



## Project Summary

# Atlanta Ozone Precursor Monitoring Study Data Report

Larry J. Purdue, James A. Reagan, William A. Lonneman, Thomas C. Lawless, Ronald J. Drago, George M. Zalaquet, Michael W. Holdren, Deborah L. Smith, Alan D. Pate, Bruce E. Buxton, and Chester W. Spicer

Monitoring was conducted during the summer of 1990 to address the measurement of ozone ( $O_3$ ) and ozone precursors in Atlanta, Georgia. Data were collected using automated gas chromatography. Resolved individual species were detected via a flame ionization detector (FID) and an electron capture detector (ECD). The study area included six continuous and six enhancement sites located in and around the greater metropolitan Atlanta area.

The collected data provide an information base to support the development and implementation of improved strategies to reduce  $O_3$  in metropolitan areas. This data base contains more than 300,000 hourly measurements of the various parameters and species identified for the study.

*This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

During the summer of 1990, the U.S. Environmental Protection Agency (EPA) conducted a major monitoring study in Atlanta, Georgia, to address the measurement of ozone ( $O_3$ ) and  $O_3$  precursors. This project was undertaken to obtain an information base to support the development and implementation of improved strategies for reducing  $O_3$  in cities that are not in compliance with EPA's National Ambient Air Quality Standards (NAAQS).

The study was sponsored jointly by EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) and

Office of Air Quality Planning and Standards (OAQPS), located in Research Triangle Park (RTP), North Carolina. It was conducted with contractual assistance from the Atmospheric Science and Applied Technology Department of Battelle Memorial Institute in Columbus, Ohio, and with operational assistance from EPA Region IV and the Georgia Department of Natural Resources (DNR) in Atlanta, Georgia.

Six primary field sites and six enhancement sites were identified and made ready for use. Approximately 1000 hourly measurements were taken for the parameters and species listed in Tables 1 and 2. The resulting data set contains more than 300,000 hourly measurements of the 60 parameters addressed. In addition, approximately 20,000 measurements resulted from analyzing 375 canister samples for hydrocarbon species, and approximately 750 measurements resulted from analyzing the 250 cartridge samples for formaldehyde.

The hourly measurements from the six primary sites and the periodic carbonyl measurements are available for assessment and interpretation on a 3.5-in disk. The measurements resulting from the analysis of the 375 canister samples also are available on a separate disk. These disks, along with the full data report, may be obtained from EPA. The back of this Project Summary provides the necessary ordering information.

### Background and Rationale

The high number of  $O_3$  nonattainment areas across the country indicates a need to develop new, improved strategies for  $O_3$  control. Extensive reviews of past and current  $O_3$  control strategies, generated over the last several years in conjunction



over the last several years in conjunction with agencywide planning, have identified promising directions for action. For example, more complete nonmethane organic compound (NMOC) emissions inventories would allow EPA and other agencies to predict and address appropriate reductions for bringing nonattainment areas into compliance with the O<sub>3</sub> standard.

The control strategies for photochemical O<sub>3</sub> that have been implemented in recent years involve reducing NMOC compounds and/or NO<sub>x</sub>. The Empirical Kinetic Modeling Approach (EKMA), as well as airshed models, often have been used to determine necessary nonmethane organic compounds (NMOC) or oxides of nitrogen (NO<sub>x</sub>) controls. These models relate NMOC and NO<sub>x</sub> to maximum O<sub>3</sub> concentrations typically observed during afternoons at sites located downwind of an urban area. They predict the NMOC and NO<sub>x</sub> control requirements needed to attain NAAQS for O<sub>3</sub>.

Although measurement requirements are somewhat different for the EKMA and airshed models, both require source-emissions data and ambient-air data for NMOC and NO<sub>x</sub>. With this information, states and local control agencies can develop control approaches aimed at bringing their nonattainment areas into compliance with the O<sub>3</sub> NAAQS. Measurements of O<sub>3</sub> precursor concentrations will be useful in carrying out the necessary modeling exercises. Interpretations of NMOC species data collected at various times of day will help determine not only whether certain control measures have been implemented but also whether they are effective.

Within the next two to three years, EPA and other agencies will pursue O<sub>3</sub> control strategies that require more monitoring data. Unfortunately, historical data bases of concurrent NMOC species and NO<sub>x</sub> are limited, and they do not provide sufficient information for design and tracking functions. They provide little information, for example, that can be used to design the ambient monitoring networks and special monitoring projects needed to support future, intensified O<sub>3</sub> control strategies. Nor do they allow for tracking the effectiveness of ongoing control programs. As a result of recent developments and improvements in NMOC and NMOC-speciation methodology, however, it is possible to obtain sufficiently accurate and precise monitoring data for these O<sub>3</sub> precursors.

The above discussion describes part of the context for the present study, which was conducted to accomplish three goals:

1. To evaluate new measurement technology.

2. To demonstrate its feasibility and applicability to emerging needs.

3. To provide the information on the spatial/temporal variability of NMOC, its component species, and NO<sub>x</sub> to develop the needed monitoring guidance.

## Objectives

The primary objective of this project was to develop a comprehensive, quality-assured data base for NMOC species, NO<sub>x</sub>, O<sub>3</sub>, carbonyls, and meteorological variables with high-time resolution, at sites distributed across the Atlanta urban area. This data base may be used to address a number of questions relating to:

- spatial and temporal variations in the concentrations of O<sub>3</sub> precursors
- specific pollutants (for example, toxic air pollutants) and pollutant ratios
- the adequacy of precursor data requirements for air-quality models
- the accuracy of emissions data used in air-quality models.

Examples of specific questions that may be addressed with the aid of the Atlanta data base are:

1. Spatial variability—
  - a. How do pollutant concentrations and precursor ratios vary from site to site across an urban area?
  - b. To what extent and under what conditions can pollutant concentrations and precursor ratios measured at one site be extrapolated to other parts of the urban area?
  - c. How do meteorological conditions influence spatial pollutant variability?
2. Temporal variability—
  - a. How do pollutant concentrations and precursor ratios vary during the day?
  - b. How representative of short-term concentrations are time integrated samples?
  - c. Does temporal variability vary from site to site?
  - d. How do meteorological conditions influence temporal variability?
3. Nature and distribution of emissions sources—
  - a. What sources contribute to urban air-pollutant concentrations?
  - b. Do ambient measurements of NMOC species substantiate existing emissions inventories?
  - c. What is the relative importance of anthropogenic and biogenic emissions?
4. Photochemical models
  - a. How well do photochemical models predict O<sub>3</sub> levels downwind of the urban area?

b. How do spatial and temporal variations in precursor ratios and levels influence model predictions?

c. Are the default reactivity assignments used in models adequate?

## Methodology

Air monitoring was conducted during the summer of 1990 for O<sub>3</sub> and its precursors at 12 sites spatially distributed across the Atlanta metropolitan area. Hourly measurements of O<sub>3</sub>, carbon monoxide (CO), NO<sub>x</sub>, meteorological parameters, total NMOC, and NMOC species were collected on a continuous basis using automated sampling and analysis techniques. Supplementary integrated measurements for total NMOC and NMOC species (canisters) and carbonyls (cartridges) were made periodically on predetermined schedules throughout the study. A schematic diagram of the field station is shown in Figure 1.

In addition, several ancillary experiments were conducted, including:

- operation of a long-path analyzer at Site 2
- operation of continuous PM<sub>10</sub> monitors at Sites 2 and 3
- limited operation of a continuous formaldehyde analyzer at Site 6
- collection of integrated samples for volatile organic C<sup>14</sup> determinations for estimating the contribution of biogenic sources
- collection of several samples for source signature determinations

Monitoring was conducted primarily at six fixed-sampling locations distributed across the Atlanta urban area. These sites were selected to satisfy the following criteria:

1. Must provide broad spatial coverage of the Atlanta area not dominated by local sources.
2. Three sites must be located along the northwest direction of prevailing winds for Atlanta in the O<sub>3</sub> season.
3. Three sites must be located along the southwest direction perpendicular to prevailing winds.
4. One site must be upwind to supply background measurements.
5. One site must be located downwind in an expected high-O<sub>3</sub> area.

The locations of the six primary sites are shown in Figure 2. These sites are identified by the numbers 1-6 and appear as circles. To increase the spatial resolution of the NMOC species portion of the data set, additional samples were collected for NMOC analysis during certain periods. These additional samples were collected

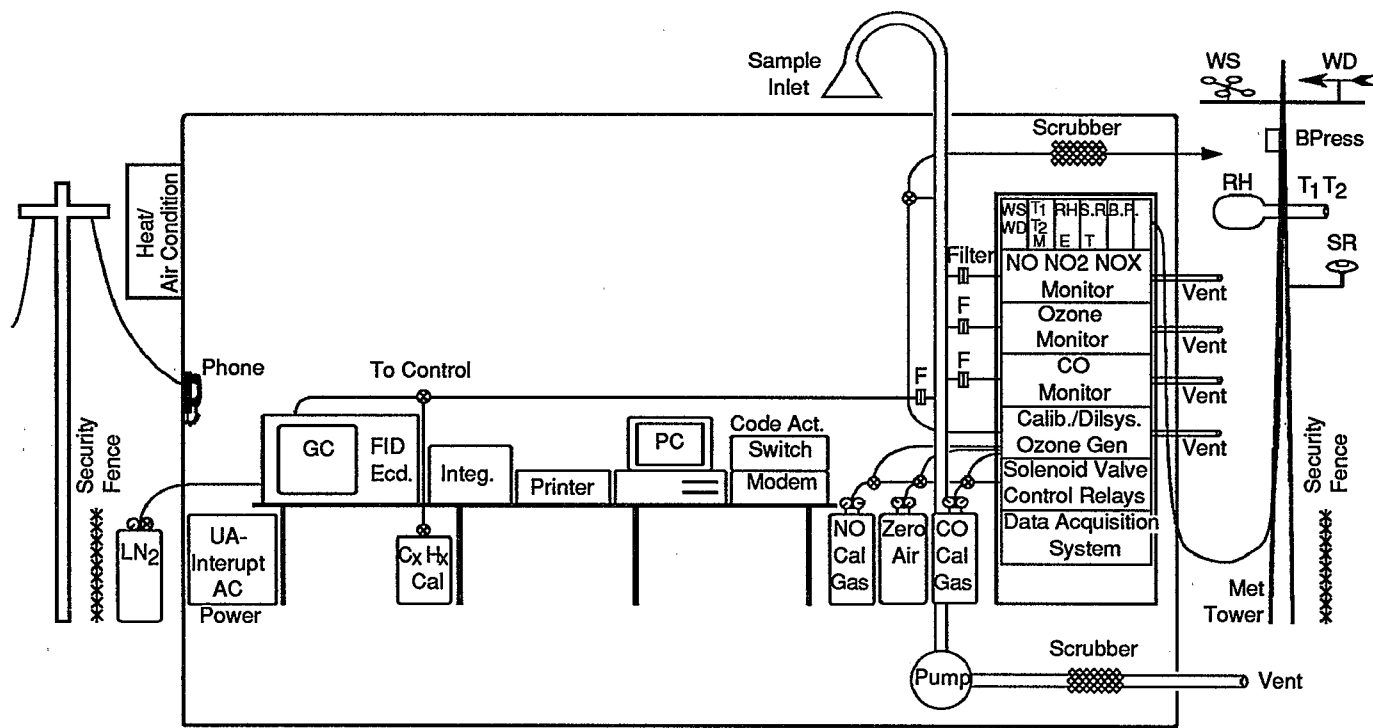


Figure 1. Station layout.

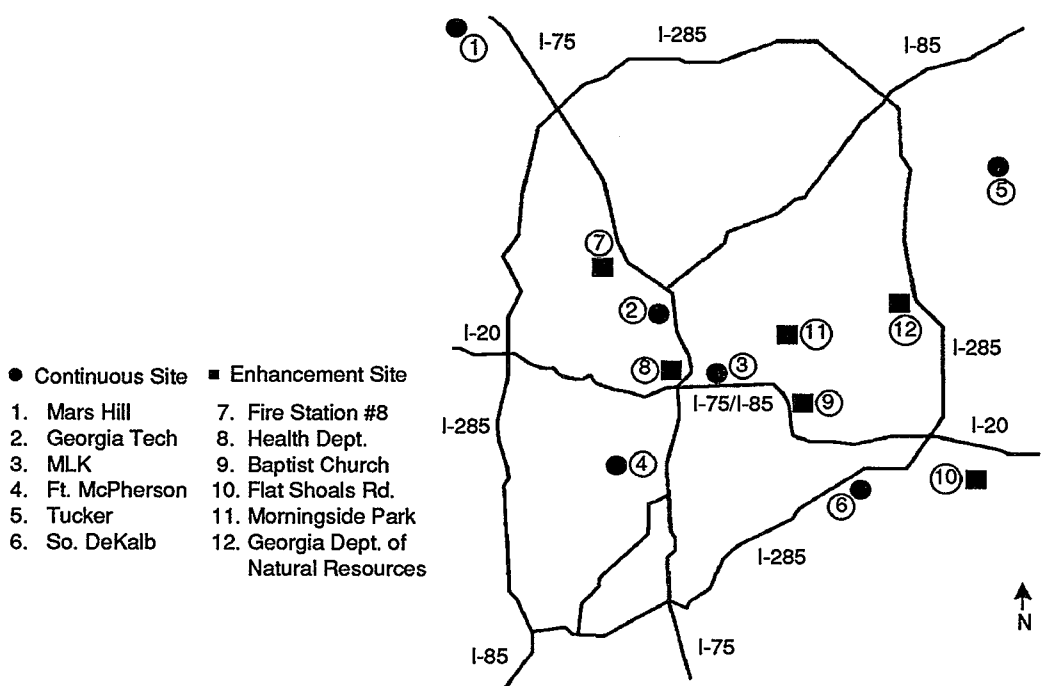


Figure 2. Location of sites in the Atlanta, Georgia, Metropolitan Area.

The names and general characteristics of the six main sites are listed below:

1. Mars Hill is located approximately 35 km NW of the Atlanta beltway (I-285). The site is in a rural, residential neighborhood with no industry and is in the predominantly upwind direction from the Atlanta metropolitan area during the O<sub>3</sub> season. Mars Hill serves as a background site to measure concentrations of pollutants transported into the Atlanta area.

2. The Georgia Institute of Technology is located in downtown Atlanta. There are several industries located from 4-5 km NE, NW, and W of the site. The site is representative of the downtown area and is located approximately 4 km NW of the Martin Luther King (MLK) site, identified below.

3. MLK is located on the fringe of downtown Atlanta. The site is located in an area with several localized sources, including a reclamation operation, scrap-metal operation, two small incinerators, and a Metro Atlanta Rapid Transit (MARTA) station. The site also is affected by the I-75/85 downtown connector. MLK is approximately 4 km SE of the Georgia Tech site and 11 km NW of the Dekalb Junior College site, identified below. MLK has been used in the past to collect NMOC and NO/NO<sub>x</sub> samples to evaluate the EKMA model.

4. Fort McPherson is located on a military base and is approximately 8 km SW of MLK. This site is approximately 1 km north of Highway 166 and 2 km west of the I-75/85 and 166 interchange. The site lies in the SW direction and is perpendicular to prevailing winds from downtown Atlanta during the O<sub>3</sub> season.

5. Tucker is located on the grounds of an inactive hospital, approximately 22 km NE of the MLK site and 23 km NNE of the Dekalb Junior College site. The site is located in a residential area affected by I-285, approximately 2 km west, and by the I-285/I-85 interchange, approximately 5 km NW. In addition, a tank farm is located 7 km NNW, and a manufacturing plant is 7 km NW of the site.

6. The Dekalb Junior College site is located on the campus approximately 1 km SE of I-285. The site is in a predominantly residential and commercial urban fringe area, and it is located 12 km SE of downtown Atlanta in the prevailing wind direction during the O<sub>3</sub> season. The site traditionally measures the highest O<sub>3</sub> levels and, of all the sites in the existing Atlanta O<sub>3</sub> monitoring network, most often exceeds NAAQS. The site was used to collect NMOC samples for the Atlanta EKMA study.

## Target Chemicals

The target pollutants and meteorological parameters for continuous monitoring at the six field sites are listed in Table 1. The hydrocarbons, halocarbons, and carbonyls initially selected for measurement at the six sites are shown in Table 2. To aid comparisons between target chemicals and those actually reported, Table 3 lists the resolved organic species.

## Continuous Monitoring Instruments

Automated analyzers approved by EPA under the Ambient Air Monitoring Reference and Equivalent Methods Regulations (40 CFR Part 53) were used for continuous measurements of O<sub>3</sub>, CO, and NO<sub>x</sub>. The instruments were calibrated in accordance with approved calibration procedures using dynamically generated gas mixtures.

## Automated Gas Chromatography

An automated gas chromatographic system was used to obtain the hourly NMOC species measurements. This system was developed and manufactured in Bilthoven, The Netherlands, and is marketed in the United States by Chrompack, Inc., of Raritan, New Jersey. It is equipped with a three-phase adsorbent trap to preconcentrate the individual species. The trap materials were Carbotrap C, Carbotrap, and Carbosieve S-III. The trap was held at -35°C during the collection of a 30-min sample at a flow rate of approximately 20 cc/min.

The collected species were thermally desorbed from the preconcentration trap at 250 °C. A second trap was used to refocus the desorbed compounds. This trap consisted of deactivated fused silica, 30-cm by 0.53-mm ID, filled with 3-in glass-wool plugs. The trap was held at -186 °C during sample transfer from the primary trap and then was heated rapidly to 200 °C to direct components onto the analytical column. A CP-Sil-5 50-m by 0.32-mm ID fused silica column with 5-μ film thickness was used to resolve the species, which ranged in carbon number from C<sub>2</sub> through C<sub>10</sub>. The critical GC parameter settings were as follows:

1. Oven initial temp. = -20 °C
2. Oven final temp. = 210 °C
3. Oven ramp temp. = 8 °C/min
4. Oven initial time = 3 min
5. Oven final time = 10 min
6. Detector temperature = 300 °C
7. Injector temperature = 200 °C

The resolved individual species were detected using an FID and an ECD con-

nected in parallel to the analytical column. From the resulting chromatograms, 54 hydrocarbon species and total NMOC, plus five halocarbon species, were identified and named on the basis of their retention-time characteristics. Based on an NIST-certified, benzene-standard response, a per-carbon response factor was determined for the FID detector for the hydrocarbon species. The targeted hydrocarbon species were quantified using the per-carbon response factor and were reported in units of ppb C. The unidentified hydrocarbon species were quantified using the same per-carbon factor. An estimate of the total NMOC was determined by summing the identified and unknown hydrocarbon species. Individual compound response factors for each of the halocarbon species were determined for the ECD based on responses from a known mixture of the species. The targeted halocarbon species were reported as ppb compound.

## Canister Samples

Approximately 375 whole-air canister samples were collected throughout the study and analyzed for total NMOC and NMOC species. These samples were collected for the following purposes:

1. To compare measurements of the automated-GC system with measurements obtained with established GC procedures.

2. To confirm the qualitative identification of selected species and to identify persistent unknown compounds.

3. To enhance the spatial representativeness of the six primary sites by collecting canister samples at six additional sites.

4. To establish source signatures at known significant emission sources.

Approximately 185 routine samples were collected in Summa polished canisters for comparison with established GC procedures to confirm compound identifications and to evaluate the adequacy of the automated-GC system. An automated canister collection system (Anderson\*, Model 87-100) was used to collect the samples. The collection system filled the evacuated canister (initial pressure less than 0.1 torr) with sample air at a flow rate of 400 cm<sup>3</sup>/min<sup>-1</sup>, resulting in a final pressure of approximately 15 psig. Samples were collected every other day at every primary site for 30-min periods concurrent with the sampling interval of the automated GC system. Sample collection was rotated through the following periods: 8:00 a.m., 10:00 a.m., 12:00 noon, 3:00 p.m., 6:00 p.m., and 12:00 midnight.

\*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

**Table 1. Continuous Measurements Performed During the Atlanta Field Study**

Target Pollutants	Meteorological Measurements
O <sub>3</sub>	Wind speed
NO	Wind direction Sigma theta
NO <sub>x</sub>	Temperature
CO	Relative humidity Solar radiation

**Table 2. Target Species Selected for Measurement by the Automated Gas Chromatograph During the Atlanta Study****Hydrocarbons**

1. ethylene	19. cis-2-pentene	38. 3-methylhexane
2. acetylene	20. 2-methyl-2-butene	39. 2,2,4-trimethylpentane
3. ethane	21. 2,2-dimethylbutane	40. n-heptane
4. propene	22. cyclopentene	41. methylcyclohexane
5. propane	23. 4-methyl-1-pentene	42. 2,3,4-trimethylpentane
6. isobutane	24. cyclopentane	43. toluene
7. 1-butene	25. 2,3-dimethylbutane	44. 2-methylheptane
8. n-butane	26. 2-methylpentane	45. 3-methylheptane
9. trans-2-butene	27. 3-methylpentane	46. n-octane
10. cis-2-butene	28. 2-methyl-1-pentene	47. ethylbenzene
11. 3-methyl-1-butene	29. n-hexane	48. m/p-xylene
12. isopentane	30. trans-2-hexene	49. styrene
13. 1-pentene	31. cis-2-hexene	50. o-xylene
14. n-pentane	32. methylcyclopentane	51. n-nonane
15. a-pinene	33. 2,4-dimethylpentane	52. isopropylbenzene
16. b-pinene	34. benzene	53. n-propylbenzene
17. isoprene	35. cyclohexane	54. 1,3,5-trimethylbenzene
18. trans-2-pentene	36. 2-methylhexane	55. 1,2,4-trimethylbenzene
	37. 2,3-dimethylpentane	56. Total NMOC

**Halocarbons**

1. chloroform
2. 1,1,1-trichloromethane
3. carbon tetrachloride
4. trichloroethylene
5. perchloroethylene

**Carbonyls**

1. formaldehyde
2. acetaldehyde
3. acetone

Table 3. Resolved Organic Species<sup>a</sup>

Hydrocarbons		
1. ethylene	19. 2,2-dimethylbutane	38. 2,2,4-trimethylpentane
2. acetylene	20. cyclopentene &	39. n-heptane
3. ethane	21. 4-methyl-1-pentene	40. methylcyclohexane
4. propene	22. cyclopentane &	41. 2,3,4-trimethylpentane
5. propane	23. 2,3-dimethylbutane	42. toluene &
6. isobutane	24. 2-methylpentane	43. 2-methylheptane
7. 1-butene	25. 3-methylpentane	44. 3-methylheptane
8. n-butane	26. 2-methyl-1-pentene	45. n-octane
9. trans-2-butene	27. n-hexane	46. ethylbenzene
10. cis-2-butene	28. trans-2-hexene	47. m/p-xylene
11. 3-methyl-1-butene	29. cis-2-hexene	48. styrene
12. isopentane	30. methylcyclopentane &	49. o-xylene &
13. 1-pentene	31. 2,4-dimethylpentane	50. n-nonane
14. n-pentane	32. benzene	51. isopropylbenzene
15. isoprene	33. cyclohexane &	52. n-propylbenzene
16. trans-2-pentene	34. 2-methylhexane	53. 1,3,5-trimethylbenzene
17. cis-2-pentene	35. 2,3-dimethylpentane	54. 1,2,4-trimethylbenzene
18. 2-methyl-2-butene	36. 3-methylhexane	55. Total NMOC

Halocarbons	
1. chloroform	
2. 1,1,1-trichloromethane	
3. carbon tetrachloride	
4. trichloroethylene	
5. perchloroethylene	

<sup>a</sup>Individual co-eluted species are indented following each ampersand.

A set of 72 additional canister samples was collected to enhance the spatial coverage of the six primary sites. Two three-day experiments were conducted at the six sites identified in Figure 2 as enhancement sites. These sites were selected to fill in the grid of primary sites and to provide spatial information at scales of less than 10 km to more than 50 km. In each three-day experiment two samples were collected per day, one at 9:00 a.m. and one at 3:00 p.m., for 30-min periods concurrent with the 30-min sampling time of the automated-GC systems operated at the six primary sites. Portable collection systems consisting of a mass-flow controller and canister were used at the six enhancement sites. The collection system filled the evacuated canisters (initial pressure less than 0.1 torr) at a flow rate of 120 cm<sup>3</sup>/min<sup>-1</sup>, resulting in a final pressure of 500-550 torr.

Another set of approximately 120 canister samples was collected at sites representing mobile sources, which are the predominant component of Atlanta's nonmethane hydrocarbon emission inven-

tory. The sites included a roadway, a parking lot, and the Hatsfield International Airport. These samples were collected with a portable 12-volt, battery-operated pump (Metal Bellows, Model 158; Sharonville, Massachusetts) and a throttle valve to control flow rate at approximately 1.2 L/min<sup>-1</sup>.

### Carbonyl Sampling

During the study, approximately 250 samples were collected during the study using silica gel cartridges coated with 2,4 dinitrophenylhydrazine (DNPH). They were analyzed for formaldehyde, acetaldehyde, and acetone using Method TO-11. All of the cartridges were shipped directly to RTP for analysis by AREAL personnel using high-pressure liquid chromatography (HPLC). Samples were collected at every site every other weekday at alternating periods of 6:00 a.m. to 12:00 noon (six hr); 12:00 noon to 6:00 p.m. (6 hr); and 6:00 p.m. to 6:00 a.m. (12 hr) each weekend at every site on alternating Saturdays and Sundays.

An automated analyzer that was capable of making continuous, real-time mea-

surements of formaldehyde was operated for a two-week period (August 8 to August 15) at the Dekalb site.

### Ancillary Experiments

In addition to the spatial and temporal variability experiment, several ancillary experiments were conducted. One involved operating a differential optical absorption spectrometer (DOAS) at the Georgia Tech site. The DOAS is a long-path analyzer manufactured by OPSIS, Inc., of Lund, Sweden. Its operation is based on the remote spectroscopic analysis of visible and ultraviolet light.

Transmitters located on the Southern Bell Building, the Coca-Cola Headquarters Building, and a near-by campus dormitory beamed light to three receivers located at the Georgia Tech site, where the light was spectroscopically analyzed for O<sub>3</sub> and several other species, including benzene and toluene. The primary purpose for operating the DOAS during the study was to compare long-path measurements with fixed-site point measurements and to determine the feasibility of

long-path measurements for addressing future regulatory and research monitoring needs.

Additional ancillary experiments included limited vertical-profile measurements of winds, temperature, moisture, and O<sub>3</sub>; limited acid aerosol measurements at selected sites; collecting samples for volatile organic C<sup>14</sup> determinations to estimate the contribution of biogenic sources; limited operation of a continuous formaldehyde analyzer at one site; and operation of continuous PM<sub>10</sub> monitors at two sites.

### **Data Acquisition and Processing**

The basic components of the data-acquisition system (DAS) included hardware and software at the field monitoring stations, the Operations Center, and the remote data-monitoring centers. DAS hardware and software were located in the shelters installed at each of the six field sites.

The Odessa Data Logger was the data-acquisition and initial data processing device for all the nonchromatographic systems. Data were stored as hourly averages and transmitted by an external modem that was attached to the data logger. Via modem, the central computer polled the data logger at each site on a daily basis. To track instrument operation, each site also was polled from a computer at RTP. The data were stored on removable

cartridges installed in the data logger. These cartridges were used to fill in areas where data were missing as a result of communication problems.

The on-site personal computer (PC) was responsible for data acquisition, initial data processing, data display, and data transmission for the automated gas chromatographs. The data from the chromatographs (raw signal files and result files) were acquired by the PC and stored on the hard drive. The data files were copied to floppy disks each day, with backups. One copy was carried to the Operations Center for archival, and one copy was stored at the field site.

### **Data Quality Objectives**

Data quality objectives (DQOs) are required by the U.S. EPA Quality Assurance Management Staff for all data collection activities. DQOs are statements of the quality of data needed to support specific program objectives. DQOs are defined in terms of the study objectives, rather than equipment or analysis method characteristics. Quality assurance objectives for the measurement data are also required, however, and are stated in the Quality Assurance Plan for this study.

The primary goal of this monitoring program was to develop a comprehensive data base with which to address a number of questions concerning spatial and temporal variations in the ambient con-

centrations of a variety of pollutants, including O<sub>3</sub> and O<sub>3</sub> precursors. Specifically, the objective was to study these spatial and temporal variations during one or more episodes of high ambient O<sub>3</sub> levels.

Assessing temporal variations statistically requires measurements with high time resolution for the complete period of a high-O<sub>3</sub> episode (i.e., one or more days). For most of the pollutants in this study, the time resolution was one hour.

Assessing spatial variations statistically requires measurements at a variety of locations that adequately characterize the entire urban area. In addition, to account for temporal variations when performing the spatial analysis, the measurements must be made simultaneously at all sampling locations. For most of the pollutants in this study, simultaneous measurements were made at six fixed locations across the Atlanta area. This basic spatial coverage for hydrocarbon species was enhanced during certain periods by sampling at six additional sites.

To meet the study objectives described above, the program DQO specified that ambient-air samples must be collected and analyzed with appropriate techniques to ensure continuous detection at six sampling locations of a target list of pollutants, including O<sub>3</sub> and O<sub>3</sub> precursors, for every sampling period covering at least one high-O<sub>3</sub> episode.

*The EPA authors, **Larry J. Purdue** (also the EPA Project Officer), **James A. Reagan**, **William A. Lonneman**, **Thomas C. Lawless**, and **Ronald J. Drago** are with the Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC 27711. **George M. Zalaquet** is with Mantech Environmental Technology, Research Triangle Park, NC 27711, and **Michael W. Holdren**, **Deborah L. Smith**, **Alan D. Pate**, **Bruce E. Buxton**, and **Chester W. Spicer** are with Battelle Memorial Institute, Columbus, OH 43201.*

*The complete report, entitled "Atlanta Ozone Precursor Monitoring Study Data Report," (Order No. PB92-220 656/AS; Cost: \$26.00; subject to change) will be available from:*

*National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650*

*For a copy of the report and the disks containing the collected data, contact **Larry J. Purdue** at:*

*Atmospheric Research and Exposure Assessment Laboratory  
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Research Triangle Park, NC 27711*

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