III. Our Research: Regional Tropospheric Chemistry

A. The Context of Our Research: What and Why?

During the past ten years, the Aeronomy Laboratory has become increasingly involved in understanding the processes that shape regional air quality. This research has focused on the processes that control the formation of ozone in the lower troposphere. This focus not only involves answering challenging scientific questions, but also embraces issues of great practical importance. Elevated and potentially harmful levels of ozone are found in many areas of the United States during summer. In 1991, the National Research Council Committee on Tropospheric Ozone Formation and Measurement published the report "*Rethinking the Ozone Problem in Regional and Urban Air Pollution*" (National Research Council, 1991). The study found summertime ozone pollution in the United States was a major and continuing problem, and that despite intensive efforts, the attempts that had been made to manage ozone air quality in the United States "largely have failed".

Ozone is a secondary pollutant, i.e., it is not emitted directly. Rather, it is produced by photochemical reactions from ozone precursors: volatile organic compounds (VOCs), carbon monoxide (CO), and nitrogen oxides ($NO_x = NO + NO_2$). Therefore, most ozone management strategies are aimed at reducing anthropogenic VOC emissions in areas unable to meet the ozone standard (i.e., non-attainment areas). However, ozone has an atmospheric lifetime much longer than many of the compounds that control its formation. Hence, once formed it can be transported over much wider regions. Consequently, understanding the distribution of ozone in the atmosphere requires understanding the chemical process responsible for its formation and destruction and the dynamics responsible for its redistribution.

The U.S. air quality research concerning ozone pollution has been centered in urban areas, with human health being the issue. However, ozone damage to crops and forests represents a major economic burden on the United States. As a result, the Aeronomy Laboratory has built a unique focus on understanding the rural (i.e., non-urban) and regional aspects of ozone pollution. With this emphasis and with our analytical techniques developed for the non-urban atmosphere, our early research in the 1980s led to a very important finding. Namely, it was discovered that natural nonmethane hydrocarbons, such as isoprene, play a critical role in the formation of ozone over the forested regions of the United States. This finding, augmented by other studies, was a cornerstone of the above-noted Academy report and was described in the previous Aeronomy Laboratory review in 1992.

Since then, the Aeronomy Laboratory has built upon that research of the late 1980s, has expanded the foci to address new scientific issues uncovered, and has added to the scientific understanding of regional tropospheric chemistry in ways that make the prediction and assessment of air quality issues more effective. We continue our approach of integrated laboratory, field, and modeling studies.

B. Some Illustrative Recent Achievements: What? And So What?

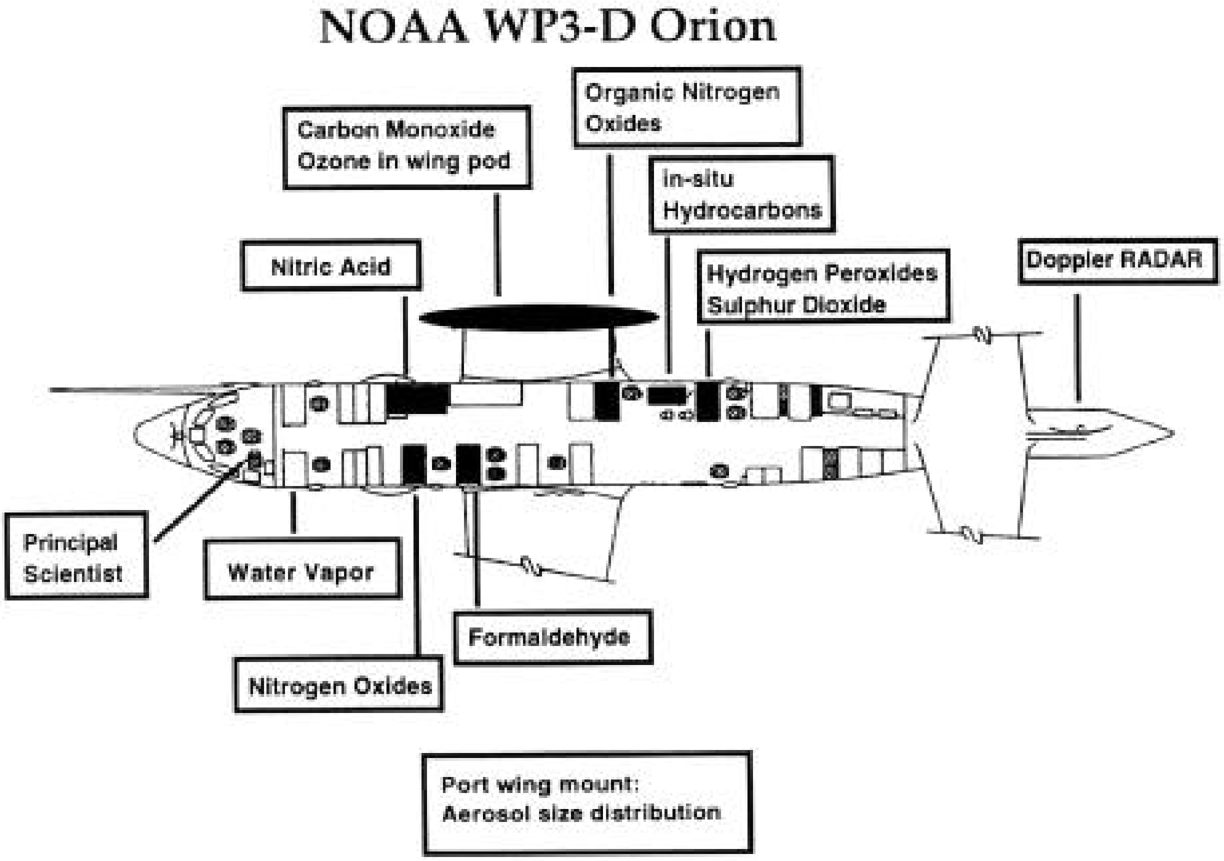
We give here *examples* of Aeronomy Laboratory research endeavors that address regional tropospheric chemistry. In each of the summaries, we explain the rationale, what was accomplished, and the significance of the results, as well as note a few of the key scientific papers that resulted. The complete set of findings is detailed in the bibliography in Appendix B, which groups together the Aeronomy Laboratory publications that address regional tropospheric chemistry. At the conclusion of the present Section, we outline the Aeronomy Laboratory research goals for the immediate future and the plans that are in place for attaining these goals.

1. Setting the Stage: Instrument and Platform Development

• The development of aircraft capabilities

Airborne measurements are needed to investigate regional air-quality problems. Most of the early air quality measurements made by the Aeronomy Laboratory were carried out at ground sites. However, to understand the processes that shape the regionality of air quality, a comprehensive set of measurements detailing the chemical and meteorological conditions for ozone photochemistry must be made using aircraft:

> Aircraft measurements help to determine if ozone pollution is a regional or a local problem. Even though ozone can be elevated over large areas, for example during stagnant high pressure periods, a question remains concerning how much of this ozone is produced locally and how much is produced remotely and then transported into the area.
> Aircraft measurements can be used to determine if and how ozone observed in a particular location can be attributed to a particular ozone-precursor source located among a complex matrix of sources. Using aircraft, the synergism associated with the interaction of power plants plumes, urban plumes, and the regional background can be investigated under a variety of conditions and in various combinations.
> Aircraft can be used to investigate exchange of air between the planetary boundary layer and the lower free troposphere. Detrainment of highly polluted boundary layer air



will reduce the local impact by removing precursors for ozone production from the local photochemistry. However, the negative side of this process is the redistribution of the burden of anthropogenic pollution over a larger area and to locales far removed from the pollution sources. Moreover, since the efficiency of ozone production depends in a non-linear fashion on the concentration of ozone precursors, these mixing processes may serve to enhance the total ozone formation potential of the atmosphere over a large region.

\> Aircraft can be used to investigate the influence of the diurnal variation of the mixed layer. During the night, the decoupling of the atmosphere from the frictional resistance to horizontal transport that occurs with the formation of the nocturnal inversion may provide a significant but yet unappreciated and unquantified mechanism for regional transport and dispersion of local pollution.

The Aeronomy Laboratory has built up a suite of airborne chemical measurements. The Laboratory has instrumented NOAA’s Lockheed Orion WP-3D with a comprehensive suite of instruments to measure ozone and ozone precursors in the troposphere. The research has been fashioned to answer the scientific questions concerning the factors that determine regional air quality and the production of distribution of tropospheric ozone. This has provided NOAA with a research platform capable of investigating critical problems associated with ozone relating to regional air quality, global tropospheric chemistry, and the atmospheric chemistry of global climate change. Using this platform, aircraft studies have been made of the physical and chemical properties of the atmosphere as part of the 1994/1995 Nashville/Middle Tennessee Ozone Studies of the Southern Oxidants Study (SOS) and the North Atlantic Regional Experiments of 1996 and 1997.

Important results have already been obtained. In the SOS flights, it was found that the rapidly expanding areas of the Southern United States are poised for significant regional air quality problems associated with elevated ozone levels and these levels appear to be directly attributable to human-made emission of ozone precursors. The influence of urban-area and large point-source emissions on regional levels of ozone and ozone precursors are documented from our measurements onboard the NOAA WP-3D during the 1994/1995 Studies. A sample of some of these results are described below. This information is used to understand the interaction between regional and urban air quality and provide policy makers with an improved scientific understanding of the processes that shape the regional and global atmosphere.

Hübler, G., R. Alvarez, P. Daum, R. Dennis, N. Gillani, L. Kleinman, W. Luke, J. Meagher, D. Rider, M. Trainer, and R. Valente, An overview of the airborne activities during the SOS 1995 Nashville/Middle Tennessee ozone study, *J. Geophys. Res., 103,* in press, 1998.

• Intercomparison and evaluation of reactive nitrogen (NO_y) measurement techniques

The importance of determining the reliability of NO_y measurements. During the 1980’s, the Aeronomy Laboratory developed a method to measure the sum of the reactive nitrogen oxides (NO_y = NO + NO_2 + PAN + HNO_3 + ...) in the atmosphere. The measurements have become an important tool that the atmospheric chemistry community is using to determine the potential of sources that emit the nitrogen oxides to influence atmospheric chemistry on local, regional and global scales. Our experience has taught us that whenever instruments are used in environments substantially different from those where they have been test, validated, and successfully operated, there is concern that the results may be compromised by factors unique to the new environment. For example, gold/CO and molybdenum catalytic reduction NO_y

detectors have been used successfully for many years in the rural and remote atmospheres. However, when these instruments are operated in an urban environment, particularly those with high levels of high molecular weight VOCs, the instrument testing and validation must be revisited.

A recent intercomparison of these measurements. A comprehensive intercomparison of ground-based NO_y measurement systems employing both gold/CO and molybdenum catalytic reduction systems was carried out in a heavily polluted suburban location that is downwind of industrialized areas in metropolitan Nashville, TN. These tests indicated good agreement between the methods and among the various groups making the measurements.

Conclusions from this intercomparison. These measurements indicated that there are no important artifacts or interferences in the measurements of NO_y made in urban and suburban locations in the southern United States and that the techniques commonly used for these measurements appear to be robust and reliable when operated under these conditions.

Williams, E.J., K. Baumann, J.M. Roberts, S.B. Bertman, R.B. Norton, F.C. Fehsenfeld, S.R. Springston, L.J. Nunnermacker, L. Newman, K. Olszyna, J. Meagher, B. Hartsell, E. Edgerton, J.R. Pearson, and M.O. Rodgers, Intercomparison of ground-based NO_y measurement techniques, *J. Geophys. Res., 103,* in press, 1998.

- **Intercomparison and evaluation of ammonia (NH_3) measurement techniques**

The importance of determining the reliability of NH_3 measurements. Ammonia (NH_3) plays a key role in the formation of fine particles in the atmosphere, in the formation of regional haze, and in the naturalization of acidic aerosols and acid precipitation. Ammonia measurements can provide insights into gas-to-particle conversion and the impact that this may have on air quality, atmospheric visibility, and human health.

The Aeronomy Laboratory has contributed to the evaluation of ammonia measurement techniques. The Aeronomy Laboratory played host to an intercomparison of ammonia measurements (see reference). In this intercomparison, the citric acid denuder tube developed at the Aeronomy Laboratory and a laser-induced fluorescence method developed at Georgia Tech University were shown to be reliable measurements of ammonia in the atmosphere over a wide range of concentration under a variety of meteorological conditions. However, because of its simplicity, the citric acid method has become the accepted technique of choice for routine NH_3 measurements in the troposphere.

What's next. Because of the increased interest in ammonia measurements and the need for sensitive, fast-response measurement methods, new ammonia measurement techniques are emerging. One of the most promising new techniques is a chemical ionization mass spectrometry (CIMS) method that is being developed in the Aeronomy Laboratory. For this reason, the Aeronomy Laboratory will hold an informal intercomparison of the CIMS technique being developed here, along with the citric acid techniques as well as another new method that is being developed in another laboratory.

Williams, E.J., S.T. Sandholm, J.D. Bradshaw, J.S. Schendel, A.O. Langford, P.K. Quinn, P.J. LeBel, S.A. Vay, P.D. Roberts, R.B. Norton, B.A. Watkins, M.P. Buhr, D.D. Parrish, J.G. Calvert, and F.C. Fehsenfeld, An intercomparison of five ammonia measurement techniques, *J. Geophys. Res., 97,* 11591-11611, 1992.

- **Ion chemistry: A tool for detection of nitric acid (HNO_3)**

Ion chemistry provides a means to specifically detect trace compounds in the atmosphere. Chemical ionization mass spectrometry is a very sensitive and selective technique for detection of trace gases for both laboratory and field measurements. However, a detailed knowledge of the ion chemistry is needed to confidently apply chemical ionization mass spectrometry (CIMS) to the measurement of atmospheric trace gases such as nitric acid.

Ion chemistry unraveled. Therefore, the kinetics and products of reactions of various ions with nitric acid and a host of other atmospheric gases were measured. The ion-molecule chemistry was studied with a flowing afterglow reactor coupled to a quadrupole mass spectrometer. The principal findings was that SiF^-_5 could be produced in copious quantities, that these ions bind strongly to nitric acid, and that the ions are unreactive to all other gaseous species present in the atmosphere, hence have the desired selectivity. Therefore, SiF^-_5 represented an excellent potential choice as a specific CIMS detector for nitric acid.

Chemistry successfully tested in the field. This work has resulted in the development of the first field-based nitric acid detector with fast time response and excellent sensitivity (see following section).

Huey, L.G., E.R. Lovejoy, Reactions of SiF^-_5 with atmospheric trace gases: Ion chemistry for chemical ionization detection of HNO_3 in the troposphere, *J. Mass Spec. Ion. Proc*. 155, 133-140, 1996.

- **Development of chemical ionization mass spectrometry (CIMS) to measure nitric acid and other trace compounds**

Importance of nitric acid measurement. One of the most important trace species present in the atmosphere is nitric acid. The formation of nitric acid from NO_x terminates the photochemical production of ozone, and once formed nitric acid becomes a major component of acid deposition. Hence, for understanding the process for the production of ozone and acid deposition, the measurement of nitric acid is critical. Yet, the analytical methods presently available are totally inadequate for its measurement, particularly from airborne platforms.

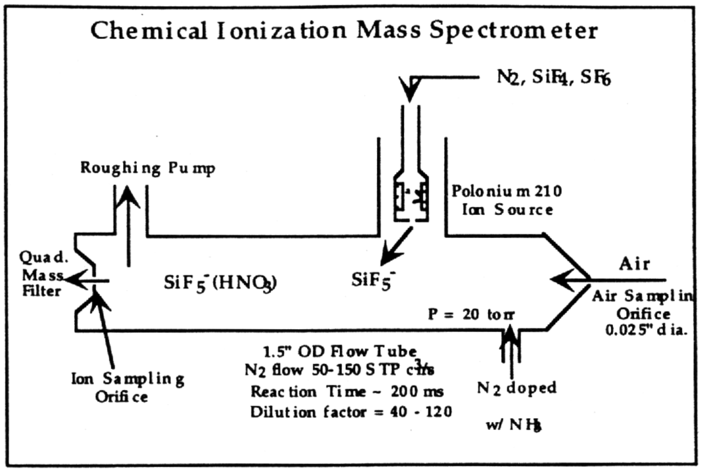
Chemical ionization detector developed. Using the Aeronomy Laboratory's extensive knowledge in ion chemistry and chemical kinetics, the Laboratory developed an ultra-sensitive, (part-per-trillion) fast response (one second or less), continuous technique to measure nitric acid. The method employs chemical ionization (CI) and mass spectrometry (MS) to specifically detect nitric acid present in the atmosphere. As the figure on the next page shows, the chemical ionization mass spectrometry (CIMS) system utilizes a high pressure flowing afterglow technique operating with diluted sampled air that features an isolated ion source and chemical equilibrium quantification using SiF^-_5 as a reagent ion (see preceding section). The system operates continuously and has a detection limit of approximately 10 pptv for a one-second integration.

System successfully measured nitric acid. The system has been successfully tested in a ground-based instrument intercomparison and flown successfully on an aircraft. A similar CI strategy can also be developed to measure a host of other important trace chemicals in the atmosphere. Additional ion chemistries have been identified that will expand the technique to the fast response measurement of ammonia and isoprene.

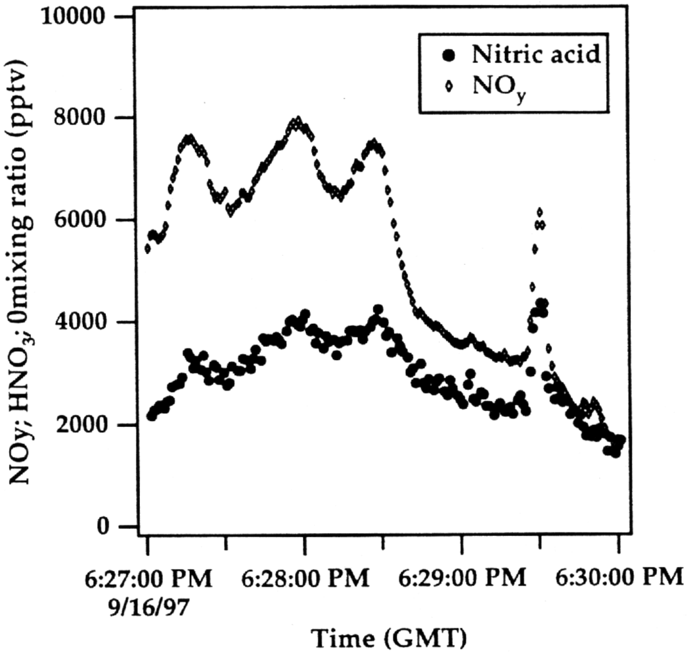
Fehsenfeld, F.C., L. G. Huey, D.T. Sueper, R.B. Norton, E.J. Williams, F.L. Eisele, R.L. Mauldin III, and D.J. Tanner, Ground-based intercomparison of nitric acid measurement techniques, *J. Geophys. Res., 103*, 3343-3353, 1998.

Huey, L.G., E.L. Dunlea, E.R. Lovejoy, D.R. Hanson, R.B. Norton, F.C. Fehsenfeld, and C.J. Howard, Fast time response measurements of HNO_3 in air with a chemical ionization mass spectrometer, *J. Geophys. Res., 103,* 3355-3360, 1998.

Apparatus to measure nitric acid and results from atmospheric measurements.



Measurements crossing a pollution plume.
NOAA WP3 Flight, September 16, 1997.



- **Building a better trap**

What is an ion-trap mass spectrometer? Traditionally, mass spectrometers sequentially measure the ions of a specific mass. They do this by a combination of electric and/or magnetic fields that allow the ions of a single mass to pass un-attenuated to the detector while ions having other masses are prevented from reaching the detector. As the name implies, ion-trap mass spectrometers trap all ions entering the filter over a given acquisition time period. The electric fields associated with the trap are then scanned in a manner that permits the trapped ions to exit the trap according to their mass and be detected. The advantages of the system compared to traditional mass spectrometers are two fold: first, ions at all masses that enter the trap during the acquisition period are collected as a group and hence the ions when detected are correlated with the same acquisition period; secondly, the collection occurs over a period of time allowing the number of ions being collected at all masses to increase over this acquisition period.

The Aeronomy Laboratory has built a better trap. A quadrupole ion trap mass spectrometer has been designed and constructed. The quadrupole ion trap is more versatile than the conventional quadrupole mass filter. The ion trap has an excellent duty cycle and a multiplex advantage, allowing a wide range of masses to be monitored simultaneously with good sensitivity. Multiple stages of mass spectrometry are also possible with the ion trap. These qualities make the trap ideally suited for the analysis of complex mass spectra.

The advantages of ion traps. The ion trap apparatus that has been constructed in the Aeronomy Laboratory has proved to be a very useful laboratory instrument in studies of ionic clusters expected to be involved in the nucleation of particles in the atmosphere. The ion trap has great potential to enhance field measurements based on mass spectrometry. The ion trap technology offers important advantages for the improved detection of trace compounds in the atmosphere and for greatly enhanced capability to determine the chemical composition of aerosols and fine particles.

Lovejoy, E.R., and R.R. Wilson, Kinetic studies of negative ion reactions in a quadrupole ion trap: Absolute rate coefficients and ion energies. *J. Phys. Chem., 102,* 2309-2315, 1998.

- **Improved meteorological measurements**

New techniques for wind and temperature measurements required testing. Wind profiling radar (profiler) and radio acoustics sounding systems (RASS) have become important tools to measure the physical properties of the atmosphere. The height of the convective atmospheric boundary layer (CBL) under daytime continental convective conditions is a key parameter in air pollution modeling. In the past, the CBL height or mixing depth has been measured by radiosondes. These measurements are not continuous and, when they are made. they are labor intensive. The profiling radar offers a continuous measurement of the CBL provided the data can be interpreted with sufficient precision and accuracy. In addition, when used in combination with the RASS, the profiler also can be used to obtain a height-resolved measurement of temperature in the lower troposphere (boundary layer). However, the algorithms used to de-convolute the RASS-measured temperature profiles must be evaluated.

Aeronomy Laboratory improves profiler measurements. The Aeronomy Laboratory has developed methods to determine the mixing depth using profilers that were deployed at various Aeronomy Laboratory field measurement sites. In the measurements, the CBL top appears as an enhancement of the profiler reflectivity. Simple algorithms were developed to find the height of this enhancement. The reflectivity patterns also include information about the strength and integrity of the capping inversion. In addition, the laboratory has undertaken theoretical and observational studies to characterize and improve the precision and accuracy of temperature measurements in the lower troposphere (boundary layer) made using the RASS in conjunction with the profilers. Intercomparisons of the RASS measurements with instrumented aircraft, radiosondes, and instruments on tall towers have provided a quantitative assessment of the precision, accuracy, and limitations of these RASS.

Measurements provide important information. The mixing depth measured using the improved profiler algorithms have been used to model chemical concentrations, to improve calculations of the entrainment of free-troposphere air at the CBL top and to aid in understanding if the measurements of chemical compounds measurements made at surface sites are representative. The laboratory has used the RASS measurements of temperature to calculate the entrainment of free-troposphere air at the boundary layer top.

Grimsdell, A.W., and W.M. Angevine, Convective boundary layer height measured with wind profilers and comparison to cloud base. *J. Atmos. Oceanic Technol.*, in press, 1998.

Angevine, W.M., P.S. Bakwin, and K.J. Davis, 1997: Wind profiler and RASS measurements compared with measurements from a 450-m tall tower. *J. Atmos. Oceanic. Technol.*, 15, 817-824, 1997.

2. Testing the Understanding of Photochemical Ozone Production

- **Kinetics of organic peroxy radicals: Is size important?**

The role of peroxy radicals in the photochemical production of ozone. The reaction of volatile organic compounds by OH leads to the formation of peroxy radicals, R_iO_2,

$$VOC + OH + O_2 \rightarrow R_iO_2 + \text{products.} \qquad (1)$$

In these processes, a variety of peroxy radicals (i.e., R_iO_2, i = 1,2,3, . . .) are formed depending on the identity the VOC that reacts with OH. These R_iO_2, as a group, play a central role in the photochemical production of ozone in the troposphere.

$$NO + R_iO_2 \rightarrow NO_2 + R_iO \quad (i = 1,2,3, \ldots) \qquad (2)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (3)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (4)$$

According to our present understanding the reactions outlined above are the only significant processes for photochemical ozone production in the troposphere. However, to quantify the ozone production rate, the kinetics of the individual R_iO_2 reactions, (2), with nitric oxide must be known.

Laboratory measurements made of peroxy radicals with NO. Previous work on these reactions led to the conclusion that the rate coefficients had a strong dependence upon the size and shape of the R_i group. Direct measurements of the rate coefficients of the RO_2 reactions with nitric oxide as a function of temperature for two different families of R groups, alkyl radicals ($R = C_nH_{2n+1}$) and acyl radicals (R-C=O) were made by the Aeronomy Laboratory using chemical ionization mass spectrometry detection. In both cases, the reaction rate coefficients were found to be practically independent of the size or shape of the R group. However, the alkyl peroxy radicals, as a group, reacted about a factor of two slower than the acyl peroxy radicals.

Improved ability to simulate photochemical production of ozone in the troposphere. These results have greatly improve our ability to accurately model the production of ozone in the troposphere and, moreover, provide a simple reliable method to predict rate data for compounds that have not been studied.

Eberhard, J. and C.J. Howard, Rate coefficients for the reactions of some C_3 to C_5 hydrocarbon peroxy radicals with NO, *J. Phys. Chem. A* , *101*, 3360-3366, 1997.

- **Verification of chemical mechanisms by interpretation of field measurements**

Mechanism for ozone production. Thus far, the oxidation of NO by reaction with peroxy radicals is the only identified source for the photochemical production of ozone in the troposphere (see preceding section). Major efforts have been made over the past decade to quantify the instantaneous rate of photochemical ozone production in the reaction of peroxy radicals and NO.

In-situ measurements and their interpretation. Measurements of ozone made at surface sites show a marked diurnal pattern that is shaped by the photochemical formation of ozone as well as by other processes such as entrainment, photochemical loss, and deposition. For a rural site in Alabama, Frost et al. used one-dimensional model simulations to estimate the combined effects of photochemical production and loss, entrainment, and deposition. The simulations used the estimates of the peroxy radical concentrations obtained by four methods along with the measured nitric oxide concentration to predict the instantaneous rate of photochemical ozone production. The various methods agree on the diurnal behavior of peroxy radical levels and ozone production rates, as well as the dependence on the nitrogen oxide concentrations.

Photochemical production and loss relative to entrainment and deposition quantified. This study represents one of the most stringent field tests of our understanding of the mechanism for the photochemical production of ozone. Within the scatter in the inferred photochemical ozone production rate from these methods, there are indications of subtle systematic differences underlying the four methods and/or the photochemical mechanisms or the assumptions used to interpret the results. These differences will be investigated in future studies. Finally, for the conditions encountered at the Alabama site, deposition and entrainment are found to be as important as photochemical production in determining the diurnal variation of ozone.

G.J. Frost, M. Trainer, G. Allwine, M.P. Buhr, J.G. Calvert, C.A. Cantrell, F.C. Fehsenfeld, P.D. Goldan, J. Herwehe, G.F. Hübler, W.C. Kuster, R. Martin, R.T. McMillen, S.A. Montzka, R.B. Norton, D.D. Parrish, B.A. Ridley, R.E. Shetter, J.G. Walega, B.A. Watkins, H.H. Westberg, and E.J. Williams, Photochemical ozone production in the rural Southeastern United States during the 1990 ROSE Program, *J. Geophys. Res.*, *103*, in press, 1998.

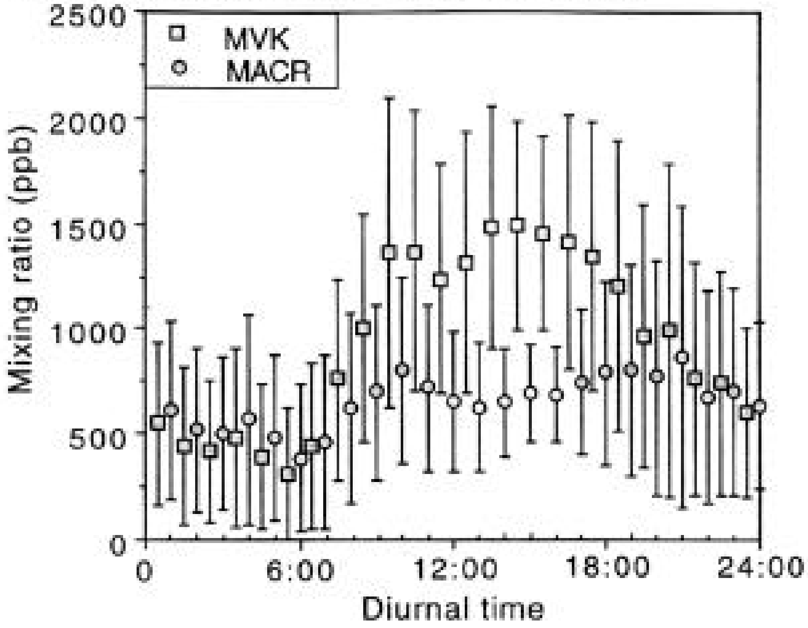
• Testing the mechanisms for isoprene oxidation

The importance of isoprene oxidation. During the last decade, largely as a result of Aeronomy Laboratory research, there has been a growing appreciation, particularly in the southeastern U.S., for the role of summertime biogenic emissions of volatile organic compounds (VOCs) from vegetation. These biogenic VOC emissions are largely in the form of a highly reactive, unsaturated hydrocarbon, isoprene. Our studies indicate that the influence of the oxidation of this isoprene on regional ozone formation can be large. Clearly, therefore, it is essential that the isoprene oxidation mechanisms identified through laboratory kinetic measurements be subjected to independent verification by field measurements.

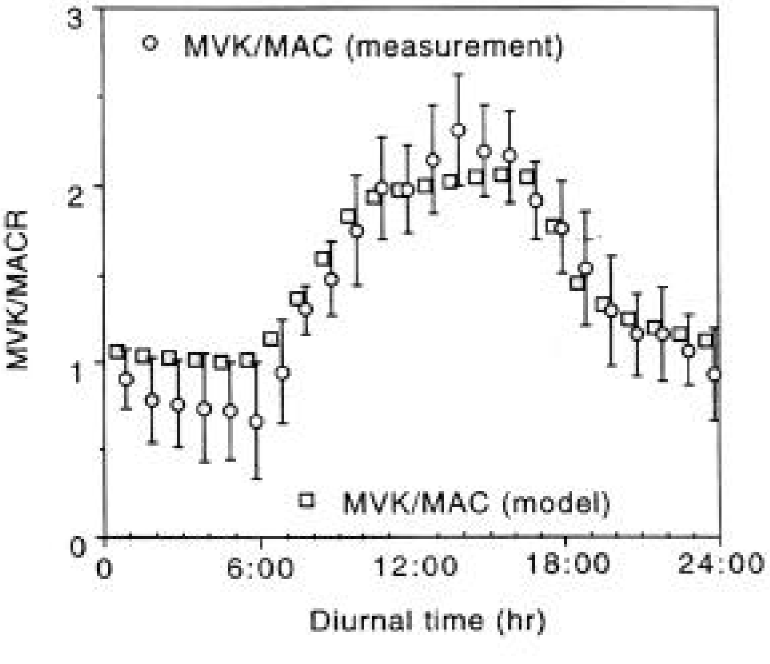
Observations of the oxidation products confirm oxidation mechanisms. Laboratory measurements have indicated that methacrolein, methyl vinyl ketone, and 3-methyl furan are the principal molecular by-products directly formed by the OH-initiated oxidation of isoprene. Measurements of these compounds along with isoprene were carried out at a rural site in Alabama. The analysis of these measurements using a one-dimensional model simulation showed that their relative and absolute concentrations are in good agreement with the present understanding of the photochemistry of isoprene. This is illustrated in the figures shown on the next page. Note that the ratio of the two oxidation products have a smaller standard deviation than that of the individual concentrations, which indicates their strong correlation. The model interpretations of these measurements also indicated that the oxidation of isoprene could adequately account for all the methacrolein, methyl vinyl ketone, and 3-methyl furan that was observed.

Implication of the research. These measurements, in addition to the measurements of the specific peroxy nitrate compound MPAN, which is formed in the oxidation of methacrolein, confirm the oxidation schemes for isoprene that have been developed in the laboratory and support the importance of the role that isoprene can play in the regional formation of ozone. It should also be noted that the development of effective ozone control strategies is dependent on the knowledge of the emission rate of natural hydrocarbons such as isoprene in urban as well as rural areas. Due to its high photochemical reactivity the concentrations of isoprene are spatially highly variable and are influenced by vegetation in close proximity to the measurement location. However, due to their longer photochemical lifetime, the concentrations of methacrolein and methyl vinyl ketone will be representative for the emissions of isoprene over a larger fetch. Ambient measurements of these oxidation products in settings with highly inhomogeneous distribution of isoprene-emitting vegetation, such as urban areas, provide a more stringent test of the role that isoprene plays in urban and regional ozone formation.

Mixing ratio of methacrolein (MACR) and methyl vinyl ketone (MVK) averaged over each hour through the diurnal cycle. Bars are the standard deviation.



Ratio of MVK/MACR averaged over each hour through the diurnal cycle. Bars are the standard deviation.



Montzka, S.A., M. Trainer, W.M. Angevine, and F.C. Fehsenfeld, Measurements of 3-methyl furan, methyl vinyl ketone, and methacrolein at a rural forested site in the southeastern United States, *J. Geophys. Res.*, 100, 11393-11401, 1995.

G.J. Frost, M. Trainer, G. Allwine, M.P. Buhr, J.G.Calvert, C.A. Cantrell, F.C. Fehsenfeld, P.D. Goldan, J. Herwehe, G.F. Hübler, W.C. Kuster, R. Martin, R.T. McMillen, S.A. Montzka, R.B. Norton, D.D. Parrish, B.A. Ridley, R.E. Shetter, J.G. Walega, B.A. Watkins, H.H. Westberg, and E.J. Williams, Photochemical ozone production in the rural Southeastern United States during the 1990 ROSE program. *J. Geophys. Res.*, *103*, in press, 1998.

• Testing the importance of biogenic volatile organic compounds (VOCs) on regional ozone formation

The relative importance of natural VOCs. If ozone concentrations are to be successfully managed by the implementation of primary emission controls, it is essential that the role of naturally produced VOCs vis-a'-vis the manmade VOCs be thoroughly understood. It has become clear in the past decade through our research that while most of the NO_x involved in regional pollution is anthropogenic in origin, both biogenic and anthropogenic hydrocarbons contribute to regional ozone formation. The relative importance of biogenic and anthropogenic compounds to O_3 formation must be properly understood so that effective control strategies for regional ozone can be formulated.

Measurements of products provide an indicator. Our research has provided a method to address this problem by providing an observational means to estimate the impact that biogenic and anthropogenic compounds have on O_3 formation chemistry. This method relies on measurements of three related peroxy nitrate compounds, known as PAN, PPN, and MPAN, that are byproducts of the same chemistry that produces ozone. However, MPAN is a unique product of isoprene, the most important reactive biogenic hydrocarbon, while PPN is essentially solely produced from anthropogenic compounds and PAN is a general product of both. The simultaneous measurement of these product species provides the opportunity to determine the relative effectiveness of biogenic as opposed to anthropogenic compounds in ozone-forming atmospheric chemistry. The three compounds were measured aboard the NOAA P3 aircraft during the 1995 Southern Oxidants Study in and around Nashville, Tennessee, along with O_3, NO_x, hydrocarbons, and a number of other chemical and meteorological quantities. These represent the first airborne measurements of PAN, PPN and MPAN. Moreover, this capability was used to arrive at quantitative estimates of the effect of biogenic and anthropogenic hydrocarbon chemistry on O_3 formation.

What was found? From these measurements, it was found that isoprene chemistry dominated ozone formation in the forested rural areas of the Nashville/Middle Tennessee region. However, the contribution of isoprene to rural ozone formation was found to decrease significantly with increasing latitude (i.e., from south to north). This decrease paralleled a similar decrease in isoprene emissions with latitude as predicted by current biogenic emission inventories.

Williams, J., J.M. Roberts, F.C. Fehsenfeld, S.B. Bertman, M.P. Buhr, P.D. Goldan, G. Hübler, W.C. Kuster, T.B. Ryerson, M. Trainer, and V. Young, Regional ozone from biogenic hydrocarbons deduced from airborne measurements of PAN, PPN, and MPAN, *Geophysical Research Letters*, *24*, 9, 1099-1102, 1997.

• Fingerprints of atmospheric photochemistry and atmospheric lifetimes: Field measurements and laboratory kinetic results complement each other

The current understanding of alkyl nitrate formation. Laboratory kinetic data provide the framework required to analyze field measurements, and the resulting analysis in turn provides tests of the laboratory data. One example is the measurement of alkyl nitrates and their parent hydrocarbons. The alkyl nitrates are formed as intermediates during the oxidation of hydrocarbons in the atmosphere. The rate-determining step of the hydrocarbon oxidation is attack by a hydroxyl radical, which extracts a hydrogen atom from the hydrocarbon to yield the alkyl radical. The alkyl radical quickly combines with O_2 to give the peroxy radical that then reacts with NO, usually to transfer an oxygen atom to oxidize it to NO_2 leaving an organic radical, which then is oxidized further. However, there is some probability that the peroxy radical simply combines with the NO to give the alkyl nitrate.

Field testing the mechanisms for alkyl nitrate formation. The mechanisms responsible for the photochemical formation of alkyl nitrates have been studied in the laboratory for many hydrocarbons. The alkyl nitrate is removed from the atmosphere by photodissociation or oxidation by hydroxyl radical. The rates of the removal reactions, as well as of the original oxidation of the parent hydrocarbon, have been carefully determined in the laboratory. The reaction sequence that constitutes the formation and removal of alkyl nitrates can be approximated by two sequential pseudo-first order reactions. The rate constants, k_A and k_B, are related to the rate constants for the hydroxyl radical reactions, and the diurnal averages of the hydroxyl radical concentration and photolysis rate. Two sequential first order reactions constitute a common kinetics example from undergraduate physical chemistry, and the time evolution of at least the ratio of the alkyl nitrate to the parent alkane can be integrated to yield

$$[RONO_2]/[RH] = \{ak_A/(k_B - k_A)\}\{1 - \exp -(k_B - k_A)t\}. \qquad (1)$$

Equation (1) cannot be directly tested, since the time between hydrocarbon emissions to the atmosphere and their later measurement is, in general, not known. However, the application of Equation (1) to the ratios of two different alkyl nitrates to their parent hydrocarbons allows the time factor to be eliminated and allows the relationship between the two ratios to be predicted solely from the kinetic data. In many cases, these predictions agree with measurements to within 50%, which is reasonable agreement considering the levels of uncertainty associated with all of the measurements, rate constants, and branching ratios that go into the analysis. In some cases, disagreement has indicated that additional formation pathways exist for some of the alkyl nitrates.

Implication of the results. These measurements have provided an additional field test of our understanding of the photochemistry that shapes tropospheric composition and is involved in ozone production and loss. Such agreement increases our confidence in both the field measurements and the laboratory results.

Bertman, S.B., J.M. Roberts, D.D. Parrish, M.P. Buhr, P.D. Goldan, W.C. Kuster, F.C. Fehsenfeld, S.A. Montzka, and H. Westberg, Evolution of alkyl nitrates with air mass age, *J. Geophys. Res.*, *100,* 22805-22813, 1995.

• NMHC measurement tests

Lessons learned by analyzing the data. The first information emerging from data reduction and interpretation of field measurements is the quality of the instrument performance. An example is nonmethane hydrocarbon (NMHC) data sets. These measurements are made using gas chromatography with flame ionization detection, which is rugged and reliable, but nonspecific. This nonspecificity, as well as sample collection, storage, and concentration procedures, introduce many opportunities for errors. Not surprisingly, when these data sets are analyzed, suspicion is often cast upon the claimed accuracy of the results.

Sorting out measurement problems. The emission of NMHCs into the atmosphere is followed by their photochemical processing and dilution. Common patterns reflecting these processes are expected in NMHC measurements. Specific tests based upon these patterns are can be used to determine the representativeness and/or credibility of NMHC measurements collected in North America. It is expected that anthropogenic NMHC data should reflect urban concentration patterns, modified by dilution and photochemical removal. The urban patterns of NMHC have been established by a large number of urban studies; one analyzed 800 ambient air samples from 39 U.S. cities. The ratios of the median concentrations of the 48 compounds seen at the highest ambient levels in this study are assumed to characterize the urban concentration pattern. Average measured ratios are expected to equal the average emission ratio of the sources, except as the ratios are modified by the differential rate of photochemical removal of the NMHCs. The primary process for removal of NMHCs from the atmosphere is attack by OH radicals; the approximate summertime lifetimes of NMHCs span the range of tens of days to one hour or less.

The suite of the aromatic NMHC ratios to benzene has been examined using 16 data sets: 11 from EPA Photochemical Assessment Monitoring Stations (PAMS) and 5 research data sets. The research data sets show, on average, significant evidence for photochemical processing - factors of 3 to 5 reduction in the concentration of the more reactive aromatic relative to benzene from the ratio of the urban medians. In contrast, the PAMS data show no consistent indication of photochemical processing. Remarkably, every mean ratio in every data set except one was found to agree with the ratio of the urban medians to within a factor of two. (The one exception was the Virginia site, which is evidently affected by some systematic error throughout the aromatic measurements.) The generally excellent agreement between the ambient PAMS data and the urban median ratios is unexpected. At least some of the PAMS sites are located where fresh emissions are not expected to dominate, especially during the photochemically active summer period of the measurements, and evidence for photochemical processing is expected as is seen for the research data sets. It may be that all of the selected PAMS stations are sited such that local, fresh automotive emissions dominate the aromatic NMHC concentrations. Such siting may well limit the usefulness of the PAMS data for evaluation of the areal NMHC levels, which is their intended purpose.

The ratio of each alkene to ethene in all of the data sets has been examined. There is little consistency in the behavior of these data in contrast to the aromatic data. Some systematic errors are obvious in data sets with ratios significantly above the U.S. urban ratios. No consistent pattern of photochemical processing emerges in the PAMS data. Substantial (approaching an order of magnitude) systematic errors are indicated in much of the PAMS alkene data. Indeed, it is not clear that any measurement technique reliably measures ambient alkenes.

The bottom line. In summary, perhaps the most pressing issue in the measurements of gas-phase species in the troposphere is the need for a rigorous, formal intercomparison of field measurements. Only then can the evident systematic measurement errors be reliably quantified, and the reliability of the techniques adequately assessed.

Parrish, D.D., and F.C. Fehsenfeld, Methods for gas-phase measurements of ozone, ozone precursors and aerosol precursors, *Atmos. Environ.*, in press, 1998.

Parrish, D.D., M. Trainer, V. Young, P.D. Goldan, W.C. Kuster, B.T. Jobson, F.C. Fehsenfeld, W.A. Lonneman, R.D. Zika, C.T. Farmer, D.D. Riemer, and M.O. Rodgers, Internal consistency tests for evaluation of measurements of anthropogenic hydrocarbons in the troposphere, *J. Geophys. Res.*, in press, 1998.

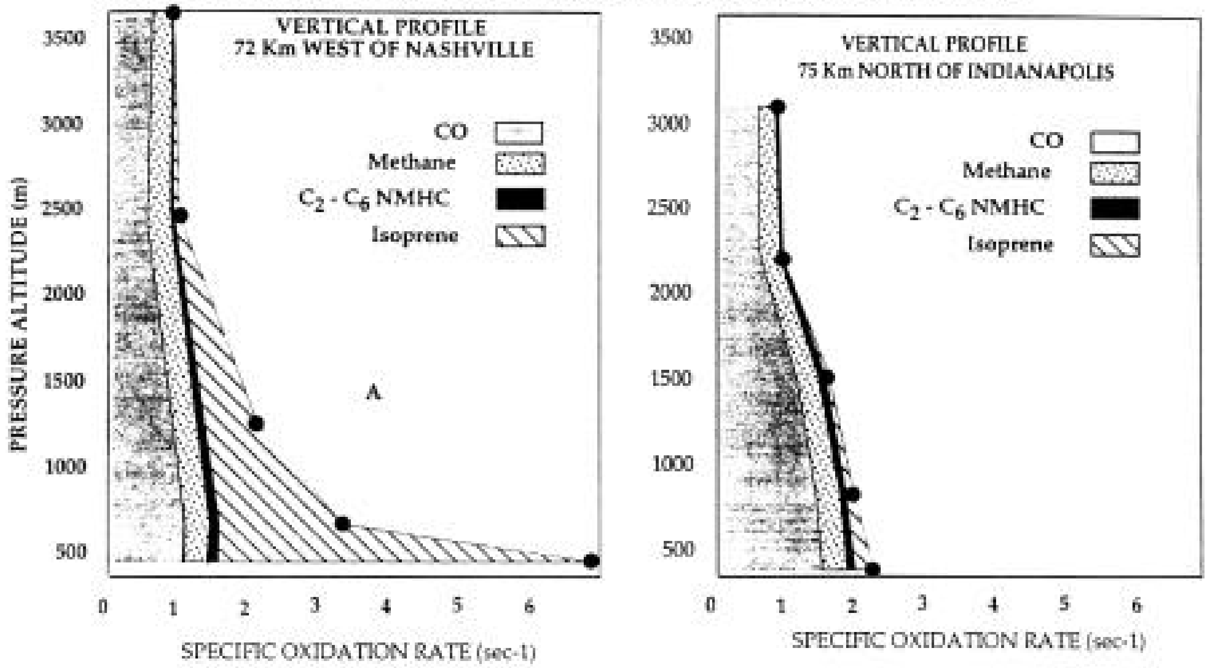
3. Investigating the Regionality of Ozone Production

• Role of carbon monoxide and methane in regional ozone formation

Long range transport of longer-lived ozone precursors can be important. It is well known that the elevated pollutant ozone concentrations that are found frequently during the summer over the Eastern United States are potentially harmful to humans and damaging to crops and forests. Once produced, the lifetimes of ozone and certain ozone precursors are sufficiently long so that they can be transported over great distances. For this reason, ozone concentrations in a particular location may depend on the amount of ozone and ozone precursors transported from outside the local region.

Importance of carbon monoxide relative to the nonmethane hydrocarbons as an ozone precursor evaluated over a wide region. An analysis of the data taken during the course of regional flights over the Southeastern and midwestern United States during the 1995 Nashville/Middle Tennessee Study of the Southern Oxidants Study (SOS) suggests that carbon monoxide makes a significant contribution to ozone formation in regions where isoprene levels are depressed (i.e., in the boundary layer in urban plumes, in the upper Midwest, and in the free troposphere). This is illustrated in the figures above that show two representative profiles of NMHCs measured from the NOAA WP3 during the summer of 1995. The figures show the specific rates of oxidation, k*[mixing ratio], of the anthropogenic compounds, the C2 through C6 hydrocarbons. This is a measure of the ability of those compounds to photochemically produce ozone. Over forested heavily regions in the Southeast, like the Nashville area, isoprene oxidation plays an important role in ozone formation. In the free troposphere, over the whole region the oxidation of CO and CH_4 are the most significant oxidizable O_3-precursors. However, in the rural regions of the commercial/ industrial/ agricultural upper midwest, like the Indianapolis area, the oxidation of CO and CH_4 is the dominant factor in ozone formation. Both CO and CH_4 have a variety of natural and anthropogenic sources and are produced by the oxidation of more complex natural and anthropogenic NMHCs. Moreover, during a typical midsummer period, both CO and CH_4 are long-lived compounds with photochemical lifetimes of approximately one to several months. Hence, the exact sources of these compounds at a particular location will be difficult to determine.

The bands represents the specific oxidation rate, k_{OH}*[mixing ratio], for CO, CH_4, and the combined man-made NMHCs measured over a forested region west of Nashville, and over a commercial/ industrial/ agricultural region north of Indianapolis(summer 1995).



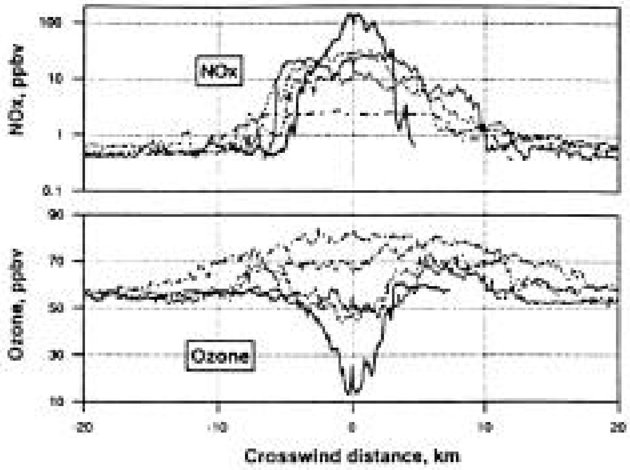
Carbon monoxide can contribute significantly to photochemical ozone formation. The apparent importance of methane and CO in ozone formation in the regions described above is new information for consideration in future ozone management strategies. The role of methane and CO should be expected to be further enhanced as emissions of more reactive VOCs continue to decline.

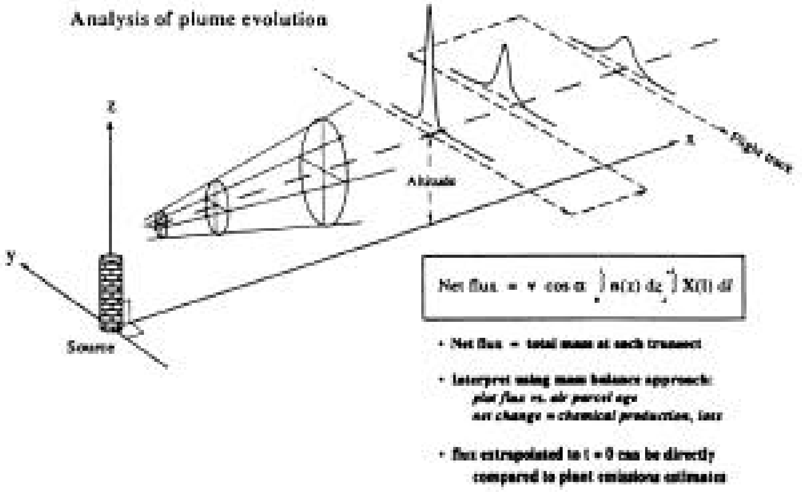
M. Trainer, D.D. Parrish, P. D. Goldan, J. Roberts and F. C. Fehsenfeld. Regional factors influencing ozone concentrations, *Atmos. Environ.*, submitted, 1998.

- **Inefficient ozone formation in plumes**

NO_x reduction to control ozone. As noted previously, the photochemical production of ozone requires NO_x. Hence, a control strategy that is presently being pursued is to reduce the photochemically formed ozone by reducing the emission of NO_x. This is being done by reducing the emissions of NO_x from large point sources such as power plants, which on a nationwide basis contribute a substantial fraction of the NO_x emitted from all sources. Since ozone production is nonlinear with the amount of NO_x emitted, the effectiveness of this approach requires further scrutiny.

Results from studies of power plant plumes. These measurements were made as part of the 1995 Nashville/Middle Tennessee Study of the Southern Oxidants Study (SOS). Cross-plume pollutant profiles obtained by the NOAA WP-3D were combined with detailed wind fields to investigate O_3 formation at various downwind distances for several pollutant sources with very different NO_x emissions. A sample of some of the measurements and the approach to their interpretation are shown in the figure below. The analysis of these data from the measurements that were made in 1994 and 1995 indicates that NO_x removal occurred quickly





and that O_3 production in these plumes was much less efficient than ozone production from more dispersed NO_x sources. Ozone production per unit of NO_x emission appears to be greatest for the Nashville urban plume and for the smaller NO_x -emitting power plants that are located in areas rich in natural VOC emissions. Ozone production was found to be less efficient for NO_x emitted from rural power plants with the higher NO_x emissions.

Implication for emission controls. The implications of these finding are significant in terms of strategies that are being proposed for controlling ozone by regulating sources of NO_x. The approach currently being pursued would reduce NO_x emissions by reducing the emission of NO_x from large point sources. However, our results would suggest that the effectiveness in reducing photochemically produced ozone pollution may be substantially less than what might be expected with relatively large reductions in NO_x. These data would suggest that one could get more "bang for the buck" by controlling smaller sources. The results also suggest that the trading of NO_x emissions from power plants over long distances may be of limited value in reducing ozone nonattainment, since ozone production appears to occur relatively near to the source.

Ryerson, T.B., M.P. Buhr, G. Frost, P.D. Goldan, J.S. Holloway, G. Hübler, B.T. Jobson, W.C. Kuster, S.A. McKeen, D.D. Parrish, J.M. Roberts, D.T. Sueper, M. Trainer, J. Williams, and F.C. Fehsenfeld, Emissions lifetimes and ozone formation in power plant plumes, *J. Geophys. Res., 103,* in press, 1998.

- **Reduced photochemical production of hydrogen peroxide in power plant plumes**

The importance of H_2O_2. The measurement of hydrogen peroxide represents an important diagnostic of the photochemistry that leads to ozone formation. As the case with nitric acid, the formation of H_2O_2 terminates the tropospheric odd-hydrogen chemistry and the production of H_2O_2 is a measure of the availability of the peroxy radicals that are involved in the photochemical formation of ozone. In addition, since H_2O_2 can be formed in the absence of NO_x while HNO_3 is formed from NO_x, the production of H_2O_2 relative to HNO_3 has been used as a measure of whether the photochemical production of ozone is most sensitive to the availability of NO_x or VOCs.

Measurements of H_2O_2 during plume studies. Hydrogen peroxide measurements were made aboard the NOAA WP-3D aircraft in the summer of 1995 as part of the Southern Oxidants Study. These measurements revealed the loss of hydrogen peroxide within fossil fuel power plant plumes and the Nashville urban plume. On July 7, the Cumberland power plant plume was intercepted at five different downwind distances. Observations from these transects show that H_2O_2 mixing ratios within the plume decreased with increasing distance from the plant. Conversely, ozone mixing ratios increased. The H_2O_2 loss is attributed to the lowered rate of formation due to suppression of HO_2 radical concentrations in the high NO_x environment, and the subsequent removal of H_2O_2 by photolysis, reaction with HO, and dry deposition. From steady-state model estimates of the chemical loss rates in the plume and an analytical approximation for the influx of H_2O_2 into the plume center due to horizontal dispersion, a simple budget for H_2O_2 was formulated, from which a dry deposition lifetime of 19 hours ± 55% was inferred.

Importance of these findings. The Aeronomy Laboratory has provided the first measurements of H_2O_2 along with a variety of other photochemical trace compounds in flights downwind of large point-source pollution plumes. The successful interpretation of the formation and loss of H_2O_2 measured in these flights provides an independent test of our understanding of the photochemistry that leads to ozone formation.

Jobson, B.T., D.D. Parrish, T.B. Ryerson, M.P. Buhr, G. Frost, M. Trainer, and F.C. Fehsenfeld. Hydrogen peroxide dry deposition lifetime in a continental boundary layer determined from observed loss rates in a power plant plume, *J. Geophys. Res., 103,* in press, 1998.

- **Estimation of source emissions and secondary pollutant production**

Importance of independent tests of emission rates. The development of ozone control strategies relies primarily on model calculations. However, due to the nonlinear behavior of ozone formation, the predictions of these photochemical models are sensitive to the emission rates of ozone precursors such as the anthropogenic and natural hydrocarbons and nitrogen oxides. Ambient measurements can provide critical tests of the relative as well as absolute emission rates of carbon monoxide, hydrocarbons, and nitrogen oxides.

Several such investigations have been carried out by the Aeronomy Laboratory. During times when the influence of photochemical processing of the emissions is small, such as during winter and during the early morning hours, ambient measurements made in the vicinity of emission sources provide a direct measure of the relative emission rates of anthropogenic precursors. During the summertime the mixing ratios of O_3 precursors at rural locations are strongly influenced by photochemistry and dilution. However, the concentrations of compounds can still provide information concerning the relative importance of the sources of these compounds when photochemical processing is properly taken into account.

Ambient measurements at a site on the western perimeter of Boulder, Colorado, during February 1991 in comparisons with the predictions of the 1985 National Acid Precipitation Assessment Program (NAPAP) inventory show (i) good agreement for CO/NO_y, (ii) significant overpredictions by the NAPAP inventory for many of the hydrocarbon to NO_y ratios, (iii) much more benzene from mobile sources (and less from area sources) than predicted by the NAPAP inventory, and (iv) large underpredictions of the light alcohols and carbonyls by the NAPAP inventory. The first two results are in marked contrast to conclusions from ambient measurements in the Los Angeles basin. This points to the need for an evaluation of the emission inventories for a variety of urban airsheds.

We have also carried out studies investigating the emissions of NO_x relative to CO and VOCs from point and area sources for a region in the southeastern United States. The studies were interpreted using a principal component analysis (PCA) using the concurrent measurements of a variety of trace gases made at Kinterbish, a rural Alabama field site, during the summers of 1990 and 1992. The results of the PCA indicated that the major sources of NO_y in the region were (i) coal-fired power plants and (ii) biomass burning and/or paper mills.

Aircraft measurements of O_3, CO, NO_x, and SO_2 have characterized the horizontal and vertical extent of plumes downwind of urban areas and power plants in the southeastern U.S. A mass balance approach has been used to derive an estimate of the flux of the primary pollutants from these sources, which can then be directly compared with emission estimates. The flux of O_3 can be calculated similarly to provide a direct estimate of the amount of O_3 that is directly produced from the emissions of a particular source.

Some findings from the tests of emissions. These tests have several important consequences. Among them:

> evaluations of the emission inventories needed for a variety of urban airsheds;

> biomass burning in the southeastern United States may be an important, but as yet poorly characterized, component in the NO_y area source; and

> the flux of O_3 can be used to estimate of the amount of O_3, H_2O_2, CO, NO_x, and SO_2 that is directly emitted from point sources or is produced from the emissions of a particular source.

Goldan, P.D., M. Trainer, W.C. Kuster, D.D. Parrish, J. Carpenter, J.M. Roberts, J.E. Yee, and F.C. Fehsenfeld, Measurements of hydrocarbons, oxygenated hydrocarbons, carbon monoxide, and nitrogen oxides in an urban basin in Colorado: Implications for Emission Inventories, *J. Geophys. Res., 100,* 22,771-22,783, 1995.

Trainer, M., B.A. Ridley, M.P. Buhr, G. Kok, J. Walega, G. Hübler, D.D. Parrish, and F.C. Fehsenfeld, Regional ozone and urban plumes in the southeastern United States: Birmingham, a case study, *J. Geophys. Res., 100,* 18,823-18,834, 1995.

Buhr, M., D. Parrish, J. Elliot, J. Holloway, J. Carpenter, P. Goldan, W. Kuster, M. Trainer, S. Montzka, S. McKeen, and F. Fehsenfeld, Evaluation of ozone precursor source types using principal component analysis of ambient air measurements in rural Alabama, *J. Geophys. Res., 100*, 22,853-22,860, 1995.

Ryerson, T.B., M.P. Buhr, G. Frost, P.D. Goldan, J.S. Holloway, G. Hübler, B.T. Jobson, W.C. Kuster, S.A. McKeen, D.D. Parrish, J.M. Roberts, D.T. Sueper, M. Trainer, J. Williams, and F.C. Fehsenfeld, Emissions lifetimes and ozone formation in power plant plumes, *J. Geophys. Res., 103,* in press, 1998.

4. Understanding Regional Air Quality: Combining Meteorology and Chemistry

• Entrainment measurements

The impact of entrainment after sunrise. As noted above, the diurnal variation of the planetary boundary layer (PBL) has a strong impact on regional air quality. In particular, the transition periods after sunrise and sunset are key to understanding the diurnal influence on atmospheric chemistry. After sunrise, the PBL grows during the morning by entraining air from the free atmosphere above. This entrainment of free tropospheric air is a key process in controlling the temperature, humidity, and chemical concentrations in the PBL and, therefore, at the surface. This can be particularly important when the overlying free atmosphere has layers with enhanced concentrations of ozone and ozone-precursors, as is commonly observed. At present, in general, it is poorly understood and crudely parameterized in numerical models.

Measurements made in Illinois. Two field experiment campaigns focused on entrainment were conducted at the Flatlands Atmospheric Observatory, near Champaign, IL in the summers of 1995 and 1996. The primary instruments used in the study were three boundary layer wind profilers deployed in a triangle. Radiosonde and surface flux measurements were also made. Entrainment was calculated from the heat budget of the boundary layer. The ratio of entrainment heat flux to surface heat flux that we found, about 0.4, was significantly larger than previously accepted values (0.2). Similar studies in other locations have found a range of values for this ratio, some agreeing with our results.

Results from the measurements. The results of the entrainment studies are being used to improve the parameterization of entrainment in atmospheric models and to improve the general understanding of the process. In addition, the use of remotely sensed data for this study has demonstrated the advantages such instruments have in continuity and availability of data and should encourage others to improve future campaigns by deploying and using profilers with radio acoustic sounding systems.

Angevine, W.M., A.W. Grimsdell, S.A. McKeen, and J.M. Warnock, Entrainment results from the Flatland boundary layer experiments. *J. Geophys. Res., 103*, 13689-13702, 1998.

- **Role of convection in redistribution of trace compounds**

Deep convection can influence regional air quality. It has been generally recognized that atmospheric convection plays an important role in the vertical distribution of ozone and other trace species. Model studies have shown the impact of the vertical mixing by convective clouds on the redistribution of chemical species. These studies have found that convection can significantly increase the O_3 column production rate because the concentrations of trace gases (particularly NO_x) become more dilute through cloud mixing, which leads to greater column production efficiency. The importance of enhanced long-range transport of pollutant species in the free troposphere after the vertical pumping by clouds also has been recognized.

Model simulations of deep convection have been improved. An improved parameterization of subgrid-scale convective cloud vertical mixing has been developed for the Aeronomy Laboratory three dimensional regional chemistry model. This parameterization was evaluated by comparison with airborne observations during the measurements that were made in the Southeastern United States campaign in Alabama and the North Atlantic Regional Experiment.

The model simulations including convection are in much better agreement with measurements. The study showed that model results with and without cloud transport differ significantly from each other when convective clouds are present. The model results with cloud transport are in much better agreement with the aircraft observations than those without. This represents a quantitative test of the importance of convection in shaping the regional ozone distribution.

Lin, X, B.A. Ridley, J. Walega, G.F. Hübler, S.A. McKeen, E.-Y. Hsie, M. Trainer, F.C. Fehsenfeld, and S.C. Liu, Parameterization of subgrid scale convective cloud transport in a mesoscale regional chemistry model, *J. Geophys. Res.*, *99*, 25,615-25,630, 1994.

5. Understanding Regional Air Quality: Processes on Fine Particles

- **Reactions on "reduced" particles**

Heterogeneous reactions may play an important role in atmospheric chemistry. Carbon and organics comprise a significant component of tropospheric aerosol. The reaction of ozone with organic aerosol could be an important sink for ozone and possibly release interesting gas-phase products. Therefore, the heterogeneous reactivities of NO_2 on soot and on organic liquids were investigated.

Studies being carried out. The Aeronomy Laboratory has begun the investigation of heterogeneous reactions on soot particles. These reactions are were studied by using flow reactors coated with soot or organic liquids, with chemical ionization detection of gas-phase reactants and products.

Important new results have been obtained. NO_2 is reduced by hydrocarbon soot to produce HONO. In the presence of water the reactivity of the soot is regenerated. This reaction sequence may be an important a.m. HO_x source. Ozone reacts efficiently with unsaturated liquid organic compounds. The importance of this result awaits a better understanding of the composition of tropospheric aerosols. Additional reactions of atmospheric species on soot and carbonaceous aerosol will be investigated.

de Gouw, J. A, and E. R. Lovejoy, Reactive uptake of ozone by liquid organic compounds, *Geophys. Res. Lett*., *25*, 931-934, 1998.

- **Formation of particles from the gas phase**

Formation of H_2SO_4 on particles may be an important source of particles. A significant fraction of gas-phase SO_2 is oxidized to gas-phase SO_3 by reactions with OH and O_2. The kinetics of the SO_3 reactions are needed to evaluate the rate of production of gas phase H_2SO_4. Since nucleation on H_2SO_4 initiates particle formation, this information is critically needed in order to understand the rate of fine particle formation in the atmosphere.

Mechanism for the formation of H_2SO_4 on ionic clusters studies. Ionic clusters may play important roles in atmospheric nucleation because of their enhanced stability. The thermodynamics of the ionic clusters are needed to evaluate the role of ions in particle nucleation. Therefore, the kinetics and mechanisms of the gas-phase reactions of SO_3 with NH_3 and H_2O were studied. The kinetics and products of reactions of atmospheric cluster ions with H_2SO_4, NH_3, and H_2O are being studied. The kinetics and products of the SO_3 reactions were measured by using a flow reactor coupled to a chemical ionization mass spectrometer. The ionic cluster reactions are being investigated with a new quadrupole ion trap mass spectrometer developed in this laboratory.

Aeronomy Laboratory studies indicate SO_3 conversion on particles is not important. The SO_3 studies show that reactive uptake by aerosol cannot compete with the gas phase reaction with water, so that SO_3 is quantitatively converted to gas phase H_2SO_4 in the troposphere and lower stratosphere. The SO_3 + NH_3 reaction produces H_3NSO_3 which may play a role in new particle formation. Further studies on formation of small clusters, which lead to particles, will be carried out.

Lovejoy, E. R., D. R. Hanson, L. G. Huey, Kinetics and products of the gas-phase reaction of SO_3 with water, *J. Phys. Chem.*, *100*, 19911-19916, 1996.

C. Future Plans: What's Next?

Ozone and fine particles: Synergies

Anthropogenic pollution can be harmful to human health, have deleterious effects on crops and forests, and degrade visibility. At present, the most serious air quality concerns are associated with ozone and fine particle pollution. All of the ozone and much of the aerosol that are attributed to human pollution are not emitted directly into the atmosphere but rather are produced as byproducts of atmospheric chemistry. The same is true about much of the fine and ultrafine particles. Therefore, the aim of the Aeronomy Laboratory air quality research over the near future is to investigate how the chemical processing and removal of compounds of anthropogenic origin can influence the regional budgets of ozone and fine particles.

A focus on the Southeastern U.S. and South Texas

During the next few years, the Aeronomy Laboratory will undertake field measurements (e.g., in the Southeastern U.S. and in South Texas) of the concentrations of O_3, fine particles, their precursors, photochemical intermediates, and other photochemical products, as well as other atmospheric parameters. Both areas have growing emerging pollution problems due to the meteorological conditions and population and industrial growth. Early knowledge will pay great dividends to the decision process. Airborne and ground-based studies will provide information required to more accurately determine the rate and amount of ozone and fine particulate that are photochemically produced in the atmosphere from human-made and natural precursors. Our research will build on the development of a new measuring technique that promises to revolutionize the determination of the chemical composition of fine particles. This technique already has be used successfully to measure the chemical composition of particles in the rural atmosphere and from these measurements infer many heretofore unrecognized chemical properties of these aerosols that may play an important role in the formation of these particles and the role that they may play in atmospheric chemistry.

Does the atmosphere couple ozone-related and fine-particle-related decisions/actions?

The expansion of our measurements to investigate fine particles and related processes is timely. Aerosols participate in a variety of chemical and physical processes in the troposphere. On a regional scale, these processes are associated with regional air quality as related to visibility and the effects of fine particles on human health. In this regard, there is a natural synergism between the ozone-related research described previously and the study of processes leading to or involving fine particles. New Federal standards have been proposed for both ozone and fine particles. These standards force the recognition that a basic scientific understanding of the chemistry and physics of the atmosphere is prerequisite in order to design effective control strategies for these pollutants and that the concentrations of the pollutants in the atmosphere are often co-dependent because of interacting chemical reactions.

With this in mind, the Aeronomy Laboratory will be emphasizing a laboratory, field, and modeling program to elucidate:

- how chemical processing on aerosols influences ozone formation;
- how the atmospheric oxidation that leads to ozone formation may also lead to aerosol formation; and
- how atmospheric chemistry influences the growth and/or the chemical composition of aerosols.

This new paradigm also has been embraced by our colleagues in The Southern Oxidants Study and the North American Research Strategy for Tropospheric Ozone and Aerosols (NARSTO).