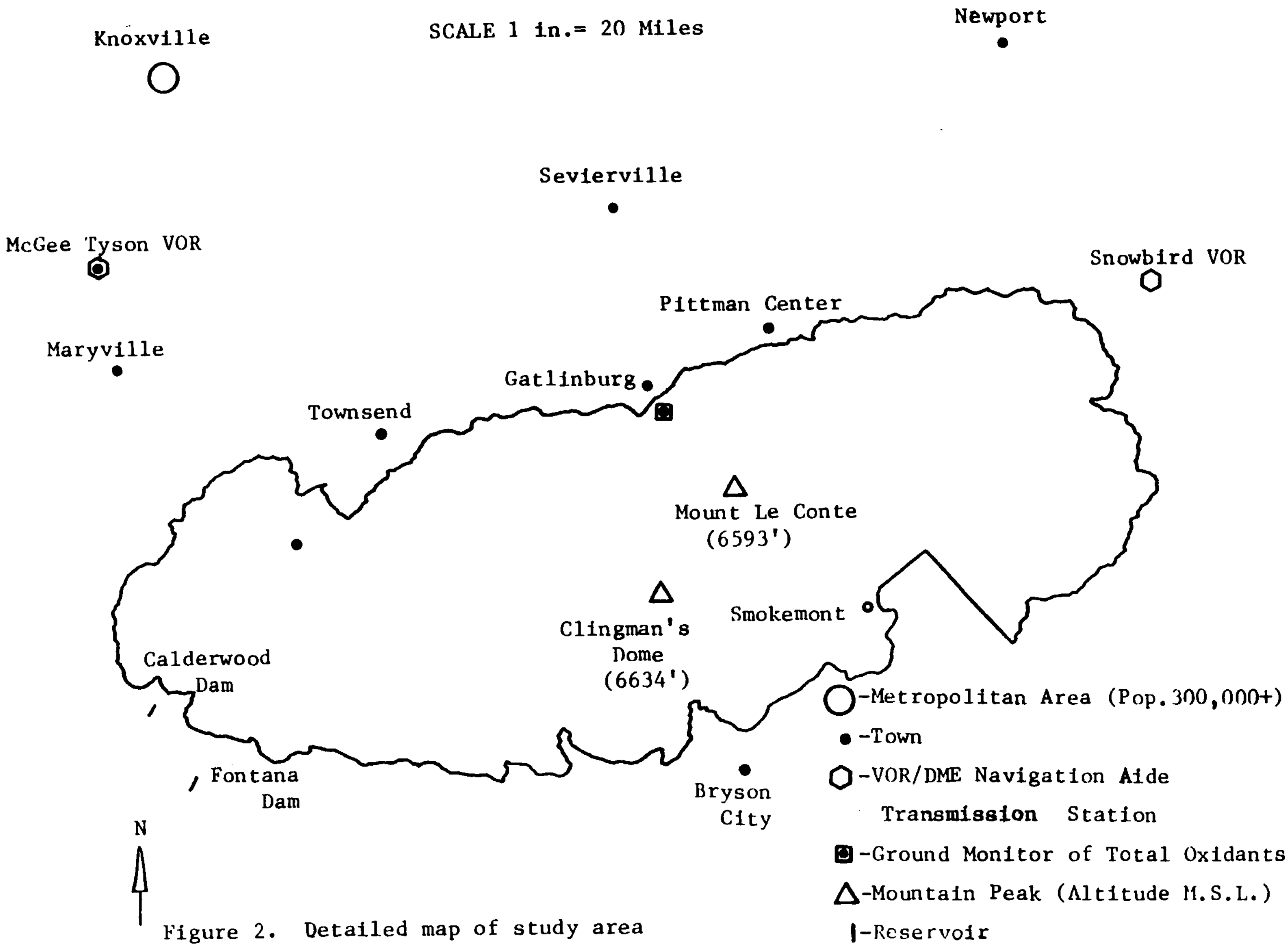



Figure 2. Detailed map of study area

## LITERATURE REVIEW

This survey begins with discussions of the two pollutants monitored, their sources and their adverse effects and the regulations which specify concentrations permitted by the NAAQS and the increases in concentrations permitted by the PSD regulations. The final section is a review of airborne air pollution monitoring.

### Photochemical Oxidants - Formation

Photochemical oxidants are defined as "a class of compounds which tend to donate oxygen atoms" (1). They are not emitted, but formed by reactions of precursors in the atmosphere. These reactions are initiated by sunlight, and primarily involve the precursors, hydrocarbons and nitrogen oxides.

Nitrogen oxides ($NO_x$) are formed very slowly by natural processes, and background concentrations are very low (2). The most important nitrogen oxides are nitric oxide (NO) and nitrogen dioxide ($NO_2$). The most important contributors of NO are motor vehicles, while both motor vehicles and power plants emit a large portion of $NO_2$ emissions (3).

Nitrogen oxides cannot cause high oxidant concentrations unless hydrocarbons are also present. Hydrocarbons are emitted by both natural, and anthropogenic sources (4). Not all hydrocarbons are photochemically reactive, and the most common natural hydrocarbon is unreactive (5). One class of compounds which is photochemically reactive is the olefin. Olefins are emitted by motor vehicles and many species of plants (6). The influence of natural olefins on oxidant concentrations is debated, however a recent study indicates that natural emissions are insignificant when compared to anthropogenic emissions (7).

Ozone ($O_3$) is the most prevalent photochemical oxidant, and it is a good indicator of the amount of photochemical pollution (8). Since ozone is a good indicator of photochemical pollution, and its concentration can be accurately determined, the NAAQS for oxidants is expressed in $O_3$ concentration. For this reason, the discussion of photochemical oxidant formation will deal mainly with reactions which lead to the formation of $O_3$.

The photochemistry of the polluted atmosphere is exceedingly complex; several authors have reviewed the important reactions (9,10, 11,12,13). Only a few reactions, those which lead to the formation of $O_3$ will be discussed.

The reactions, as mentioned previously involve hydrocarbons, nitrogen oxides and atmospheric gases in the presence of sunlight. Nitrogen dioxide absorbs light in the blue to near ultraviolet range and releases an oxygen atom (Reaction 1). Free oxygen atoms react quickly with molecular oxygen ($O_2$) to form ozone (Reaction 2). The third body (M) involved in Reaction 2 absorbs the energy of bond formation, and is probably nitrogen ($N_2$) or $O_2$. Nitric oxide (NO) reacts with $O_3$ quickly to form $O_2$ and $NO_2$.

$$(1) \quad NO_2 + \text{light} \rightarrow NO + O$$

(2) $O + O_2 + M \quad O_3 + M^*$

(3) $NO + O_3 \rightarrow NO_2 + O_2$

This series of ractions occurs when there are few hydrocarbons present and leads to equilibrium with only a small oxidant concentration (14).

The following series of reactions is more prevalent when hydrocarbons (R) are present. Some hydrocarbons are oxidized by oxygen atoms formed by dissociation of $NO_2$ (Reaction 1) to produce hydrocarbon radicals (RO·) as seen in Reaction 4. Due to the high reactivity of RO·, they can initiate reactions with other species to form more oxidized hydrocarbons, ozone and other oxidants as seen in Reactions 5 through 9.

(4) $O + R \rightarrow RO\cdot$

(5) $RO\cdot + O_2 \rightarrow ROOO\cdot$

(6) $ROOO\cdot + NO \rightarrow ROO\cdot + NO_2$

(7) $ROOO\cdot + R \rightarrow ROO\cdot + RO\cdot$

(8) $ROOO\cdot + O_2 \rightarrow O_3 + ROO\cdot$

(9) $RO\cdot + NO_2 \rightarrow$ Other Oxidants

Hydrocarbons are quite important since they not only lead to $O_3$ production, as seen in Reactions 4, 5, and 8, but also decrease the amount of $O_3$ destruction by NO by Reaction 6.

The rate of $O_3$ formation is dependant on solar radiation, temperature, and precursor concentrations (15). High oxidant levels are most common during the summer months, in high pressure weather systems, where skies are clear and wind speeds are generally low (16). These conditions facilitate $O_3$ production and lead to slow dilution of $O_3$ at its precursors.

$O_3$ is also formed in the upper atmosphere where the ultraviolet light intensity is strong enough to dissociate oxygen molecules. Downward transport of $O_3$ and natural emissions maintain background concentrations of $O_3$ which are estimated to be from 0.020 ppm to 0.040 ppm (17).

Man is known to be the cause of high $O_3$ concentrations in areas of abundant vehicular emissions and $O_3$ levels higher than twenty times the natural background have been observed (18). The impact of natural emissions on $O_3$ levels is still debated because $O_3$ or its precursors can be transported great distances.

Photochemical Oxidants - Transport

The theory that $O_3$ could be transported was advanced when photochemical oxidant plant damage was found downwind from a metropolitan area. Subsequent study showed that precursors from a large urban area caused high ozone concentrations over 70 miles away (19). Later studies showed that an urban area could have a significant impact on oxidant concentrations over 150 miles downwind (20). High rural oxidant concentrations ($>0.08$ ppm) are not uncommon in the south central United States (21).

Some regional oxidant episodes were attributed to natural sources, but a recent study has shown that anthropogenic influences on oxidant levels are great enough to cause episodes on a regional scale (22). The details of these and other airborne air pollution studies will be discussed in more detail in the section or airborne monitoring.

Photochemical Oxidants - Adverse Effects

Studies on the adverse effects of $O_3$ and other photochemical oxidants are well documented (8) and a few effects which are pertinent to the study area will be discussed.

Although $O_3$ is invisible, there is often a strong correlation between $O_3$ concentration and decreased visibility (23). Many photochemical reactions lead to the formation of aerosols in the light scattering size range (13).

Oxidants also have adverse effects on plants at ambient concentrations. Plant injury has been observed by Skelly et al. (21) in rural areas of Virginia, only 200 miles from the Great Smoky Mountains National Park. Plant injury was one of the earliest indicators of photochemical pollution, and is one of the most important economic effects of an air pollutant (8).

Sulfur Dioxide

Sulfurous gasses are emitted by natural as well as anthropogenic sources and are present in all parts of the globe. Most sulfurous gasses are from natural sources and are most commonly emitted as hydrogen sulfide ($H_2S$). Background $SO_2$ concentrations formed by conversion of $H_2S$ to $SO_2$ in the atmosphere are around 1 ppb (24).

Anthropogenic sources emit about one third of all sulfurous pollutants and more than 95% is emitted as $SO_2$. Coal and petroleum combustion account for almost all manmade emissions of $SO_2$ (24). In most populated areas $SO_2$ concentrations are much greater than background levels due to local combustion of fossil fuels.

Unlike photochemical oxidants, after $SO_2$ is emitted it constantly decreases in concentration due to dilution, deposition, and oxidation. The oxidation of $SO_2$ takes place by a number of mechanisms including photochemical oxidation, chemical oxidation, and catalyses (10). Photochemical oxidation of $SO_2$ is a process which is the result of reactions of $SO_2$ molecules in an excited state from absorbing sunlight. Chemical oxidation is due to the interaction of $SO_2$ with photochemical oxidants. Catalytic oxidation often takes place on particulates or aerosols which contain transition metals such as iron (25). Oxidation of $SO_2$ eventually leads to complete conversion to sulfates ($SO_4^{=}$), which can take from a few hours to days (25). Since $SO_2$ and $SO_4^{=}$ may remain in the air for days, they can be transported hundreds of miles from their source of emission (26).

The formation of sulfates is important since they are aerosols which cause visibility degradation . $SO_4^{=}$ may be concentrated in precipitation and have adverse effects on materials as well as biotic systems (26).

## Pertinent Legislation

The primary and secondary National Ambient Air Quality Standards (NAAQS) for photochemical oxidants (at the time of writing) are both 160 μg/$m^3$ (0.08 ppm) measured as ozone. This standard is not to be exceeded for more than one hour per year (27). There is no Prevention of Significant Deterioration (PSD) increment established for photochemical oxidants.

The secondary NAAQS for $SO_2$ is 1300 μg/$m^3$ (0.5 ppm) not to be exceeded more than once a year for a three hour time period. The primary NAAQS is 365 μg/$m^3$ (0.14 ppm) not to be exceeded more than once a year for a 24 hour period (27).

The PSD increment for $SO_2$ for a Class I area such as (national parks and monuments is 25 μg/$m^3$ (0.0096 ppm) (28).

## Airborne Monitoring

Early airborne studies reported were conducted using a single instrument or two fastened with seat belts, and data was observed and recorded by hand. Most current airborne studies are much more sophisticated, and require that much more information be recorded and processed. A discussion of the development of airborne monitoring systems, and studies in which they were used follows.

Pioneer studies were limited by the state of the art of instrumentation. Some studies were conducted by collecting and preserving samples for later analysis on the ground (29). The samples were generally taken over a long period of time and represent an average over a large area rather than a discreet point. These studies were usually conducted near large stationary sources where concentrations of pollutants are very high.

Another generation of airborne studies was made possible when samplers and recording instruments were made compact and light enough to be taken aloft. Stephens and McCaldin investigated parameters such as the conversion of $SO_2$ to other species (29), and small particulates (30) in power plant plumes. Another plume dispersion study was reported by Gartrell (31).

Adams et al. (32) reported an elaborate airborne system for recording flight parameters and pollutant concentrations (32). Instruments for measuring various pollutants continuous and provisions for taking "grab samples" were included. The data was recorded on magnetic tape in flight, and could be reduced and plotted by computer. The system included a chart recorder so that one or two parameters could be monitored to determine if any changes in flight patterns should be made.

A new dimension in airborne sampling was opened up with the investigation of ozone concentrations by Lovill and Miller (33). Vertical soundings indicated that the highest levels of ozone were above the inversion layer. Initial studies were followed by more comprehensive studies which included mapping of the ozone levels in an urban area and surrounding areas (34). A further development of these sampling studies yielded ozone isopeths which showed ozone variations with altitude and distance (35). High ozone levels were conducted tracking ozone plumes of cities. White et al. (36) tracked the St. Louis ozone plume up to 100 miles downwind from the city. Sipple (37) and Cleveland (38) tracked high ozone levels due to urban complexes over the Atlantic Ocean up to distances of 160 miles. These studies confirmed the idea that ozone pollution was a regional problem.

The most recent development in airborne ozone studies is the integration of air parcel trajectory. Wolff et al. (22) investigated ozone transport in the Washington, D.C. to Boston, Massachusetts corridor. Airborne data were used to confirm theories of transport. Ground data from various stations were analyzed along with airborne data and air parcels which contained high $O_3$ concentrations. Analysis of ground and airborne data permits a better understanding about both, the relationship between ground observations, and ozone levels aloft.

# EXPERIMENTAL METHODS

In addition to the traditional items - materials and methods, this chapter contains a brief discussion of the criteria used for selection of aircraft and instruments. Details on specific instruments used for this study may be found in Appendix A.

The process of selecting an aircraft has been discussed elsewhere (32) so aircraft selection criteria are limited to ones peculiar to this study. Special consideration was given because of the mountainous terrain in the sampling area. A twin engine centerline thrust aircraft was chosen for safety and maneuverability in the event of an engine failure. Another factor in the selection of the aircraft was its wide range of operating speeds. A high-wing configuration was chosen because many of the position determinations had to be made visually using navigation charts and landmarks. Finally, the cabin space had to be large enough to accommodate the desired instrumentation.

The aircraft chosen for this study was a Cessna 337, one of the few aircraft which met the criteria outlined earlier. Navigational aids include a VOR/DME (visual omni range distance measuring equipment), and an RDF (Radio Direction Finder). Both of these instruments have limitations because of rough terrain interference with line of sight transmission characteristics; however, both were useful supplements to visual observations.

Instruments were mounted using slotted 1-1/4" steel angle stock which proved very versatile since shelves could be moved simply to accommodate changes in instrumentation. A 1,000 watt solid state 28 volt direct current to 110 volts alternating current inverter supplied power to sampling instruments as well as data logging equipment.

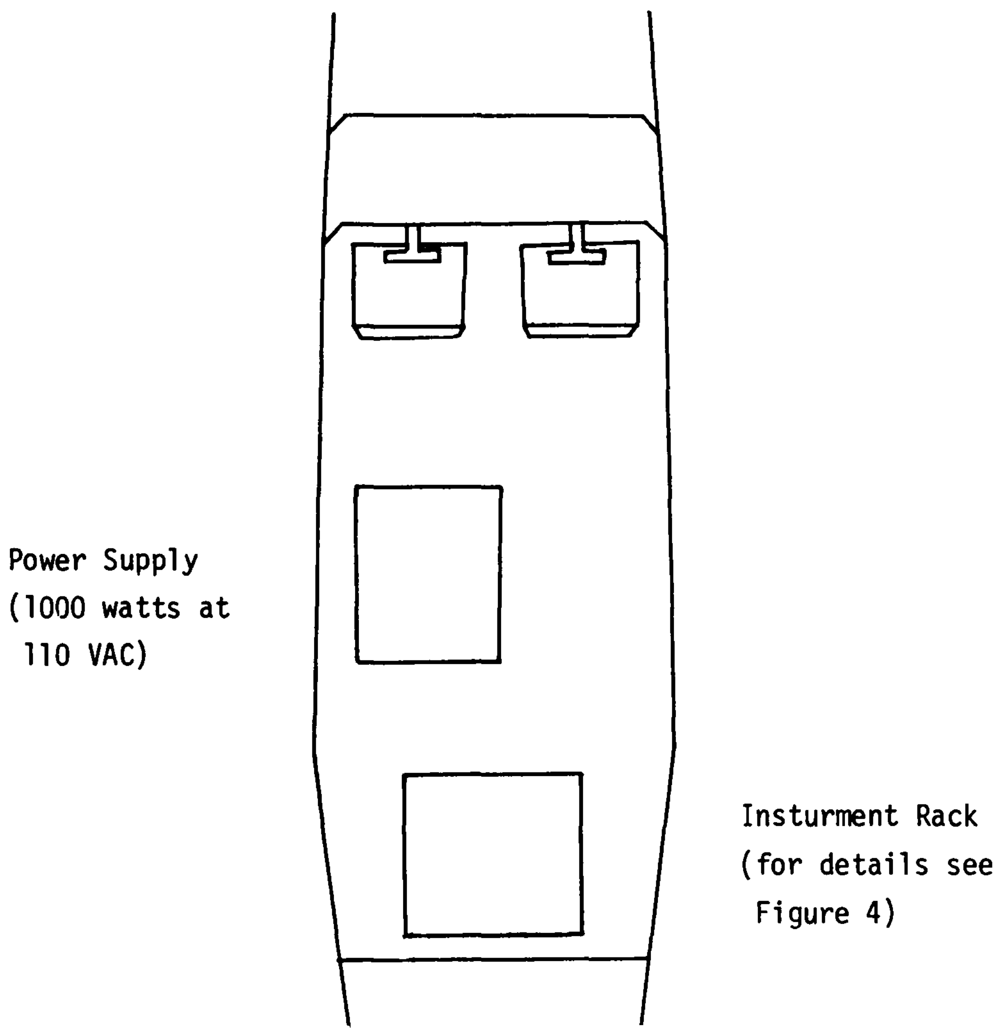
Since new instruments were obtained during the study, the instrument package had several configurations, and only the current configuration is shown in Figures 2 and 3.

Temperature and pressure altitude were determined using variable resistors. Dry cell batteries supplied current and voltage changes, due to resistance change, were monitored directly by the data logging system. The sensitivity of the temperature probe is less than one degree Fahrenheit; the altimeter indicates pressure altitude within an accuracy of $\pm$ 250 feet.

The sample intake line consists of a one-half inch inside diameter teflon tube which extends forward to the leading edge of the wing, and is not contaminated by engine exhaust (32).

The residence time required for an air sample to traverse the six foot line to the instruments is less than two seconds.

Different instruments were acquired for monitoring $SO_2$ and $O_3$ during the study and were incorporated in the system. $O_3$




SCALE 1 in.= 2ft.

Figure 3. Top View of Aircraft Insturmentation

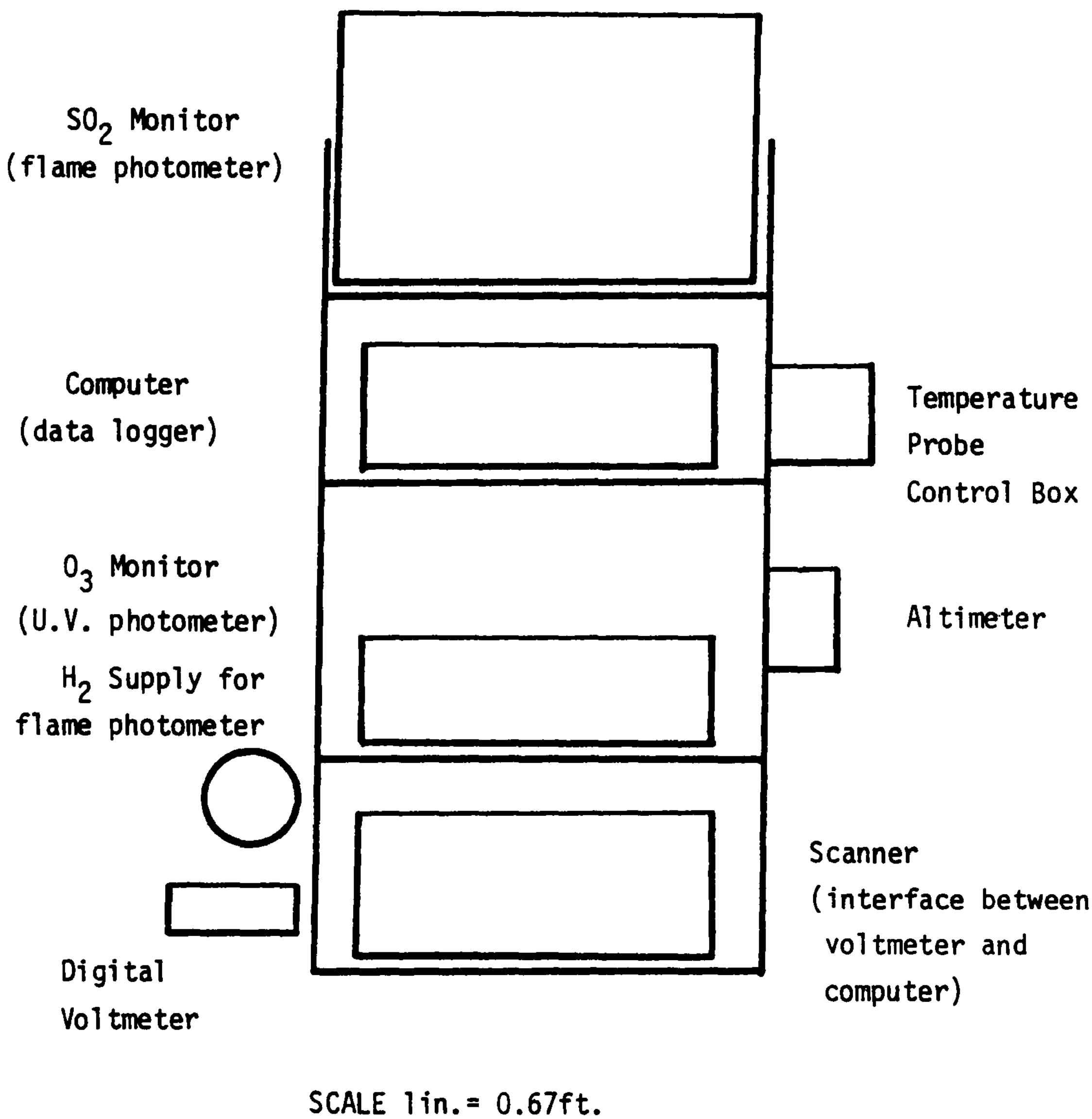



Figure 4. Front View of Aircraft Insturmentation

measurements were made with either an ultraviolet $O_3$ photometer (39), or a chemiluminescent monitor (40). Calibration of the $O_3$ monitor was performed by the Virginia State Air Pollution Control Board in accordance with the Environmental Protection Agency (EPA) methods (41). The accuracy of the $O_3$ monitors was determined to be $\pm$ .003 PPM. Calibration curves for the two $O_3$ monitors used are shown in Figures 14 and 15.

When the study was initiated, $SO_2$ measurements were attempted using a SIGN-X conductiometric instrument. The concentrations were below the limit of sensitivity of this instrument, and it was later replaced by a flame photometric analyzer.

The conductiometric $SO_2$ (42) analyzer was calibrated using a dilution chamber and bottled $SO_2$. The limit of sensitivity was $\pm$ .050 PPM.

A Meloy flame photmetric $SO_2$ analyzer (43) replaced the conductiometric instrument, and sensitivity was increased to $\pm$ 0.002 PPM. The flame photometric analyzer was calibrated using a Meloy permeation tube calibrator. Data were initially recorded on a Texas Instrument four channel strip chart recorder; however, this was replaced by a Hewlett Packard data logging system. Supplementary data, including visual navigational instrument position determinations and flight parameters, were recorded verbally using a tape recorder.

Specific instruments used for this study are listed in Appendix A.

Sampling was usually conducted when the area was under the influence of a high pressure weather system. High $O_3$ levels are often recorded during these periods, which are characterized by low wind speeds and clear skies (22). In general the flight plan consisted of traveling along the perimeter of the Park, with vertical spirals as time and weather permitted.

The flights were conducted between March 29 and September 27 of 1978. Values of $O_3$ and $SO_2$ concentrations were recorded continuously; however, only selected data at points for which position was well defined, are presented in this thesis. For points where more than two altitudes were sampled during a flight, tabular data are presented on the pages following concentration maps. A brief description of individual flights follows:

On the first sampling day, March 29, the area was under the influence of a low pressure system. High winds and clear skies dominated local weather. Sampling was conducted over most of the perimeter except the southeast end of the Park.

On May 26 the area was under the influence of a high pressure system and wind speeds were lower. Airborne samples were made for sections of all areas over the perimeter of the study area.

On June 20, due to limited visibility, sampling was limited to an area north of the Park.

On the July sampling days, the area was under the influence of a high pressure system and the highest $O_3$ concentrations for most locations were recorded. During the September 25 flight, the area was under the influence of a low pressure system and flights were modified due to limited visibility in the southern portion of the Park.

Ground level concentrations of $O_3$ are included for two stations in the vicinity of the Park. Data were provided for Knoxville, Tennessee, a downtown site, about 20 miles NW of the Park, by the Knox County Department of Air Pollution Control (44). $O_3$ concentration in downtown Asheville, North Carolina, about 25 miles east of the Park were provided by the Western North Carolina Regional Air Pollution Control Agency (45). Both instruments are chemiluminescent monitors and hourly averages were computed.

Total oxidant measurements were recorded at the Great Smoky Mountains National Park Uplands Research Center (U.R.C.) near Gatlinburg, Tennessee using a Mast colorimetric instrument. Details of this instrument are included in Appendix A.

Limited Trajectories of air parcels were determined using wind data from the National Oceanic and Atmospheric Administration. These data are not intended to provide a complete air mass trajectory analysis, but they are intended to determine the following:

(1) the residence time of air parcels in the area, and

(2) the uniformity of flow through the area.

The residence time of the air parcel is a measure of the amount of local influence on pollutant levels in that air parcel since higher residence times allow air parcels to take on more characteristics of the local area (46).

The accuracy of air parcel trajectory is dependent upon uniformity of flow (22). High pressure cells usually have uniform flow (22). Local and regional wind data are reviewed to determine if uniform flow conditions prevail.

## RESULTS

The data are presented for each sampling day, including $O_3$ concentrations and meteorological conditions of the region. Since $SO_2$ concentrations were below the limit of detection for the sign-x analyzer, $SO_2$ results are presented for September 25 only.

March 29: The sampling area was under the influence of a low pressure system located north of the Park. Ground wind speeds were low as shown in Table I. However winds at the first standard level (approximately 1000 ft above ground level) were from the west and were 25 to 30 miles per hour (mph) for the 24 hours ending with the sampling time. Westerly winds continued at 30 mph for a period of at least seven hours after sampling.

Ground level oxidant concentrations reached maximums in the afternoon at all three sampling sites. The Knoxville $O_3$ concentration reached a maximum of 0.070 PPM at 2:00 p.m. and the Asheville $O_3$ concentration peaked at 0.060 PPM. The total oxidant monitor (U.R.C.) recorded the maximum concentration of 0.078 PPM at 11:00 a.m. The hourly $O_3$ and total oxidant concentrations observed at ground stations on the sampling day are listed on Table 2.

Afternoon observations of $O_3$ concentrations increased with altitude as can be seen in observations 12 and 13 on Figure 4. The observations for the afternoon flight indicate that $O_3$ concentrations were significantly lower (.057 to .059 PPM) on the south side of the Park (North Carolina) than the northwest side of the Park (0.067 to .070 PPM) (near Knoxville, Tennessee).

TABLE 1. Hourly Averages of Wind Speed and Direction on March 29

| | Knoxville, Tennessee | | Asheville, North Carolina | |
|---|---|---|---|---|
| Hour | Direction* | Speed (mph) | Direction | Speed (mph) |
| 1:00 a.m. | 0 | 0 | 0 | 0 |
| 2:00 | 0 | 0 | 0 | 0 |
| 3:00 | 0 | 0 | 320 | 3 |
| 4:00 | 0 | 0 | 330 | 8 |
| 5:00 | 0 | 0 | 320 | 5 |
| 6:00 | 0 | 0 | 330 | 8 |
| 7:00 | 0 | 0 | 340 | 6 |
| 8:00 | 0 | 0 | 350 | 0 |
| 9:00 | 0 | 0 | 350 | 8 |
| 10:00 | 240 | 4 | 350 | 11 |
| 11:00 | 290 | 12 | 330 | 12 |
| 12:00 noon | 260 | 8 | 340 | 7 |
| 1:00 p.m. | 250 | 10 | 340 | 9 |
| 2:00 | 260 | 11 | 340 | 16 |
| 3:00 | 320 | 8 | 330 | 17 |
| 4:00 | 10 | 4 | 310 | 15 |
| 5:00 | 310 | 10 | 300 | 14 |
| 6:00 | 20 | 8 | 290 | 11 |
| 7:00 | 360 | 6 | 290 | 11 |
| 8:00 | 360 | 6 | 350 | 8 |
| 9:00 | 350 | 5 | 350 | 7 |
| 10:00 | 360 | 9 | 340 | 8 |
| 11:00 | 30 | 8 | 350 | 8 |
| 12:00 | 30 | 7 | 360 | 10 |

*Wind direction in degrees from true North.

TABLE 2. Ground Level Ozone and Total Oxidant Concentrations on March 29, 1978 in PPM

| HOUR | U.R.C.[2] | KNOXVILLE, TN.[1] | ASHEVILLE, N.C.[1] |
|---|---|---|---|
| 1:00 A.M. | .025 | .005 | .005 |
| 2:00 | .022 | .005 | .005 |
| 3:00 | .022 | .005 | .005 |
| 4:00 | .025 | .005 | .005 |
| 5:00 | .023 | .005 | .005 |
| 6:00 | .027 | .005 | .005 |
| 7:00 | .028 | .005 | .005 |
| 8:00 | .027 | .005 | .005 |
| 9:00 | .030 | .017 | .005 |
| 10:00 | .075 | .032 | .020 |
| 11:00 | .078 | .041 | .030 |
| NOON | .073 | .052 | .030 |
| 1:00 P.M. | .070 | .061 | .040 |
| 2:00 | .070 | .070 | .050 |
| 3:00 | .075 | .066 | .060 |
| 4:00 | .073 | .059 | .060 |
| 5:00 | .072 | .061 | .060 |
| 6:00 | .075 | .057 | .040 |
| 7:00 | .072 | .050 | .040 |
| 8:00 | .067 | .050 | .040 |
| 9:00 | .025 | .044 | .030 |
| 10:00 | .024 | .044 | .040 |
| 11:00 | .021 | .044 | .030 |
| 12:00 | .025 | .044 | .030 |

[1]State Air Agency observations of ozone determined by chemiluminescence.

[2]U.R.C. Uplands Research Center near Gatlinburg, TN., determined by Mast meter.

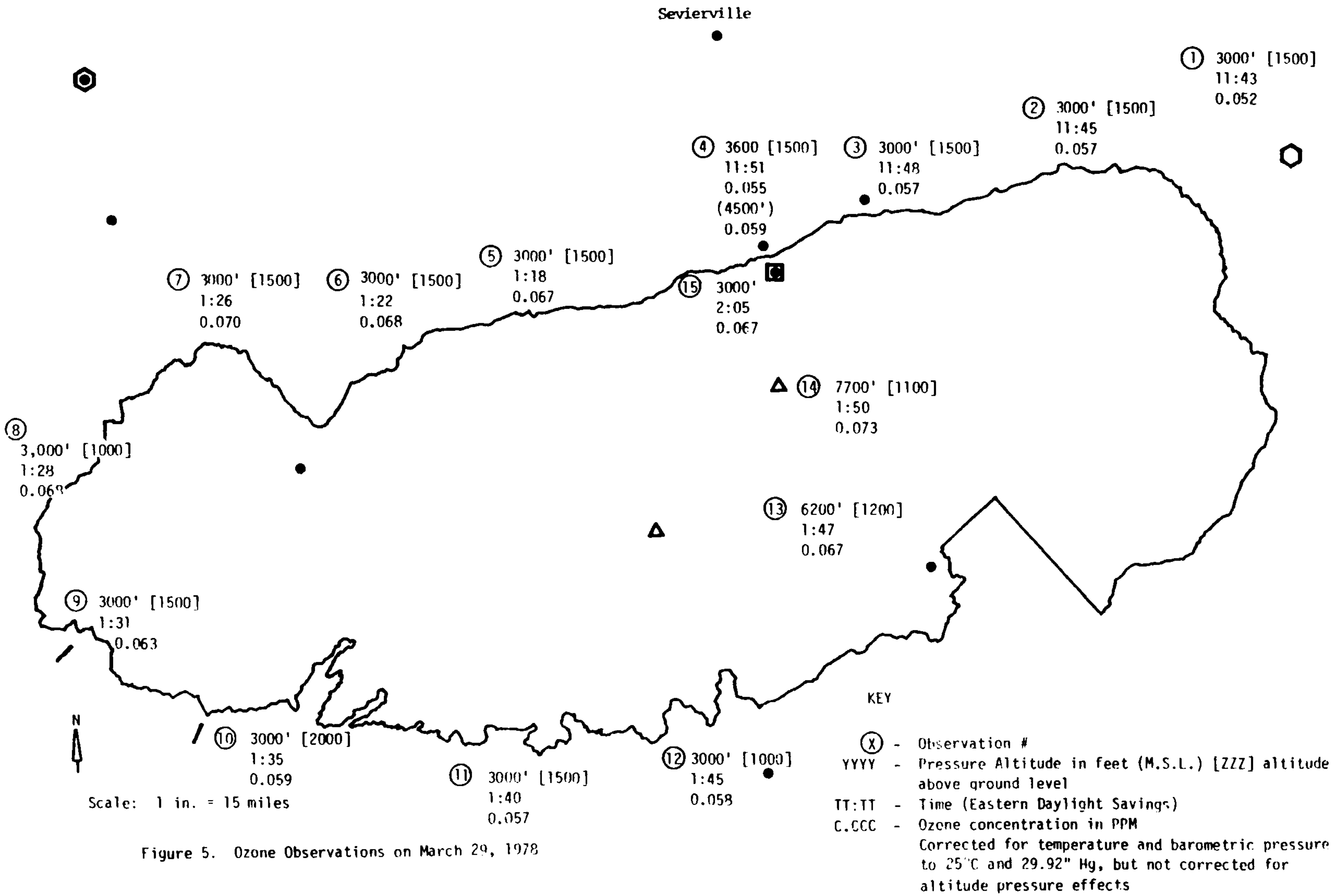



Figure 5. Ozone Observations on March 29, 1978

The $O_3$ concentrations observed at 3000' above sea level (M.S.L.) approximately 1500' above ground level (A.G.L.) were higher than the observations at any ground stations for the same time period, but were less than the maximum observed in Knoxville.

May 26: During this sampling period, the Park was under the influence of a high pressure area to the west centered in Southern Kentucky. At Knoxville, winds were light and variable 10 mph during the morning and variable and from 5 to 15 mph from the northeast during the afternoon. Winds at Asheville were southeast and velocity ranged from three to seven mph (see Table 3).

The $O_3$ data for Knoxville and U.R.C. on May 26 are incomplete and concentrations for 3:00 a.m. through 8:00 a.m. are not recorded (see Table 4). $O_3$ concentrations were above the NAAQS for three consecutive hours, at Knoxville beginning at 3:00 in the afternoon.

$O_3$ concentrations were generally lower throughout the day at Asheville, than at U.R.C., but the variations of oxidant level were very similar to those observed in Knoxville, as seen in Table 4.

Airborne observations of $O_3$ concentrations indicate there was little $O_3$ variation with height and only a 0.01 PPM change was seen over a change in altitude of 5000' (between 3500' and 8500' MSL).

$O_3$ levels closer to Knoxville were similar to those in the Park as can be seen in Figure 5.

June 20: The area was under the influence of a low to the south and there was a solid cloud cover at 2200' near the Park. No observations were made in the Park on this flight due to poor

TABLE 3. Hourly Averages of Wind Speed and Direction on May 26

| | Knoxville, Tennessee | | Asheville, North Carolina | |
|---|---|---|---|---|
| Hour | Direction* | Speed (mph) | Direction | Speed (mph) |
| 1:00 a.m. | 240 | 4 | 310 | 4 |
| 2:00 | 0 | 0 | 320 | 3 |
| 3:00 | 50 | 6 | 320 | 4 |
| 4:00 | 0 | 0 | 0 | 0 |
| 5:00 | 30 | 4 | 0 | 0 |
| 6:00 | 30 | 6 | 340 | 4 |
| 7:00 | 50 | 5 | 0 | 0 |
| 8:00 | 0 | 0 | 310 | 3 |
| 9:00 | 50 | 7 | 180 | 2 |
| 10:00 | 0 | 0 | 150 | 5 |
| 11:00 | 360 | 3 | 150 | 6 |
| 12:00 noon | 340 | 3 | 140 | 7 |
| 1:00 p.m. | 360 | 4 | 170 | 9 |
| 2:00 | 150 | 4 | 170 | 13 |
| 3:00 | 330 | 5 | 150 | 8 |
| 4:00 | 50 | 4 | 160 | 6 |
| 5:00 | 20 | 6 | 150 | 8 |
| 6:00 | 50 | 8 | 140 | 7 |
| 7:00 | 30 | 6 | 140 | 4 |
| 8:00 | 50 | 5 | 0 | 0 |
| 9:00 | 60 | 4 | 0 | 0 |
| 10:00 | 50 | 6 | 150 | 3 |
| 11:00 | 0 | 0 | 130 | 4 |
| 12:00 | 0 | 0 | 130 | 4 |

*Wind direction in degrees from true North.

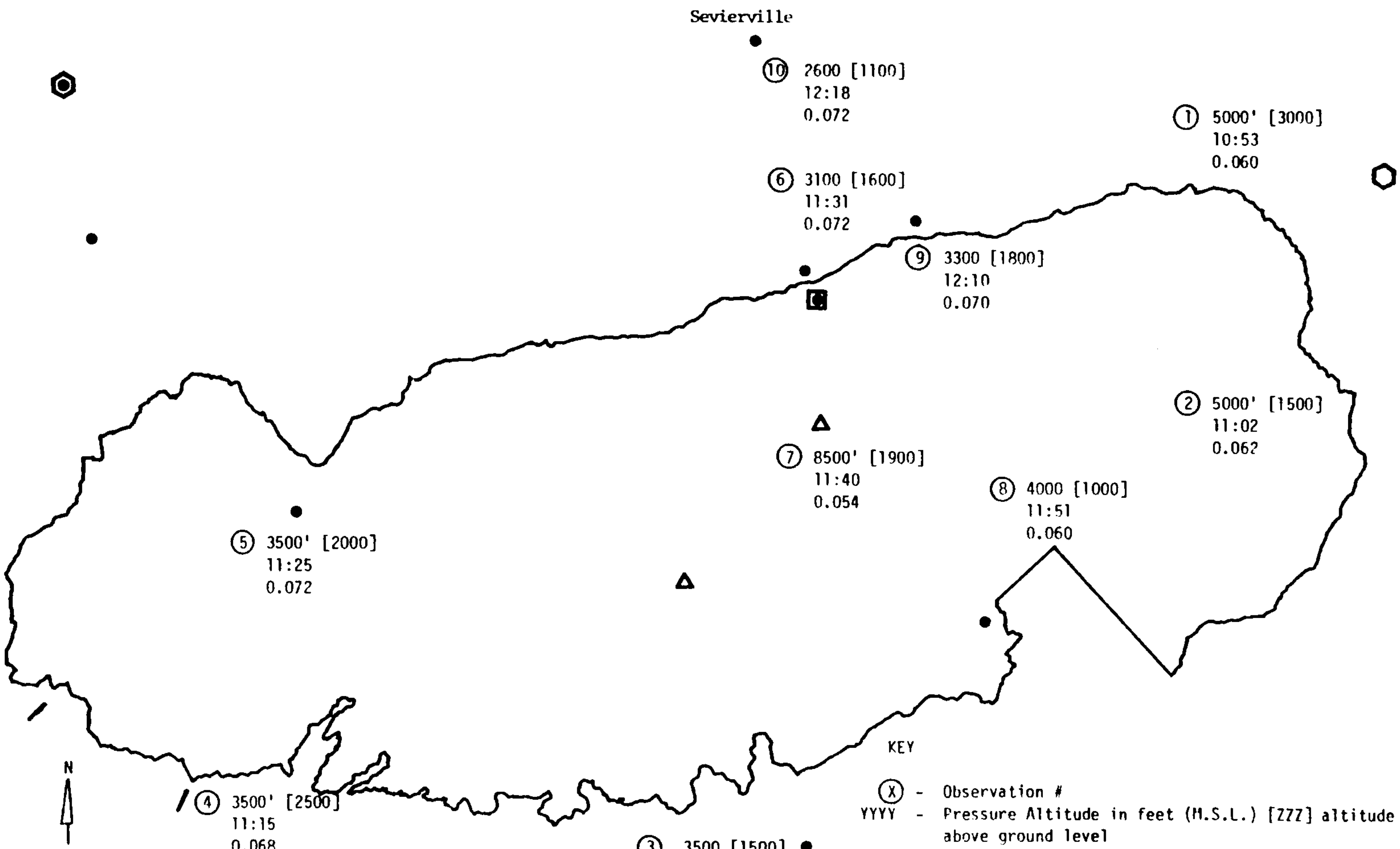
TABLE 4. Ground Level Ozone[1] and Total Oxidant[2] Concentrations on May 26, 1978

| HOUR | U.R.C.[2] | KNOXVILLE, TN.[1] | ASHEVILLE, N.C.[1] |
|---|---|---|---|
| 1:00 A.M. | NDA* | .005 | .005 |
| 2:00 | NDA | .005 | .005 |
| 3:00 | NDA | NDA | .005 |
| 4:00 | NDA | NDA | .005 |
| 5:00 | NDA | NDA | .005 |
| 6:00 | NDA | NDA | .005 |
| 7:00 | NDA | NDA | .005 |
| 8:00 | NDA | NDA | .005 |
| 9:00 | NDA | .011 | .005 |
| 10:00 | NDA | .031 | .010 |
| 11:00 | NDA | .041 | .015 |
| NOON | .018 | .066 | .015 |
| 1:00 P.M. | .042 | .076 | .020 |
| 2:00 | .058 | .089 | .020 |
| 3:00 | .062 | .091 | .030 |
| 4:00 | .062 | .083 | .040 |
| 5:00 | .060 | .078 | .050 |
| 6:00 | .058 | .076 | .050 |
| 7:00 | .057 | .066 | .050 |
| 8:00 | .053 | .026 | .015 |
| 9:00 | .038 | .005 | .015 |
| 10:00 | .012 | .005 | .015 |
| 11:00 | .007 | .005 | .020 |
| 12:00 | .002 | .005 | .020 |

*No Data Available

[1]State Air Agency observations of ozone determined by chemiluminescence.

[2]U.R.C.-Upland Research Center, Gatlinburg, Tennessee, Total Oxidants determined by Mast meter.




Scale: 1 in. = 15 miles

Figure 6. Ozone Observations on May 26, 1978

KEY

Ⓧ - Observation #

YYYY - Pressure Altitude in feet (M.S.L.) [ZZZ] altitude above ground level

TT:TT - Time (Eastern Daylight Savings)

C.CCC - Ozone concentration in PPM
Corrected for temperature and barometric pressure to 25°C and 29.92" Hg, but not corrected for altitude pressure effects

TABLE 5. Ozone[1] Concentrations Observed During Spirial on May 26, 1978 in PPM

| Altitude M.S.L. Gatlinburg 11:00 A.M. | $O_3$ Uncorrected for Altitude |
|---|---|
| 3300 | 0.062 |
| 4000 | 0.060 |
| 4500 | 0.064 |
| 5000 | 0.062 |
| 5500 | 0.062 |
| 6000 | 0.059 |
| 6500 | 0.059 |
| 7000 | 0.058 |
| 7500 | 0.055 |
| 8000 | 0.054 |
| 8500 | 0.052 |

[1] Determined by chemiluminescence.

visibility and rain. Winds shifted from the south at 3 to 6 mph to the southwest at 5 to 10 mph at 9:00 a.m.

Asheville winds were light and variable and were only steady from the south from 2:00 to 4:00 at 5 to 10 mph. Complete wind data for June 20 are contained in Table 6.

There are no $O_3$ data from the Knoxville ground station for June 20. Ozone concentrations in Asheville reached a peak of 0.030 PPM for the hours of 1:00 and 2:00 p.m. Total oxidant concentration at U.R.C. peaked at 2:00 and 3:00 p.m. at a value of 0.043 (Table 7). The Knoxville $O_3$ monitor was reported as operating for seventeen days during the month of June. On six days, $O_3$ concentrations exceeded 0.08 PPM. Oxidant concentrations were consistently lower in Asheville and the highest recorded concentration was 0.070 PPM.

Due to the low ceiling and cloud cover, no flights were conducted in the Park on June 30. Observations were made north of the Park and large variations in $O_3$ concentrations were observed near Sevierville, Tennessee on either side of a 1500' mountain ridge rising 500' above the surrounding terrain. Replications were performed to insure that there was no error in the data, and the results can be seen in Figure 8. The two different $O_3$ levels were observed on opposite sides of a ridge running northeast to southwest.

July 17: Knoxville winds were from the northeast at 5 to 10 mph from 8:00 a.m. until 3:00 p.m. when they shifted to northwest at the same speed until 6:00 p.m. Winds were light in Asheville until 6:30 a.m. when the northwest breeze began. Winds ranged from

TABLE 6. Hourly Averages of Wind Speed and Direction on June 20

| | Knoxville, Tennessee | | Asheville, North Carolina | |
|---|---|---|---|---|
| Hour | Direction* | Speed (mph) | Direction | Speed (mph) |
| 1:00 a.m. | 360 | 3 | 0 | 0 |
| 2:00 | 40 | 5 | 0 | 0 |
| 3:00 | 360 | 3 | 0 | 0 |
| 4:00 | 360 | 6 | 130 | 5 |
| 5:00 | 70 | 3 | 0 | 0 |
| 6:00 | 130 | 5 | 0 | 0 |
| 7:00 | 60 | 4 | 0 | 0 |
| 8:00 | 350 | 4 | 0 | 0 |
| 9:00 | 320 | 5 | 0 | 0 |
| 10:00 | 210 | 3 | 360 | 5 |
| 11:00 | 240 | 5 | 10 | 3 |
| 12:00 noon | 230 | 6 | 90 | 4 |
| 1:00 p.m. | 260 | 5 | 180 | 10 |
| 2:00 | 210 | 7 | 190 | 6 |
| 3:00 | 260 | 7 | 180 | 7 |
| 4:00 | 230 | 7 | 140 | 4 |
| 5:00 | 240 | 8 | 0 | 0 |
| 6:00 | 220 | 8 | 0 | 0 |
| 7:00 | 220 | 5 | 220 | 3 |
| 8:00 | 230 | 6 | 0 | 0 |
| 9:00 | 200 | 5 | 120 | 3 |
| 10:00 | 240 | 4 | 130 | 3 |
| 11:00 | 270 | 5 | 0 | 0 |
| 12:00 | 310 | 4 | 0 | 0 |

*Wind direction in degrees from true North.

TABLE 7. Ground Level Ozone[1] and Total Oxidant[2] Concentrations on June 20, 1978 in PPM

| HOUR | U.R.C.[2] | KNOXVILLE, TN.[1] | ASHEVILLE, N.C.[1] |
|---|---|---|---|
| 1:00 A.M. | NDA | NDA | .005 |
| 2:00 | .037 | NDA | .005 |
| 3:00 | .028 | NDA | .005 |
| 4:00 | .027 | NDA | .005 |
| 5:00 | .020 | NDA | .005 |
| 6:00 | .018 | NDA | .005 |
| 7:00 | .017 | NDA | .005 |
| 8:00 | .017 | NDA | .005 |
| 9:00 | .018 | NDA | .005 |
| 10:00 | .017 | NDA | .005 |
| 11:00 | .012 | NDA | .005 |
| NOON | .012 | NDA | .005 |
| 1:00 P.M. | .013 | NDA | .030 |
| 2:00 | .030 | NDA | .030 |
| 3:00 | .043 | NDA | .015 |
| 4:00 | .040 | NDA | .010 |
| 5:00 | .038 | NDA | .010 |
| 6:00 | .038 | NDA | .010 |
| 7:00 | .037 | NDA | .010 |
| 8:00 | .028 | NDA | .005 |
| 9:00 | .020 | NDA | .005 |
| 10:00 | .018 | NDA | .005 |
| 11:00 | .018 | NDA | .005 |
| 12:00 | .023 | NDA | .005 |

[1] State Air Agency observations of ozone determined by chemiluminescence.

[2] U.R.C. Uplands Research Lab, Gatlinburg, Tennessee, total oxidants determined by Mast meter.

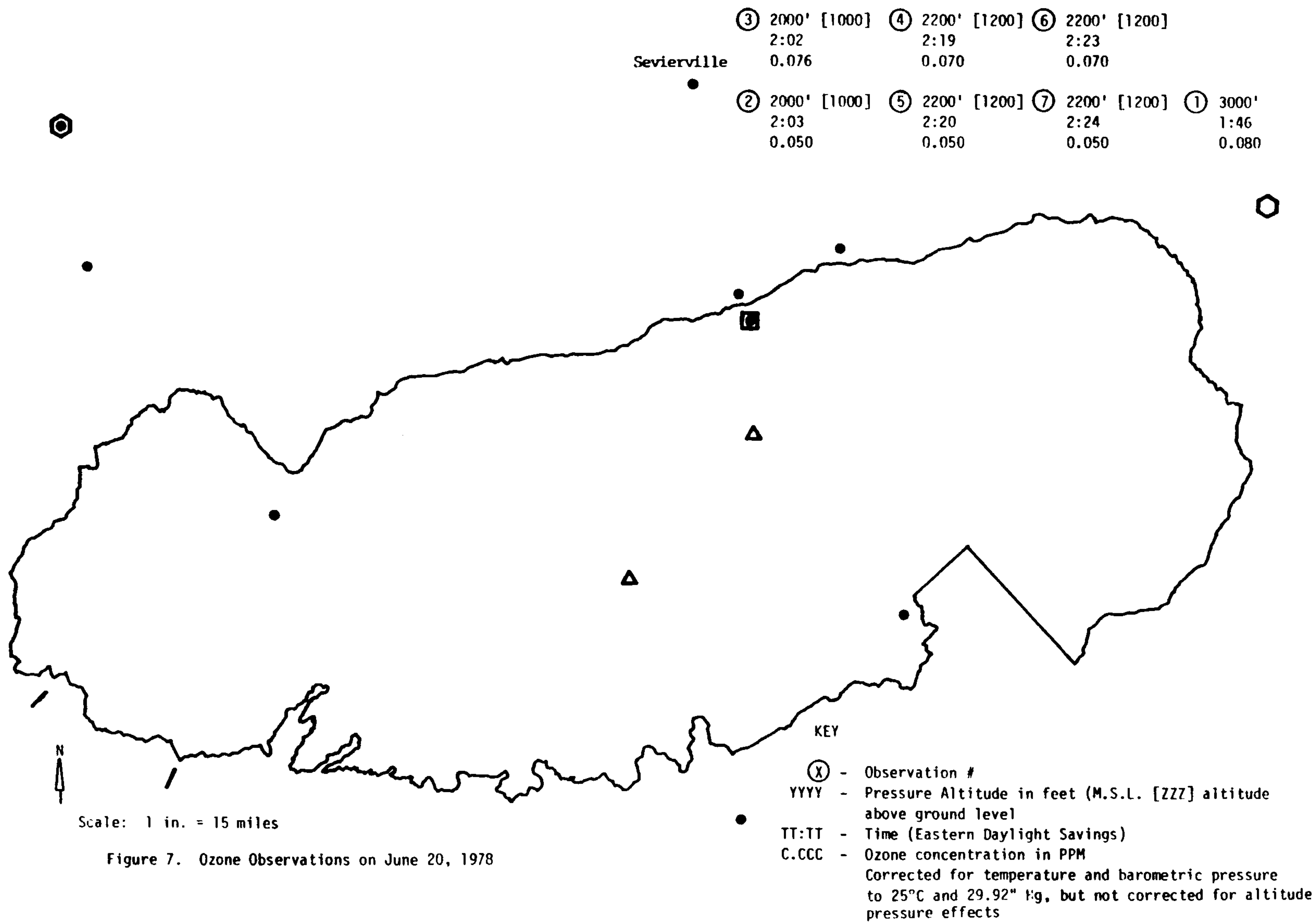



Figure 7. Ozone Observations on June 20, 1978

TABLE 8. Hourly Averages of Wind Speed and Direction on July 17

| | Knoxville, Tennessee | | Asheville, North Carolina | |
|---|---|---|---|---|
| Hour | Direction* | Speed (mph) | Direction | Speed (mph) |
| 1:00 a.m. | 0 | 0 | 190 | 3 |
| 2:00 | 0 | 0 | 310 | 3 |
| 3:00 | 0 | 0 | 0 | 0 |
| 4:00 | 0 | 0 | 0 | 0 |
| 5:00 | 0 | 0 | 0 | 0 |
| 6:00 | 340 | 3 | 0 | 0 |
| 7:00 | 0 | 0 | 350 | 6 |
| 8:00 | 60 | 5 | 340 | 6 |
| 9:00 | 60 | 7 | 350 | 10 |
| 10:00 | 60 | 9 | 320 | 13 |
| 11:00 | 50 | 11 | 10 | 11 |
| 12:00 noon | 70 | 8 | 360 | 10 |
| 1:00 p.m. | 50 | 6 | 350 | 12 |
| 2:00 | 60 | 8 | 20 | 8 |
| 3:00 | 70 | 6 | 330 | 9 |
| 4:00 | 340 | 7 | 350 | 10 |
| 5:00 | 360 | 6 | 300 | 8 |
| 6:00 | 40 | 7 | 330 | 8 |
| 7:00 | 20 | 5 | 330 | 7 |
| 8:00 | 10 | 6 | 330 | 6 |
| 9:00 | 30 | 5 | 0 | 0 |
| 10:00 | 30 | 4 | 0 | 0 |
| 11:00 | 70 | 3 | 0 | 0 |
| 12:00 | 40 | 5 | 170 | 3 |

*Wind direction in degrees from true North.

TABLE 9. Ground Level Ozone and Total Oxidant Concentrations for July 17, 1978 in PPM

| HOUR | U.R.C.[2] | KNOXVILLE, TN.[1] | ASHEVILLE, N.C.[1] |
|---|---|---|---|
| 1:00 A.M. | NDA | .008 | NDA |
| 2:00 | NDA | .008 | NDA |
| 3:00 | NDA | .008 | NDA |
| 4:00 | NDA | .023 | NDA |
| 5:00 | NDA | .029 | NDA |
| 6:00 | NDA | .005 | NDA |
| 7:00 | NDA | .005 | NDA |
| 8:00 | NDA | .023 | NDA |
| 9:00 | NDA | NDA | NDA |
| 10:00 | NDA | .050 | .015 |
| 11:00 | NDA | .055 | .030 |
| NOON | .043 | .052 | .030 |
| 1:00 P.M. | .055 | .055 | .040 |
| 2:00 | .060 | .052 | .040 |
| 3:00 | .060 | .052 | .020 |
| 4:00 | .062 | .052 | .020 |
| 5:00 | .065 | .052 | .030 |
| 6:00 | .067 | .055 | .030 |
| 7:00 | .062 | .052 | .040 |
| 8:00 | .063 | .037 | .030 |
| 9:00 | .053 | .013 | .020 |
| 10:00 | .035 | .018 | .010 |
| 11:00 | .035 | .029 | NDA |
| 12:00 | .037 | .023 | NDA |

[1] State Air Agency observations of ozone determined by chemiluminescence.

[2] U.R.C.-Uplands Research Lab, Gatlinburg, Tennessee, total oxidants determined by Mast meter.

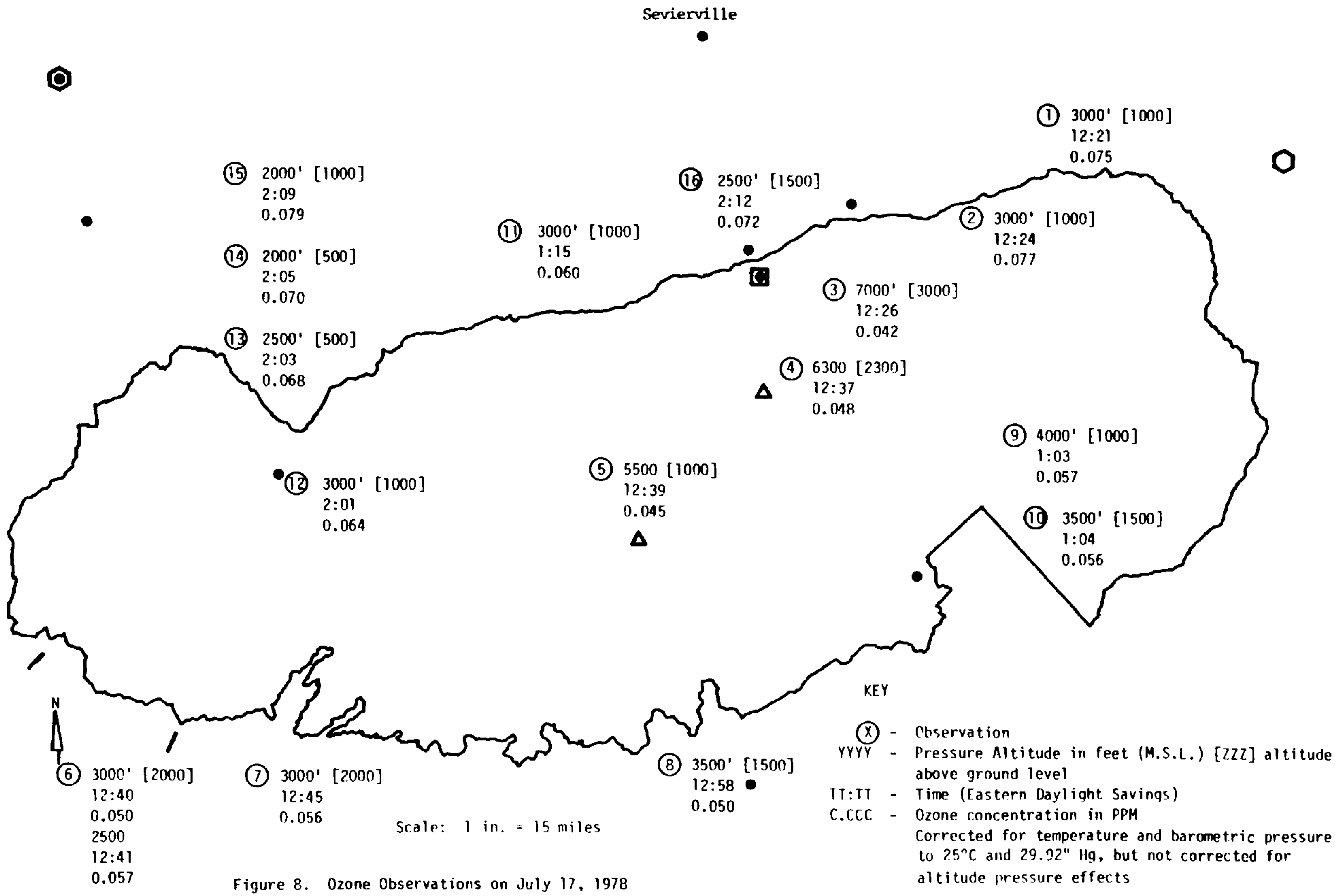



Figure 8. Ozone Observations on July 17, 1978

TABLE 10. Ozone Concentrations Observed During Spirals on July 17, 1978

| ALTITUDE M.S.L. | $O_3$ in PPM Uncorrected for Altitude |
|---|---|
| Fontana Dam (12:45 P.M.) | (1:00 P.M.) |
| 2500 | 0.057 |
| 3500 | 0.056 |
| 5000 | 0.050 |
| 6000 | 0.048 |
| 6500 | 0.054 |
| 7000 | 0.040 |
| 7500 | 0.053 |
| 8000 | 0.052 |
| 8500 | 0.053 |
| *8000 | 0.050 |
| 7500 | 0.044 |
| 7000 | 0.041 |
| 6500 | 0.041 |
| 6000 | 0.044 |
| 5500 | 0.046 |
| 5000 | 0.048 |
| 3500 | 0.050 |
| U.R.C. (1:10 P.M.) | |
| 3000 | 0.060 |
| 3500 | 0.058 |
| 4000 | 0.058 |
| 5500 | 0.052 |

*Descending portion of spiral not for same area, but heading east towards Bryson City.

[1]Determined by chemiluminescence.

5 to 15 mph as the wind shifted to the north. Tabular wind data for July 17 is on Table 8.

The maximum $O_3$ concentration recorded on July 17 was 0.055 PPM which occurred at noon. Ozone levels at Asheville reached a maximum of 0.040 PPM in the early afternoon. Total oxidant concentration did not reach the maximum (.067 PPM) until 6:00 p.m. and the U.R.C. (see Table 9).

Knoxville $O_3$ concentrations in excess of the NAAQS were recorded seven days during July. This is quite a high frequently of occurrance, since there were oxidant values above 0.80 ppm reported on almost 40% of the days monitored. There are oxidant data reported for 28 days in July at Asheville and no violations of the NAAQS occurred at U.R.C. The maximum $O_x$ concentration that day (0.067 PPM) occurred at 6:00 p.m.

Uncorrected airborne observations of $O_3$ concentrations slightly less than the NAQS were recorded between Knoxville and the Park, and in the northeastern section of the Park, as seen in Figure 6. $O_3$ levels decreased with height as can be seen in observations 3 and 4 on Figure 7, and in vertical profiles at the U.R.C. and Fontana Dam (Table 10). The descending part of the Fontana Dam spiral was not done over one area but was taken while heading east to Bryson City. Concentrations determined at 500' increments can be seen on Table 10.

July 20: The area was under the influence of a stagnant high centered about 30 miles east of the Park. Wind directions in the Knoxville area were vairable and ranged from 0 to 7 mph light and

TABLE 11. Hourly Averages of Wind Speed and Direction on July 20

| | Knoxville, Tennessee | | Asheville, North Carolina | |
|---|---|---|---|---|
| Hour | Direction* | Speed (mph) | Direction | Speed (mph) |
| 1:00 a.m. | 0 | 0 | 0 | 0 |
| 2:00 | 60 | 4 | 0 | 0 |
| 3:00 | 40 | 3 | 120 | 3 |
| 4:00 | 330 | 4 | 90 | 3 |
| 5:00 | 110 | 6 | 180 | 3 |
| 6:00 | 0 | 0 | 0 | 0 |
| 7:00 | 50 | 4 | 170 | 4 |
| 8:00 | 180 | 4 | 170 | 3 |
| 9:00 | 240 | 3 | 140 | 3 |
| 10:00 | 260 | 3 | 170 | 7 |
| 11:00 | 270 | 4 | 210 | 7 |
| 12:00 noon | 140 | 3 | 130 | 6 |
| 1:00 p.m. | 320 | 6 | 120 | 5 |
| 2:00 | 250 | 5 | 130 | 8 |
| 3:00 | 280 | 7 | 130 | 10 |
| 4:00 | 0 | 0 | 160 | 8 |
| 5:00 | 10 | 4 | 160 | 8 |
| 6:00 | 150 | 5 | 180 | 6 |
| 7:00 | 300 | 4 | 140 | 4 |
| 8:00 | 230 | 4 | 130 | 5 |
| 9:00 | 0 | 0 | 0 | 0 |
| 10:00 | 220 | 4 | 120 | 3 |
| 11:00 | 240 | 7 | 170 | 3 |
| 12:00 | 250 | 6 | 160 | 4 |

*Wind direction in degrees from true North.

TABLE 12. Ground Level Ozone[1] and Total Oxidant[2] Concentrations for July 20, 1978 in PPM

| HOUR | U.R.C.[2] | KNOXVILLE, TN.[1] | ASHEVILLE, N.C.[1] |
|---|---|---|---|
| 1:00 A.M. | NDA | NDA | .015 |
| 2:00 | NDA | NDA | .015 |
| 3:00 | NDA | NDA | .010 |
| 4:00 | NDA | NDA | .015 |
| 5:00 | NDA | NDA | .005 |
| 6:00 | NDA | NDA | .005 |
| 7:00 | NDA | NDA | .005 |
| 8:00 | NDA | NDA | .005 |
| 9:00 | NDA | NDA | .005 |
| 10:00 | NDA | NDA | .015 |
| 11:00 | .018 | NDA | .020 |
| NOON | .045 | NDA | .030 |
| 1:00 P.M. | .058 | NDA | .030 |
| 2:00 | .060 | NDA | .020 |
| 3:00 | .065 | NDA | .030 |
| 4:00 | .057 | NDA | .020 |
| 5:00 | .058 | NDA | .040 |
| 6:00 | .050 | NDA | .040 |
| 7:00 | .045 | NDA | .040 |
| 8:00 | .032 | NDA | .040 |
| 9:00 | .028 | NDA | .030 |
| 10:00 | .033 | NDA | .020 |
| 11:00 | .042 | NDA | .020 |
| 12:00 | .045 | NDA | .020 |

[1]State Air Agency observations of ozone determined by chemiluminescence.

[2]U.R.C.-Uplands Research Lab, Gatlinburg, Tennessee, total oxidants determined by Mast meter.

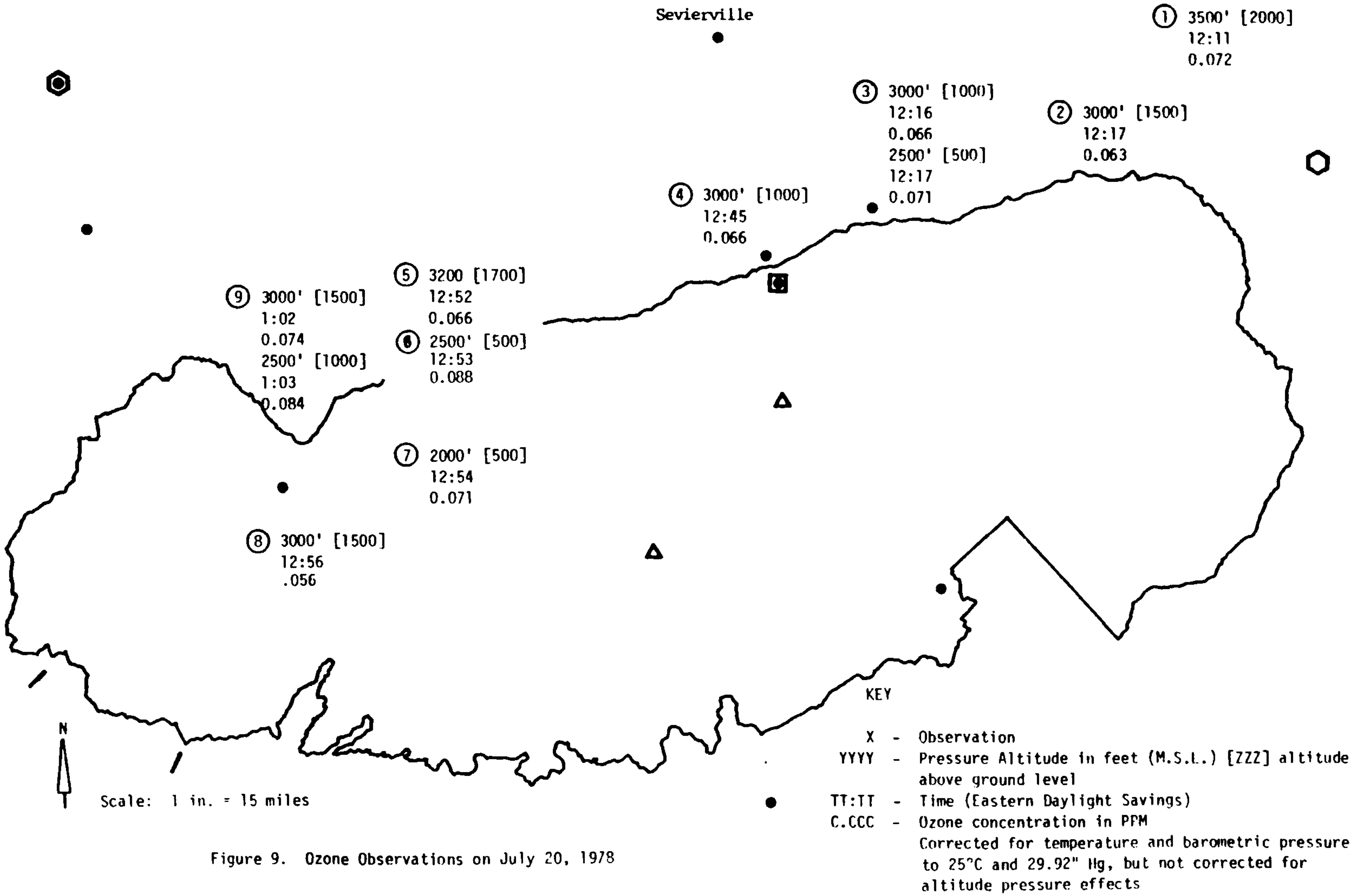



Figure 9. Ozone Observations on July 20, 1978

TABLE 13. Ozone[1] Concentrations Observed During Spirals on July 20, 1978

| ALTITUDE M.S.L. | $O_3$ Uncorrected for Altitude (PPM) |
|---|---|
| Snowbird 12:17 P.M. | |
| 3000 | 0.066 |
| 4000 | 0.063 |
| 4500 | 0.063 |
| 5000 | 0.068 |
| 5500 | 0.068 |
| 6000 | 0.067 |
| 6500 | 0.070 |
| 7000 | 0.068 |
| 7500 | 0.066 |
| 8000 | 0.052 |
| Cade's Cove 1:00 P.M. | |
| 2100 | 0.049 |
| 2500 | 0.047 |
| 3000 | 0.049 |
| 4000 | 0.046 |
| 4500 | 0.047 |
| Over Route 73 1:05 P.M. | |
| 1500 | 0.105 |
| 2000 | 0.099 |
| 2500 | 0.079 |
| One Mile East 1:05 P.M. | |
| 1500 | 0.087 |
| 2000 | 0.090 |
| 2500 | 0.084 |

[1]Determined by chemiluminescence.

variable until noon, while in the afternoon, the winds ranged from 5 to 10 mph from the southeast.

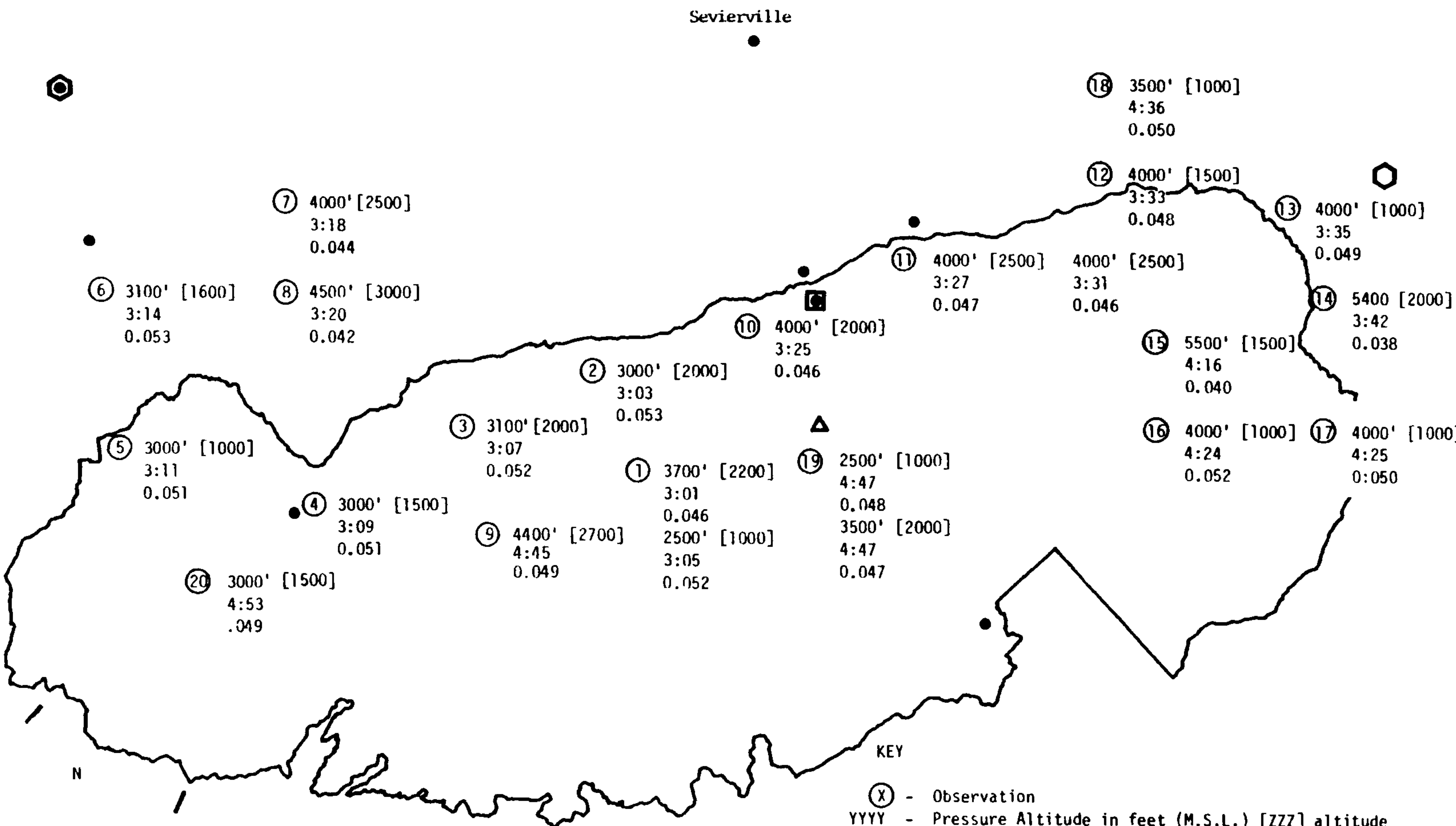
There are no data available from the Knoxville $O_3$ monitor for this date. Asheville reported a maximum of 0.030 PPM for three hours in the afternoon. Total oxidant concentration peaked at 3:00 p.m. at the U.R.C. where the concentration was 0.065 ppm.

Oxidant levels aloft reached a maximum near 6500' M.S.L. and dropped off sharply above 7500' M.S.L., the estimated mixing height as indicated in Table 13.

Interesting horizontal distributions of $O_3$ were again observed north of the western boundary. Within the Park boundary, uncorrected oxidant levels ranged from 0.056 PPM to 0.071 PPM near Cades Cove as seen in Observations 7 and 8 in Figure 9.

One area north of Cades Cove (Route 73 runs north from Cades Cove towards Knoxville) had significantly higher $O_3$ (as a difference of 0.018 PPM) concentrations than those measured one mile away (see Table 13 and Figure 9). This was verified by making duplicate traverses of the area at each altitude.

On September 25 flights were limited to the northern and eastern sections of the Park by clouds. Winds were mostly from the north and ranged from 5-15 MPH. Ozone concentrations were lower than other sampling days and the maximum concentration observed was 0.053 PPM, and there was not as great a range (the minimum concentration was 0.038 PPM (see Figure 10).




Scale: 1 in. = 15 miles

Figure 10. Ozone Observations on September 25, 1978

KEY

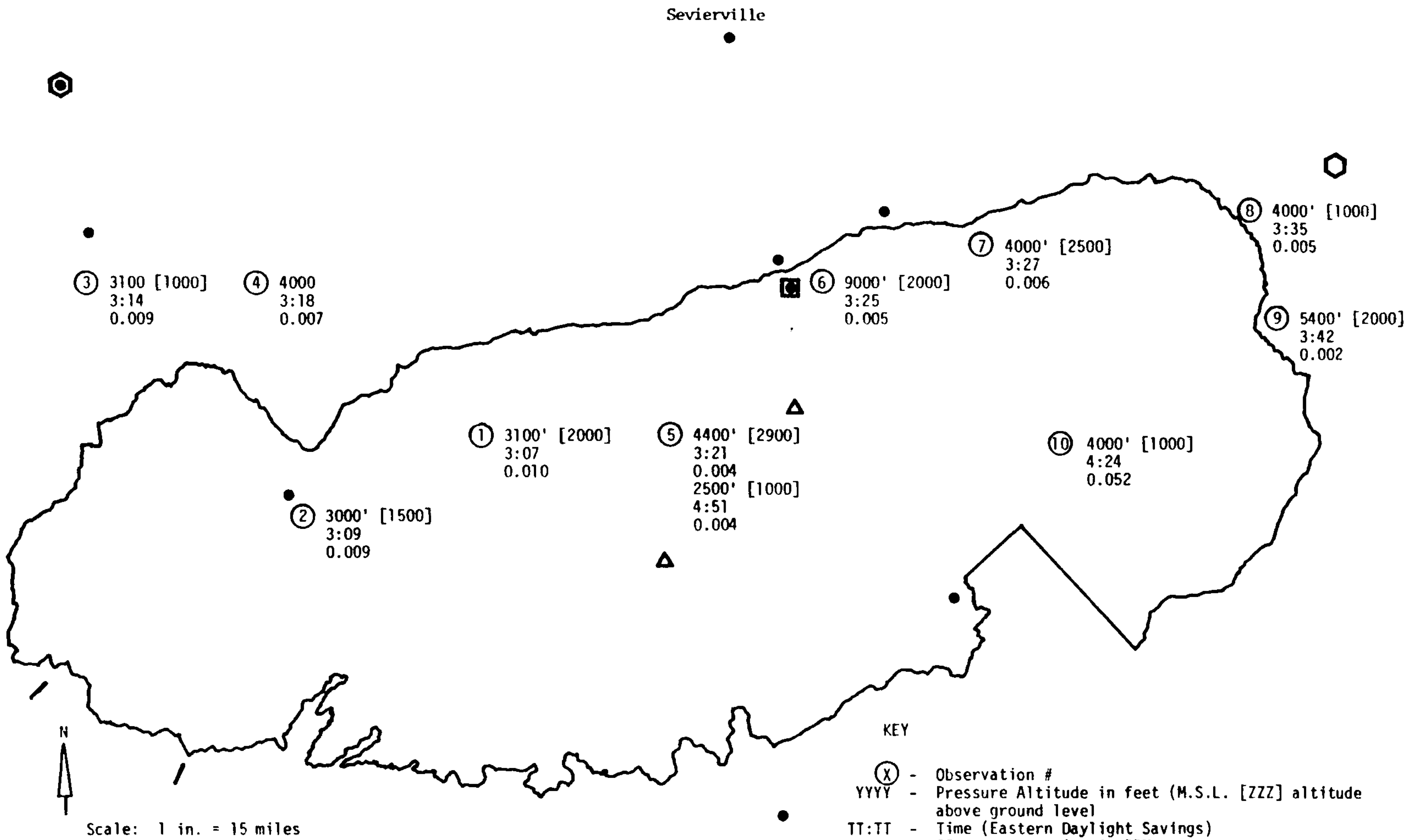
(X) - Observation
YYYY - Pressure Altitude in feet (M.S.L.) [ZZZ] altitude above ground level
TT:TT - Time (Eastern Daylight Savings)
C.CCC - Ozone concentration in PPM
Corrected for temperature and barometric pressure to 25°C and 29.92" Hg, but not corrected for altitude pressure effects

TABLE 14. Ozone[2] Concentrations Observed During Spirals on September 25, 1978

| Altitude, M.S.L. | $O_3$ in PPM Uncorrected for Altitude |
|---|---|
| Bryson City, 4:00 P.M. | |
| 4500 | 0.055 |
| 5000 | 0.052 |
| 5500 | 0.051 |
| 6000 | 0.051 |
| 6500 | 0.050 |
| 7000 | 0.050 |
| 7500 | 0.050 |
| 8000 | 0.054 |
| 8500 | 0.049 |
| 9000 | 0.057 |
| 9500 | 0.054 |
| 10000 | 0.038 |
| Cades Cove, 5:00 P.M. | |
| 2100 | 0.061 |
| 2500 | 0.061 |
| 3000 | 0.055 |
| 4000 | 0.066 |
| 4500 | 0.062 |

## $SO_2$ Data

The results from flights during March through July indicate that $SO_2$ concentrations in and around the Park were below the limit of detection of the conductometric analyzer (0.05 PPM or less). The results of observations on September 27 can be seen in Figure 11. Sulfur dioxide levels were generally low, but there was a steady increase with altitude as can be seen in Table 15.




KEY

(X) - Observation #

YYYY - Pressure Altitude in feet (M.S.L. [ZZZ] altitude above ground level

TT:TT - Time (Eastern Daylight Savings)

C.CCC - $SO_2$ concentration in PPM
Corrected for temperature and barometric pressure to 25°C and 29.92" Hg, but not corrected for altitude pressure effects

Figure 11. $SO_2$ Observations on September 25, 1978

TABLE 15. Sulfur Dioxide Concentrations Observed During Spirals on September 25, 1978

| Altitude M.S.L. Bryson City, 4:00 P.M. | Sulfur Dioxide Uncorrected for Altitude (PPM) |
|---|---|
| 4500 | 0.001 |
| 5000 | 0.002 |
| 5500 | 0.003 |
| 6000 | 0.004 |
| 6500 | 0.003 |
| 7000 | 0.002 |
| 7500 | 0.001 |
| 8000 | 0.001 |
| 8500 | 0.001 |
| 9000 | 0.001 |
| 9500 | 0.001 |
| 10000 | 0.001 |
| Cades Cove, 5:00 P.M. | |
| 2100 | 0.003 |
| 2500 | 0.003 |
| 4500 | 0.001 |

## DISCUSSION

A discussion of the results of an airborne study should include a description of the method of standardization of the results. Unfortunately results of airborne observations are not corrected for altitude, which decreases concentrations by about 15% for every 2500 feet increase in altitude. A recent EPA publication recommends reporting concentrations in micrograms per cubic meter if the pressure correction factor is not included (8). Corrected values reported here may be converted to micrograms per cubic meter by multiplying by the factor $2 \times 10^4$. To correct other values to standard conditions use the correction factors in Table 16.

Due to strong west winds in the area, $O_3$ sampled in the Park on March 29 may have resulted from emissions hundreds of miles away. March is not normally considered a part of the oxidant season, however the NAAQS was exceeded on this sampling day. The $O_3$ concentration (observations 13 and 14 in Figure 5) converted to standard conditions are 0.085 and 0.096 PPM and generally $O_3$ concentrations increased with elevation. Ozone concentrations were significantly about 14% (0.010 PPM) higher on the north (Tennessee) side of the Park than on the south side.

Winds were light (0-7 mph) and mostly ranged from the northeast to northwest on May 26. The highest $O_3$ concentration observed in the Park was 0.072 PPM, at 3500' (Figure 6, observation 5) converted to standard conditions in 0.082 PPM.

TABLE 16. Correction Factors for Altitude at STD Temperature and Pressure

| Altitude (M.S.L.) Evaluation (ft.) | Correction Factor |
|---|---|
| 0 | 1.000 |
| 500 | 1.018 |
| 1000 | 1.037 |
| 1500 | 1.056 |
| 2000 | 1.075 |
| 2500 | 1.095 |
| 3000 | 1.116 |
| 3500 | 1.136 |
| 4000 | 1.158 |
| 4500 | 1.179 |
| 5000 | 1.202 |
| 5500 | 1.225 |
| 6000 | 1.248 |
| 6500 | 1.272 |
| 7000 | 1.296 |
| 7500 | 1.321 |
| 8000 | 1.347 |
| 8500 | 1.372 |
| 9000 | 1.399 |
| 9500 | 1.426 |
| 10000 | 1.454 |

Multiply the ozone measurement by the correction factor to give the equivalent PPM at sea level.

On June 20 the afternoon winds were mostly from the west at Knoxville and ranged from 5-10 mph. A high oxidant air parcel (HOAP) was observed north of the Park, near Sevierville, Tennessee. The sampling area was directly downwind from Knoxville during the three hours preceeding sampling. Although wind speeds were not high enough to transport precursors from the downtown area to the sampling area by the time our flight was conducted. There was, however, sufficient time, and windspeed to transport precursors from suburban areas to the sampling area.

A high oxidant air parcel (or HOAP) was observed near Sevierville, Tennessee. A ridge which rose about 500' above the surrounding terrain provided a landmark, and apparently a mixing barrier between these two air parcels. Ozone concentrations differed by up to 0.020 PPM over a distance of one mile. Ozone levels when converted to standard conditions (observation 3, 0.082 ppm and observation 1, 0.089 PPM) were in excess of the NAAQS for $O_3$.

On July 17 winds were 5-10 mph from the northeast from 8:00 a.m. until 3:00 p.m. Ozone levels in excess of the NAAQS were observed in the northeast section of the Park. Figure 8, observation 3 at standard conditions was 0.086 PPM.

A HOAP was observed about 20 miles north of Cades Cove and $O_3$ levels were also in excess of the NAAQS (observation 15, Figure 8 at standard conditions is 0.085 PPM), while $O_3$ concentrations were below the standard in Cades Cove (corrected $O_3$ concentration 0.071 PPM).

Vertical sounding indicates that there was no large change of $O_3$ concentration with altitude.

Light and variable winds persisted in the area between July 17 and 20 so another flight was made to investigate the characteristics of an air parcel with a relatively long residency.

Light and variable winds occurred again on July 20 and no air-mass trajectory analysis was made. Although no violations of the NAAQS were observed during the early afternoon, $O_3$ concentrations within 10 miles of the Park exceeded the NAAQS (Observation 6, Figure 10).

More HOAPs were observed north of Cades Cove and corrected $O_3$ concentration were as high as 0.111 PPM and concentrations within one mile were 0.018 PPM lower (see Table 13). Vertical profiles on this date show no large variations of $O_3$ with altitude.

None of the ground monitors were in good positions for oxidant monitoring according to EPA guidelines. They suggest that monitors not be placed within 120 meters of heavy auto traffic (8), and both the Knoxville and Asheville monitors were located downtown. Another guideline is that oxidant monitors be placed at least 40 meters from large trees (8); which was impossible in the heavily forrested area near the U.R.C. Ozone concentration at Knoxville and Asheville generally peaks during the afternoon and is quite low at night, which indicates $O_3$ levels were strongly influenced by local sources (22). Maximum total oxidant concentrations occur later at the U.R.C. and nighttime lows were not as low, which indicates this station was more influenced by transported oxidants than ones produced by local emissions (22).

Except for March 29, when there were high winds, $O_3$ levels observed aloft were greater than ground level $O_x$ concentrations. The $O_x$ method tends to yield 25-30% higher results due to interferences of other oxidants (8). This evidence supports the EPA warning (8) that nearby trees scavenge oxidants to such a degree that they invalidate data. The U.R.C. data at least provides a qualitative indication of the diurnal variation of oxidant concentration.

Sulfur dioxide concentrations (maximum observed was 0.010 PPM) were well below the three hour secondary standard (0.5 PPM) and decreased with altitude.

Accurate measurements of $SO_2$ concentrations were made only on the last flight since levels were below the limit of detection (0.05 PPM) of the conductiometric instrument which was used for the other flights. The maximum $SO_2$ concentrations observed on September 25 was 0.011 PPM (corrected for altitude), well below the three hour secondary NAAQS of 0.5 PPM).

# CONCLUSIONS

1. The airborne platform was suitable for determining and recording the concentrations of air pollutants, and other parameters monitored in the Great Smoky Mountains National Park from March through September of 1978.
2. Violations of the $O_3$ NAAQS were observed during most investigations, and $O_3$ concentrations as high as 0.096 PPM were observed in the Park.
3. Existing state and local monitors did not provide a good indication of $O_3$ concentrations in the Park.
4. Oxidant concentrations are generally highest in the northwest section of the Park.
5. The $SO_2$ concentrations in the Park were less than 0.05 PPM and preliminary results of improved sampling technique indicate that concentrations were in the 0.002 to 0.010 PPM range during this time period.

# BIBLIOGRAPHY


1. Heicklen, J., Atmospheric Chemistry, Academic Press, New York, 1976.

2. Air Quality Criteria for Nitrogen Oxides, AP-84, U.S. EPA, Research Triangle Park, North Carolina, 1971.

3. Robinson, E., and Robbins, R. C., "Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants," Stanford Research Institute Project PR-6755, Menlo Park, California, 1968.

4. Ibid.

5. Wark, K., and Warner, C. F., Air Pollution - Its Origin and Control, Dunn-Donnelley, New York, 1976.

6. Stern, A. C., Wohlers, H. C., Boubel, R. W., Loury, W. P., Fundamentals of Air Pollution, Academic Press, New York, 1973.

7. Lonneman, W. A., Seika, R. C., Bufalini, J. J., "Ambient Air Hydrocarbon Concentrations in Florida," Environmental Science and Technology, 12:459-463, 1970.

8. Ozone and Other Photochemical Oxidants, National Academy of Sciences, Washington, 1977.

9. Altshuller, A. P. and Bufalini, "Photochemical Aspects of Air Pollution - A Review," Photochemical Photobiology, 4:97-146, 1965.

10. Leighton, P. A., Photochemistry of Air Pollution, Academic Press, New York, 1961.

11. Levy, H., II, Photochemistry of the Troposhere, Advanced Photochemistry, 9:369-524, 1974.

12. McEwan, M. J., and Phillips, L. F., Chemistry of the Atmosphere, Wiley and Sons, New York, 1975.

13. Demerjian, K. L., Kerr, J. A., Calvert, J. G., "The Mechanism of Photochemical Smog Development," Environmental Science and Technology, 4:1-262, 1974.

14. Gartrell, F. E., and Carpenter, S. B., "Aerial Sampling by Helicopter: A Method for Study of Diffusion Patterns," Journal of Meteorology, 12:215-224, 1955.

15. Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors, U.S. Environmental Protection Agency Publication No. 450/2-77-021a, Washington, 1977.

16. Di Marris, G. A., "The Ozone Problem in the Norfolk Virginia Area," U.S. Environmental Protection Agency Publication No. A-600/4-78-000, Washington, 1978.

17. Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors: Supporting Documentation, U.S. Environmental Protection Agency Publication No. 450/2-77-021b, Washington 1978.

18. Altshuller, A. P., "Evaluation of Oxidant Results at CAMP Sites in the United States," Journal of the Air Pollution Control Association, 25:19-24, 1975.

19. Miller, P. R., McCutchan, M. H., Milligan, H. P., "Oxidant Air Pollutio in the Central Valley, Sierra, Nevada Foothills, and Mineral King Valley California," Atmospheric Environment, 6:623-633, 1970.

20. Siple, G. W., Fitzsimmons, C. K., Zeller, K. F., Evans, R. B., "Long Range Airborne Measurements of Ozone of the Coast of the Northeastern United States," International Conference on Photochemical Oxidant Pollution and its Control Proceedings, U.S. Environmental Protection Agency Publication No. 600/3-77-001, Washington, 1977, pp. 249-259.

21. Skelly, J. M., Croghan, C. F., Hayes, E. M., "Oxidant Levels in Remote Mountainous Areas of Southwestern Virginia and their Effects on Native White Pine," Ibid, pp. 611-620.

22. Wolff, G. T., Lioy, R. J., Meyers, R. E., Calderwall, R. T., Wight, G. D., Parceri, R. E., Taylor, R. S., "Anatomy of Two Ozone Transport Episodes in the Washington, D.C. to Boston, Mass., Corridor," Environmental Scinece and Technology 2:506-510, 1977.

23. Husar, H. B., Patterson, P. E., Paley, C. C., Gillani, N. V., "Ozone in Hazy Air Masses" International Conference on Photochemical Oxidant Pollution and its Control Proceedings, U.S. Environmental Protection Agency Publication No. 600/3-77-001, Washington, 1977.

24. Robinson, E., and Robbins, R. C., "Gaseous Sulfur Pollutants from Urban and Natural Sources," Journal of the Air Pollution Control Association 20:233-235, 1970.

25. Kikens, G. E., and Bormann, H. F., "Acid Pair: A Serious Regional Environmental Problem," Science 18:1176-1179, 1974.

26. Likens, G. E., "Acid Precipitation," Chemical and Engineering News, 21:29-44, 1976.

27. Federal Register, 36(84) Part II, pp. 8186-8201, April 30, 1971.

28. Clean Air Act Amendments of 1977, Public Law 95-95, Statute 685-796, August 7, 1977.

29. Stephens, N. T., and McCauldin, "Attenuation of Power Station Plumes as Determined by Instrumented Aircraft," Environmental Sciences and Technology, 5:615-621, 1971.

30. McCauldin, R. O. and Johnson, L. W., "The Use of Aircraft in Air Pollution Research," Journal of the Air Pollution Control Association, 19(6), 405-409, 1969.

31. Gartrell, F. E., Thomas, J. W., Carpenter, S. M., "Atmospheric Oxidation of $S)_2$ in Coal Burning Power Plant Plumes," Industrial Hygene Journal, March-April, 116-121, 1963.

32. Adams, P. F., and Koppe, R. K., "Insturmenting Light Aircraft for Air Pollution Research," Journal of the Air Pollution Control Association, 19(6), 410-415, (1969).

33. Lovill, J. E., and Miller, A., "The Vertical Distribution of Ozone in the San Francisco Bay Area," Journal of Geophysical Research, 73:5073-5079, (1968).

34. Lea, D. A., "Vertical Ozone Distribution is the Lower Troposphere Near an Urban Pollution Complex," Journal of Applied Meteorology, 7:252-267, 1968.

35. Edinger, J. G., "Vertical Distribution of Photochemical Smog in the Los Angeles Basin," Environmental Science and Technology, 7:247-252, 1973.

36. White, W. H., Bleethemthal, D. L., Anderson, J. A., Husar, R. B., and Wilson, W. E., "Ozone Formation in the Saint Louis Urban Plume," International Conference on Photochemical Oxidant Pollution and its Control Proceedings, U.S. Environmental Protection Agency Publication No. 600/3-77-001, Washington, pp. 237-248, 1977.

37. Siple, G. W., Fitzsimmons, C. K., Zeller, K. F., Evans, R. B., "Long Range Airborne Measurements of Ozone off the Northeastern United States," Ibid., pp. 249-258.

38. Cleveland, W. S., Kleiner, B., McRae, J. E., Warner, J. L., Photochemical Air Pollution: Transport from the New York City Area into Connecticut and Massachusetts," Science, 191179-181, 1976.

39. Gloria, H. R., Bradburn, G., Reinisch, R. F., Pitts, J. N., Behar, J. V., Zafonte, B. L., "Airborne Survey of Major Air Basins in California," Journal of the Air Pollution Control Association, 24:645-652, 1974.

40. Findlay, W. J., Dowel, D. G., Quickert, N., "Detailed Evaluation of Three Chemiluminescent Ozone Monitors," Science of the Total Environment, 4: 135-155, 1975.

41. Daniel, J., Personal Communication, Virginia State Air Pollution Control Board, Richmond, Virginia.

42. Simon, C. and Proudfit, B. W., "Some Observations of Plume Rise and Plume Concentration Distribution Over New York City," Paper #67-83 presented at the 60th annual meeting of the Air Pollution Control Association, Cleveland, Ohio, June 11-16, 1967.

43. Baumgardner, R. E., Clark, T. A., and Stevens, R. K., "Increased Specificity in the Measurement of Sulfur Compounds with a Flame Photometric Detector." Analytical Chemistry, 47:563-566, 1975.

44. West, R. R., Personal Communication, Knox County Department of Air Pollution Control, Knoxville, Tennessee.

45. Legy, R., Personal Communication, Western North Carolina Regional Air Pollution Control Agency, Asheville, North Carolina.

46. DeMorris, G. A., The Ozone Problem in the Norfolk, Virginia Area, U.S. Environmental Protection Agency Publication No. 600/4-78-006, 1978.

# APPENDIX A

## AIRCRAFT INSTRUMENTATION

A. Power Supply - Abacus model #413-4-28

Abacus Controls Inc., Somerville, New Jersey.
Input 28 volts direct current from two 50 ampere alternators (optional on Cessna 337)
Output 1,000 watts at 120 volts alternating current

B. Data Recording Systems

1. Texas Instruments model #F62206D
   Texas Instruments Inc., Houston, Texas
   Four channel strip chart recorder
2. Hewlett Packard model #9825A
   Hewlett Packard, Loveland, Colorado
   Details of data logging system and data recording program are included in Appendix B

C. Analysis Instrumentation

1. Temperature: Rosemont temperature probe model #101
   Power supplied by 1.5 volt dry cell
   Calibration curve Figure 12
2. Altitude: Giannini pressure transducer model #451545
   AST/SERVO Systems Inc., Newark, New Jersey
   Power supplied by 1.5 volt dry cell
   See calibration curve Figure 13
3. Ozone
   a. Dasibi model #1003AAS
      Dasibi Environmental Inc., Glendale, California
      See calibration curve Figure 14
   b. Bendix model #8002
      Bendix Corporation, Lewisburg, West Virginia
      See calibration curve Figure 15
4. Sulfur Dioxide
   a. SIGN-X model #605A
      SIGN-X Laboratories Inc., Essex Connecticut
      See calibration curve Figure 15

b. Meloy model #285FR
   Meloy Laboratories Inc., Springfield, Virginia
   See calibration curve Figure 17

c. Hydrogen Supply
   Billings model #AHT-5
   Billings Energy Research Corporation, Provo, Utah

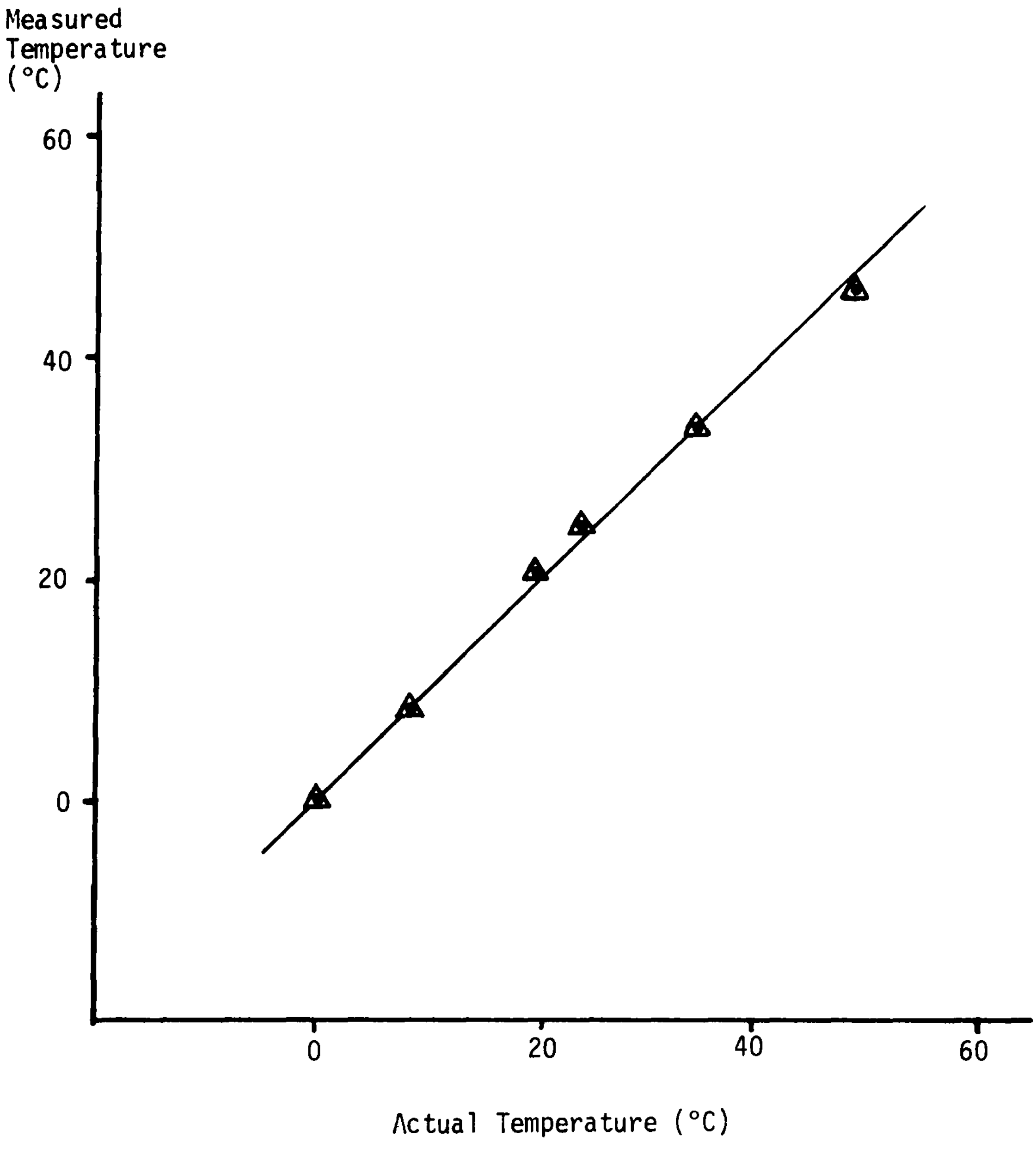



Figure 12. Temperature Probe Calibration Curve

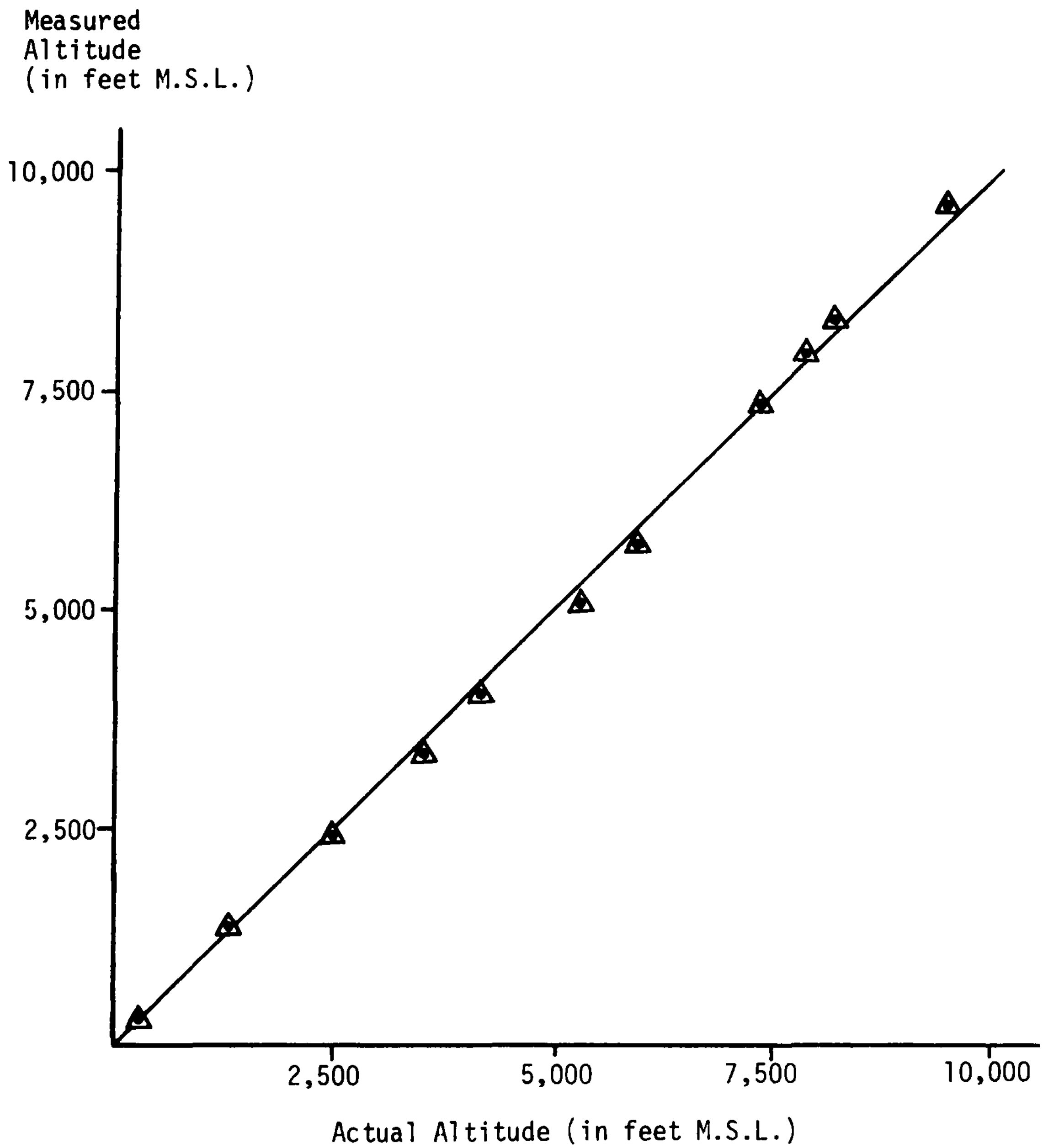



Figure 13. Altimeter Pressure Transducer Calibration Curve

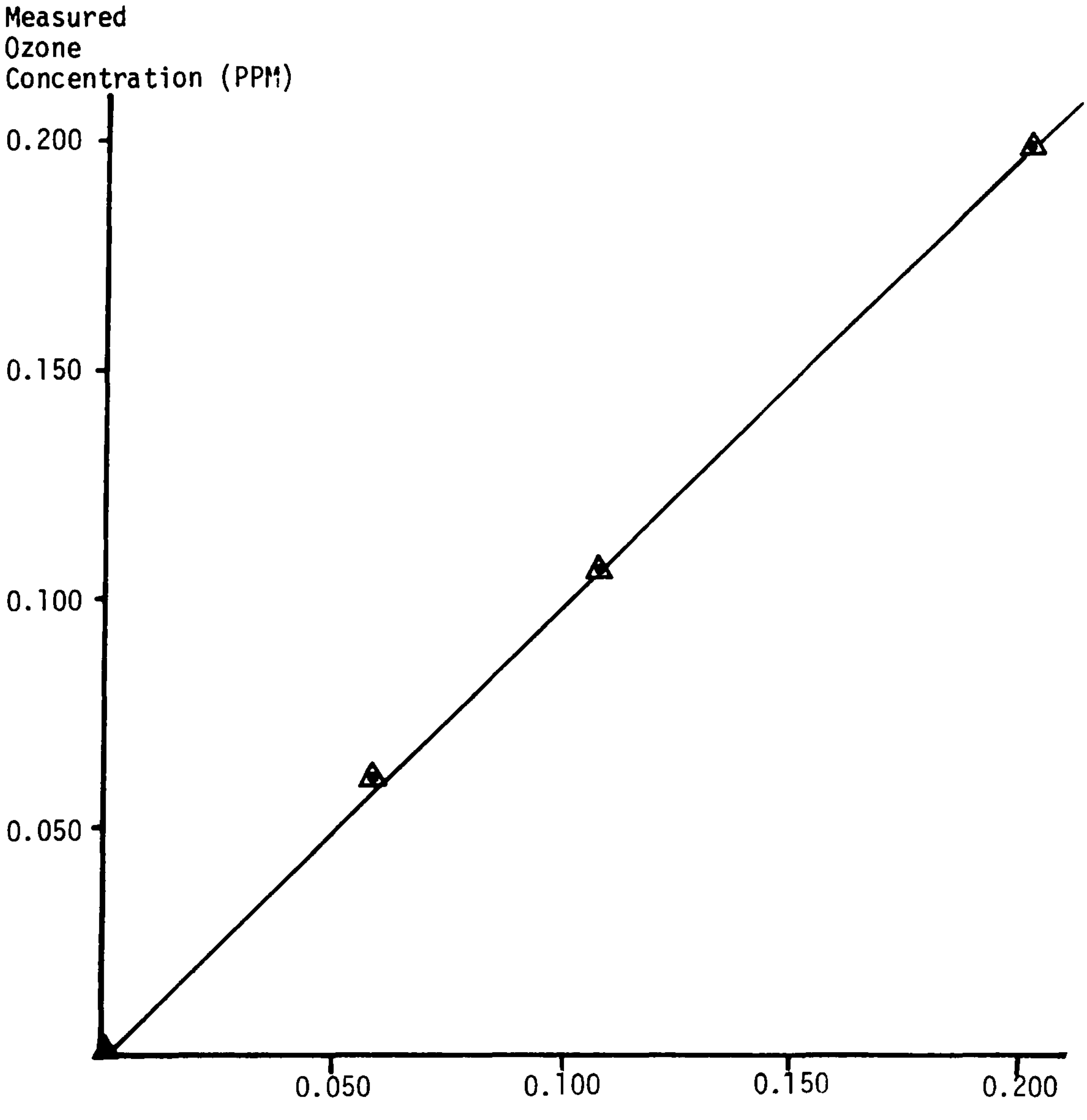



Figure 14. Ozone Photometer Calibration Curve

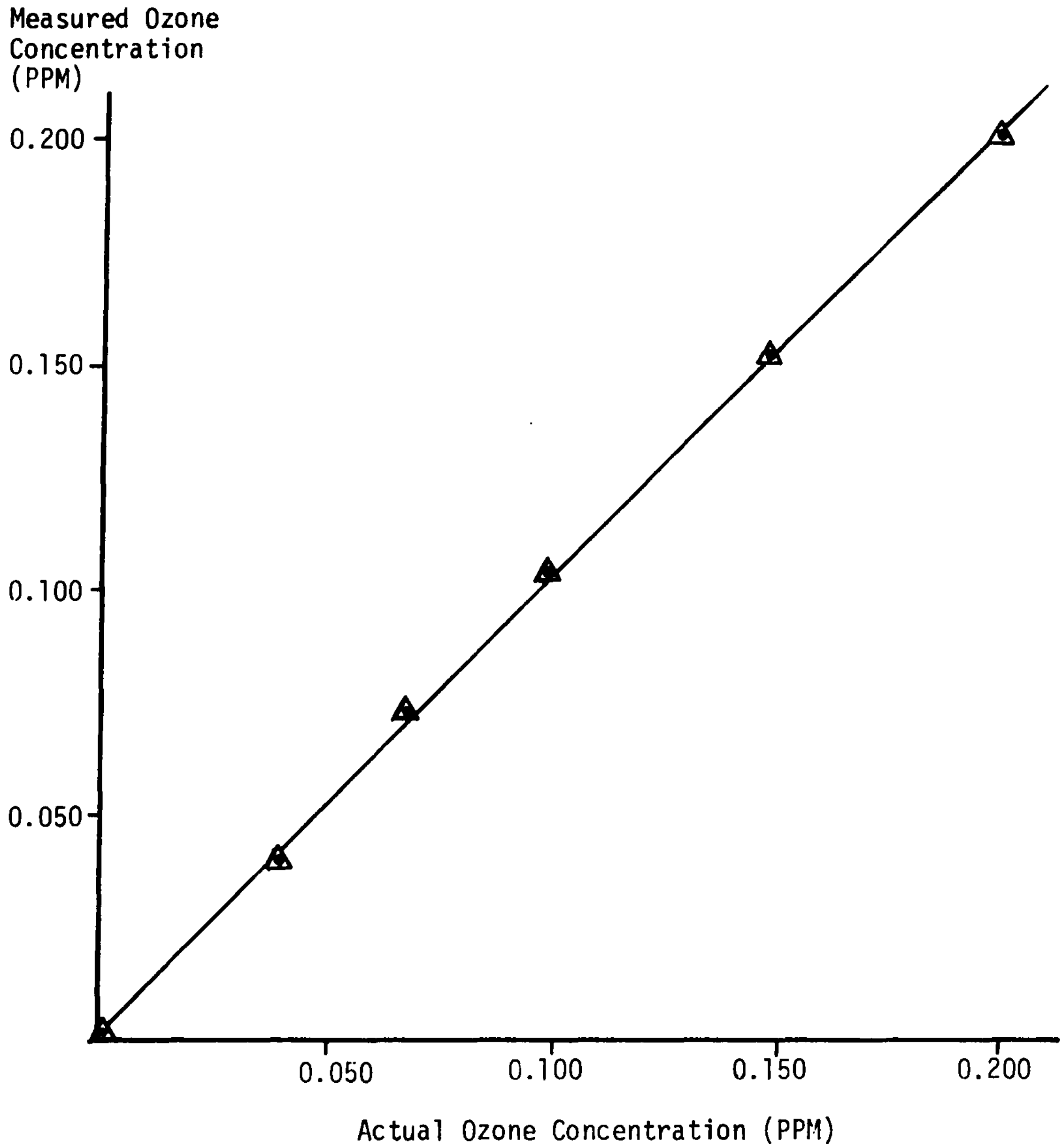



Figure 15. Chemiluminescent Ozone Monitor Calibration Curve

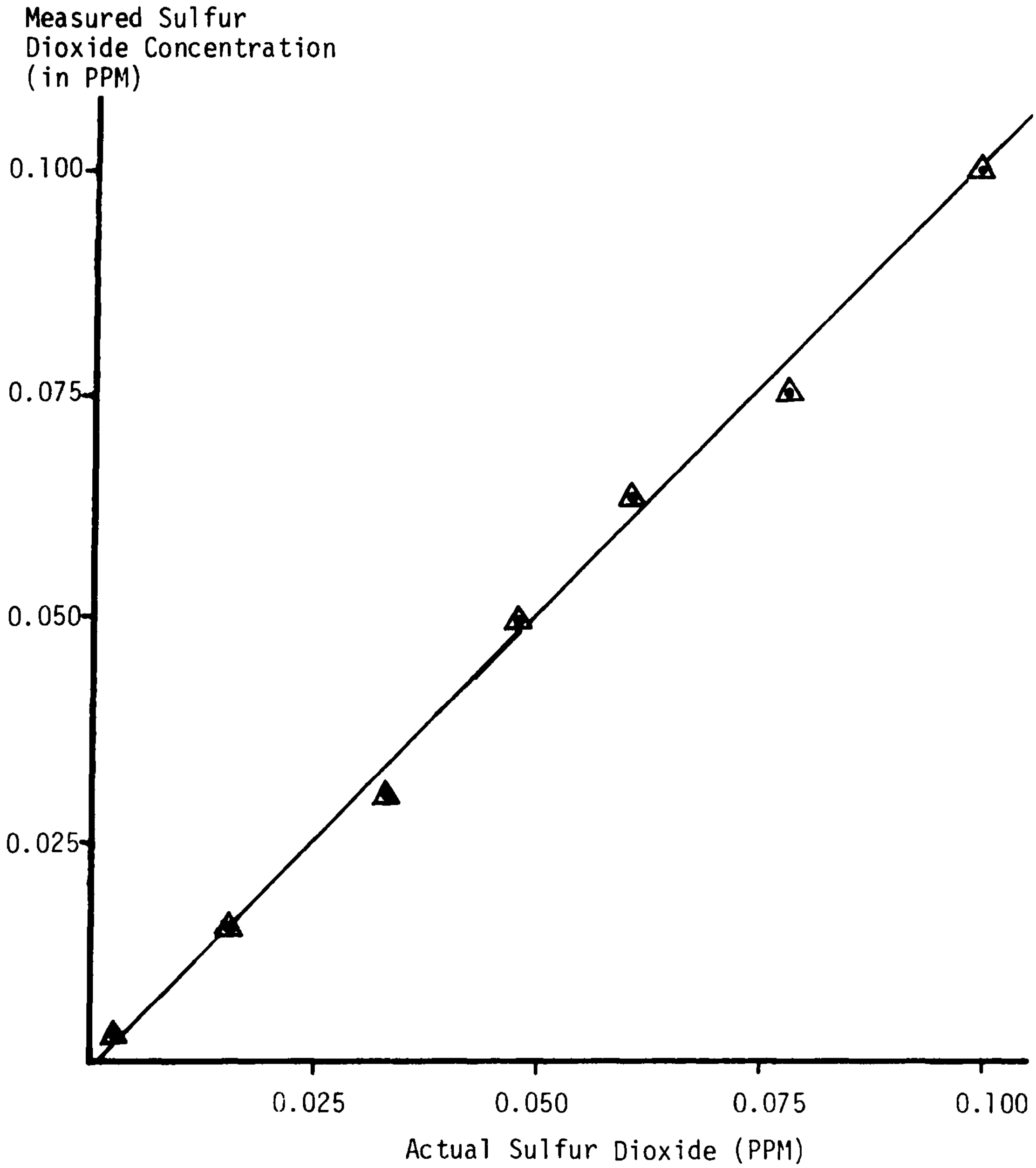



Figure 16. Conductometric Sulfur Dioxide Monitor Calibration Curve

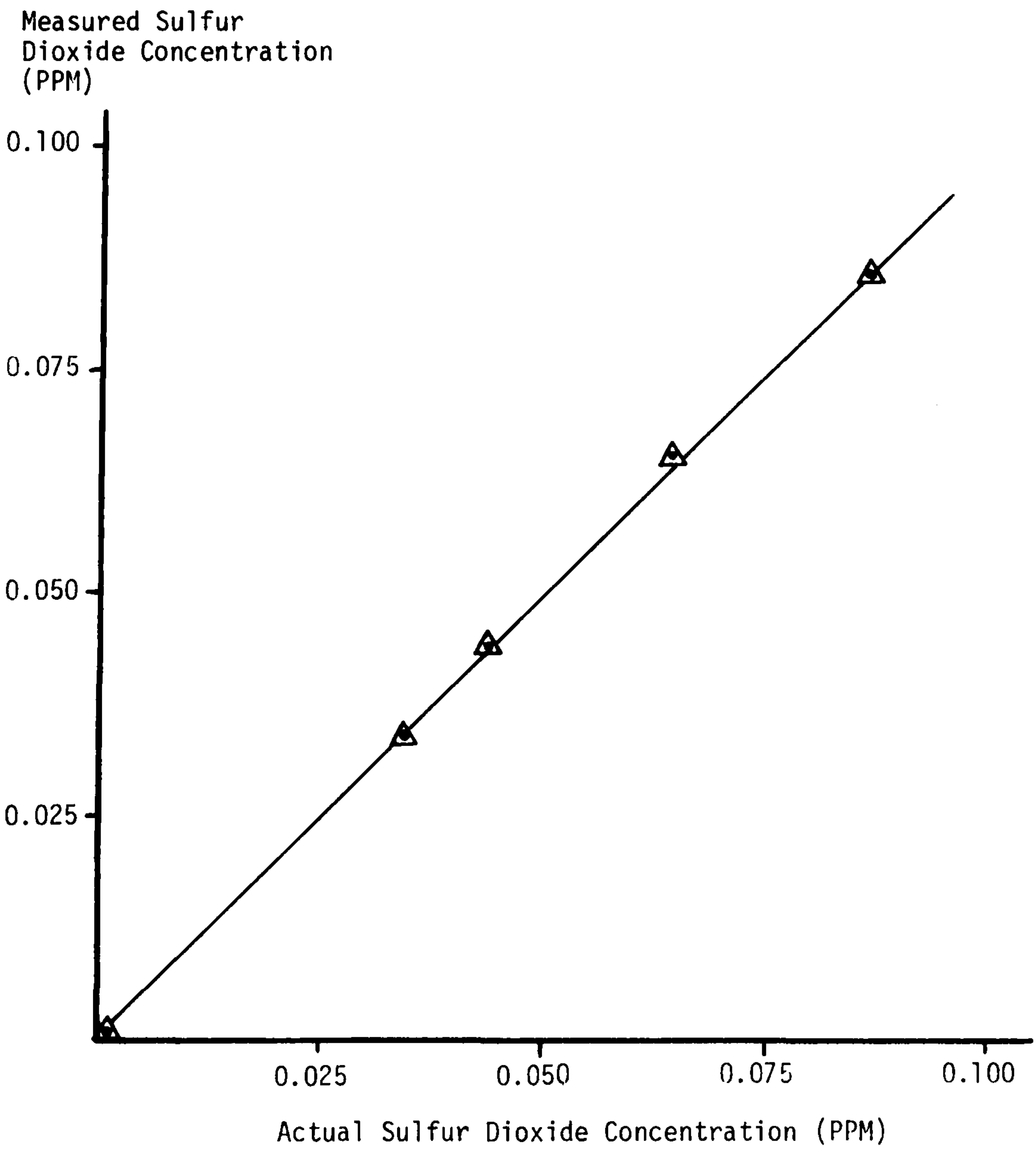



Figure 17. Flame Photometric Monitor Calibration Curve

## APPENDIX B

DATA LOGGING SYSTEM EQUIPMENT LIST

1. MINI-COMPUTER - Hewlett Packard model #9825A (addresses peripheral devices and records data on magnetic tape). A complete listing of data recording programs is in Table 19.

2. INTERFACE - Hewlett Packard 10631AHP-1B (interfaces mini-computer with scanner).

3. SCANNER - Hewlett Packard model #3495A (switching device which connects voltmeter to instruments and allows computer to record voltage).

4. VOLT METER - Hewlett Packard model # (a digital voltmeter which automatically selects the proper range to measure instrument output).

5. REAL TIME CLOCK - Hewlett Packard model #98035A (self contained quartz timer-clock which is read directly by mini-computer).

TABLE 17. Data Recording Program

```
 W[25],X[25],
 Y[25],Z[25]
1: dim C,D,H,M,
 S,Z,T,Q,F,R,O;
 723→V;fxd 3
2: for J=1 to
 144 by 1;for
 I=1 to 25;wait
 10;dsp I
3: wrt 709,"01";
 rem V;trg V;
 red V,A;A→W[I]
4: wrt 709,"02";
 rem V;trg V;
 red V,A;A→X[I]
5: wrt 709,"03";
 rem V;trg V;
 red V,A;A→Y[I]
6: wrt 709,"04";
 rem V;trg V;
 red V,A;A→Z[I]
7: next I
8: wrt 9,"R";
 fmt 1,f3.0;red
 9,C,D,H,M,S;
 dsp C,D,H,M,S
9: fxd 0;prt
 "FILE#",J
10: prt "HOURS",
 H,"MINUTES",M,
 "SECONDS",S;
 fxd 6
11: W
 W[25
 prt

 prt "CHAN2",X
13: Y[23]+Y[24]
 Y[25]→W;W/3→X;
 prt "CHAN3",X
14: Z[23]+Z[24]
 Z[25]→W;W/3→X;
 prt "CHAN4",X
15: Z[23]+Z[24]
 Z[25]→W;W/3→X;
 prt "CHAN4",X;
 spc
16: 0→Z→X→W→Y→T→
 O→Q→R→F;dsp
 "POSITION?type
 gto18";wait
 5000
17: gto 21
18: ent "altitud
 e",Z;ent "TEMP"
 ,T
19: ent "MILES
 DME",Q;ent "DME
  FREQ",F
20: ent "RDF",R;
 ent "HEADING",O
21: mrk 2,910
22: rcf J,W[*],
 X[*],Y[*],Z[*],
 C,D,H,M,S,Z,T,
 Q,F,R,O
23: next J
24: dsp "NEW
 APE PLEASE";
 tp
 6925
```

The vita has been removed from the scanned document

AN INVESTIGATION

OF

OZONE AND SULFUR DIOXIDE CONCENTRATIONS

IN

THE GREAT SMOKY MOUNTAINS NATIONAL PARK

by

John Michael Rosenquest

(ABSTRACT)

Airborne measurements of ozone and sulfur dioxide concentrations were made in remote areas of the Great Smoky Mountains National Park using an instrumented aircraft. The study was conducted because the Park was designated an area to receive maximum protection from air pollutants and it was deemed desirable to determine the existing levels of pollutant concentrations in the area.

This report includes the results of observations made between March and September of 1978 during airborne monitoring, as well as the results of observations from two ground level ozone monitors located in nearby cities (Asheville, North Carolina, and Knoxville, Tennessee) and a total oxidant monitor located in the Park.

Flights, which were made at monthly intervals, provided data which indicate that ozone levels in the Park frequently exceed the NAAQS by late morning and concentrations as high as 0.096 PPM were measured.

Comparison of ground level and airborne data indicate that ground level ozone data were significantly lower possibly due to scavenging of ozone by trees or losses by other mechanisms.

Sulfur dioxide concentrations were below the limit of detection of the conductometric sulfur dioxide monitor used during the first flights. The results of the one flight (during September) using a flame photometric $SO_2$ monitor indicates that concentrations in the Park were below 0.010 PPM.

Improvement and modification of the system are continuing, including the addition of electronic data logging equipment and visibility monitoring instruments.