FINAL (draft) ACD Strategic Plan

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Executive Summary

Today society faces many challenges due to population growth and non-sustainable use of natural resources. These challenges are likely to become more acute in the near future, as urban population in less-developed regions is projected to double over the next 25 years. This trend has led to unprecedented changes in atmospheric composition, resulting in reductions in global air quality, and to the build-up of gases and particles in the atmosphere that influence the climate system and contribute to global warming. Atmospheric chemists will continue to make significant advances in the description and understanding of the perturbations to atmospheric processes that impact air quality and the climate system. This understanding is an essential underpinning of predicting future changes to the Earth climate system.

Laboratory and chamber experiments have determined many of the parameters that characterize fundamental atmospheric chemical process. Many observational techniques adapted from the laboratory setting have produced great advances in our capacity to observe the full complexity of atmospheric composition. We can now measure the miniscule concentrations of many of the radical species that provide the engine of almost all atmospheric chemical processes including hydrocarbon oxidation, tropospheric ozone production, and stratospheric ozone destruction. It is now possible to determine the atmospheric composition of many of the myriad volatile organic chemicals as well as many of the intermediate products that play a role in ozone and particle formation in the troposphere. Many of these measurements can now be made *in situ* with a frequency on the order of seconds, enabling detailed measurements of atmospheric gradients from airborne platforms and fluxes between the Earth's surface and atmosphere from ground- based systems. Remote sensing from space has revealed the global extent of atmospheric pollution. Advances in computer power have made feasible sophisticated three dimensional models of the atmosphere that simulate the co-evolution of tens of chemical species on realistic length and time scales, allow data assimilation of chemical measurements, and provide forecasts and simulations for integrated field campaigns. The challenges of constraining the complex multi-species systems characteristic of atmospheric chemistry problems have been met through the integration of process understanding, advanced instrumentation and measurements, and extensive numerical simulations with comprehensive field campaigns. ACD scientists have played leading roles in MLOPEX (Mauna Loa Photochemistry Experiment), STERAO (Stratosphere-Troposphere Experiments: Radiation, Aerosols, and Ozone), SAFARI (Southern African Fire-Atmospheric Research Initiative), and ISCAT (Investigation of Sulfur Chemistry in the Antarctic Troposphere).

Scientists in the Atmospheric Chemistry Division (ACD) have made significant contributions to all aspects of these advances. ACD uniquely integrates a broad range of disciplinary skills from analytical chemistry, laboratory kinetics, spectroscopy, atmospheric dynamics, biology, ecology and numerical modeling into multi-disciplinary projects necessary to yield progress in many of the most difficult problems in atmospheric chemistry. The division will continue to play a major role in atmospheric chemistry studies, leading NSF-sponsored endeavors alongside university collaborators, as well as supporting multi-agency studies. Over the next half decade, the division staff will organize and direct their research efforts at two grand challenges that confront society and where atmospheric chemical processes play a crucial role, namely ***Regional and Global Air Quality*** and ***Chemistry in the Climate System***. These have also been identified as important areas for research by the International Global Atmospheric Chemistry program (IGAC) of the International Geosphere Biosphere Program (IGBP) and Stratospheric Processes and their Role in Climate (SPARC) of the World Climate Research Program (WCRP). The directions of the division's research efforts have been chosen for their societal relevance, and because they represent a good fit with the skills, enthusiasm, and scientific interests of ACD staff. These plans also focus on the exciting opportunities presented by the availability of the National Science Foundation (NSF) C-130, the deployment of the HIRDLS (High-Resolution Dynamics Limb Sounder) satellite instrument in January 2004, and the NSF Gulfstream -V (G-V) (HIAPER--High-Performance Instrumented Airborne Platform for Environmental Research) aircraft in 2006. These plans are developed with the recognition that the accomplishment of any of the major goals will require significant collaboration with other NCAR divisions and with the university community.

The main goal for ***Regional and Global Air Quality*** will be to understand and quantify the impact of pollution on air quality. Priority will be given to studying the large-scale impacts of intense pollution originating from megacities, and the multiphase (gas-aerosol-cloud) processes that transform pollutants in the atmosphere. To achieve this goal will require an integrated, multidisciplinary research program. The components of that program will include development of comprehensive regional and global chemistry-transport models, data assimilation of chemical and aerosol observations, and laboratory studies of fundamental gas and condensed-phase processes. These developments will support multi-instrument airborne- and ground-based process studies of the evolving chemical, microphysical, and radiative characteristics of aging urban outflow, as well as studies of plume transport and dispersion based on observations from satellite instruments such as MOPITT (Measurement Of Pollution In The Troposphere), MODIS (Moderate Resolution Imaging Spectroradiometer), and TES (Tropospheric Emission Spectrometer). Understanding the evolution and fate of these urban plumes is a necessary component in the prediction of future air quality trends and in the accurate simulation of the influence of atmospheric composition on climate forcing. These goals will contribute to the objectives of IGAC "*to accurately determine global distributions of both short and long lived chemical species in the atmosphere and to document their changing concentrations over time*," and "*to provide a fundamental understanding of the processes that control the distributions of chemical species in the atmosphere and their impact on global change and air quality*" (IGAC, 2003).

The goals for ***Chemistry in the Climate System*** will be to understand the interactions between the physical climate system, the chemical climate system, and the biosphere. Priority will be given to the simulation of the recent past and future chemical climate states based on current climate simulations and to the study of the crucial role of the upper troposphere/lower stratosphere (UT/LS) in the physical and chemical climate system. These priorities will require research into the development of Earth system models that couple the physical, chemical, and biological processes relevant to the forcing of the climate system, including the middle atmosphere. Laboratory studies measuring fundamental chemical and aerosol properties, the characterization and quantification of biogenic emissions, and measurements from integrated multidisciplinary field studies are necessary for improving model simulations. Airborne field studies, particularly of the tropopause region, will combine measurements from satellite instruments such as HIRDLS, and *in situ* observations from high flying aircraft such the NSF G-

V (HIAPER), with meso- and synoptic-scale numerical model simulations. Evaluation of Earth system models with atmospheric observations from ground-, aircraft-, and space-based platforms will build confidence in present-day climate simulations, and consequently in the reliable simulation of the future climate state. These goals will help answer the questions posed by SPARC: "*What changes have occurred in the atmosphere? What processes are / might be causing them? How well can models reproduce these changes?*" (SPARC, 1998). Our objectives will also contribute to the IGAC goal "*to improve our ability to predict the chemical composition of the atmosphere over the coming decades by integrating our understanding of atmospheric processes with the response and feedbacks of the Earth System*" (IGAC, 2003).

The current document is the "Science Plan of the Atmospheric Chemistry Division of the National Center for Atmospheric Research (NCAR) for the Next Five Years and Beyond." The plan describes what the Division staff intend to accomplish between 2003 and 2008, and why those choices have been made. The plan describes both the individual efforts that form the essential components of the larger integrative studies as well as the integrative studies themselves. Details of how the Division plans to meet these goals are described at the MIRAGE (Megacity Impacts on Regional and Global Environments) web site (http://mirage-mex.acd.ucar.edu/), the UT/LS "Integrated study of dynamics, chemistry, clouds and radiation of the upper troposphere and lower stratosphere" web site (http://www.acd.ucar.edu/UTLS/), the Chemistry-Climate Interactions website (http://www.acd.ucar.edu/chemistry-climate/), the WACCM (Whole Atmosphere Community Climate Model) web site (http://acd.ucar.edu/models/WACCM/), and the Biogeosciences web site (http://www.acd.ucar.edu/oppFund/BGS/HOME.htm). Furthermore, the requirements for the development of instrumentation, models and remote sensing are described in companion documents. These documents, together with the document describing our plans for community service and education and outreach, constitute the ACD Strategic Plan for the coming years.

1.0 Introduction

1.1 Mission

The ACD mission is (1) to understand the chemical composition of the atmosphere, the processes that modify and control the composition, and potential changes that may result from natural and human induced forcings; (2) to provide relevant, reliable, accessible, unbiased, and timely information on atmospheric chemistry to government and society; and (3) to act as an intellectual resource and enabler to the wider atmospheric sciences community through the development of new measurement capabilities and methodologies, development and application of numerical models that reliably simulate present and future atmospheric conditions, and the planning and execution of field experiments to address specific scientific questions of regional and global significance.

1.2 Scientific Scope and Societal Relevance

By the end of the 20th century the human population of the planet had risen to over 4 billion. Growth in population is the principal driver of global change that in its many forms challenges society. Currently, global change is manifest by unprecedented changes in atmospheric composition. For example, increased concentrations of sulfates and nitrates in the atmosphere produce acid rain which damages many ecosystems; extensive fossil fuel combustion leads to nitrogen oxide (NO_x) emissions to the atmosphere resulting in increased concentrations of ground level ozone (O_3) that causes health effects and damages crops and ecosystems; many human activities lead to the release and increased concentrations of volatile organic compounds (VOCs) that contribute to ground level ozone; increased concentrations of methane (CH_4), nitrous oxide (N_2O), and chlorine and bromine compounds have upset the natural balance of stratospheric ozone and have resulted in polar stratospheric ozone depletion and increased surface UV radiation; long-lived compounds (CH_4, N_2O, chlorofluorocarbons [CFC], halons) released to the atmosphere accumulate and significantly perturb the radiative forcing of the climate system; and short-lived compounds (NO_x, sulfur dioxide [SO_2], VOCs) released to the atmosphere contribute to the formation of inorganic and organic aerosols that cause respiratory problems and influence radiative forcing both directly and indirectly through the modification of cloud properties and precipitation.

Many of these processes are either coupled directly in the atmosphere or indirectly through interactions with other components of the physical or biological climate system. These different processes can act synergistically or antagonistically or there may be compensation points where different processes might offset each other. For example, it is believed that the destruction of the ozone layer and the increase in near-surface aerosol loadings may have counteracted the increased radiative forcing due to the growth of many greenhouse gases, including ozone depleting chemicals, and therefore masked the early indicators of climate change. As population continues to grow and steps undertaken to remediate environmental problems become effective, it is likely that compensation points will change.

Population will continue to increase, likely doubling over the next 50 years before stabilizing and reducing sometime near the end of the 21st century. Much of that population growth will occur in the tropics and will be accommodated in megacities surrounded by intensively farmed agricultural zones that will have replaced much of the tropical rainforest and grasslands. The tropics are a critical component of the climate system because incoming solar energy is at its most intense and perturbations to the flow of solar energy there will likely be greater than perturbations at high latitudes.

Progress in understanding the science underlying the consequences of these societal challenges will come through complex integrative efforts well-suited to the coordination and underpinning that ACD/NCAR can provide. Understanding of atmospheric composition has always been led by the observation of new phenomena and relationships in the atmosphere. Increasingly these multidisciplinary/multi-investigator studies involve satellite remote sensing of key components that enable local observations to be placed in a broader context. Results from such extensive field observations along with fundamental laboratory and chamber studies will be integrated with simulations from next generation Earth system models that represent both the interactions within and between the principal components of the climate system. The resulting synthesis will provide a profound understanding of the Earth system and how its components interact and will provide the necessary underpinning for scientific assessments sponsored by the Intergovernmental Panel on Climate Change (IPCC), World Meteorological Organization (WMO)/ United Nations Environment Programme (UNEP), and the U.S. Environmental Protection Agency (EPA) that are required for thoughtful policy decisions.

1.3 Approach and Strengths

ACD has advanced understanding in atmospheric chemistry from the integration of knowledge gained from three major disciplines:

1. Process studies--Laboratory studies of fundamental reaction rates and mechanisms involving gas phase and multiphase systems, and flux measurements of trace compounds from a variety of plant species.
2. Observations--Development of trace gas, aerosol, and radiation measurement instrumentation, and the deployment of this instrumentation in field and satellite programs which provide comprehensive data on atmospheric composition, trends, and variability over a range of spatial and temporal scales.
3. Models--Numerical model simulations of complex mixtures of trace gases found in the atmosphere and how they respond to changes in external forcing.

Activities in these major disciplines are highly synergistic. For example, parameters determined in fundamental process studies provide the input to numerical models of atmospheric composition and often suggest exploratory field studies. New field measurement instruments often evolve from techniques employed and developed in the laboratory. Results from model simulations may be used to identify key processes requiring further laboratory study, or to aid in the planning of field campaigns. Finally, comparisons of numerical model simulations with comprehensive measurements of atmospheric composition (obtained from major field programs) test basic hypotheses, and highlight gaps in our understanding of atmospheric processes.

1.4 Future Research

The coming years will be an exciting time for ACD and the atmospheric science community that it serves. NSF will augment the fleet of atmospheric research aircraft with the G-V (HIAPER), a long-range, high-flying aircraft ideally suited to atmospheric chemistry studies.

New satellite instruments such as HIRDLS on board the Aura spacecraft will soon be making unique observations ranging from the upper troposphere to the mesosphere. Ever increasing computational power means that chemistry-climate studies unthinkable a few years ago can now be pursued.

Given the ACD heritage in field and laboratory studies, numerical simulations, and remote sensing, and with new tools becoming available in the near future, ACD is poised to make significant advances in two areas of societal importance - Regional and Global Air Quality, and Chemistry in the Climate System. We have identified several research themes within each of these areas (listed below), which will be described in Sections 2 and 3 of this document.

Regional and Global Air Quality
- Influence of urban pollution on regional and global air quality
- Reactive carbon research
- Multiphase processes in the troposphere

Chemistry in the Climate System
- Chemistry-climate modeling studies
- Biogeochemical cycles
- Integrated studies of dynamics, chemistry, clouds, and radiation of the upper troposphere and lower stratosphere
- Middle atmosphere science

1.5 Partnerships, Synergism and Integration

ACD has significant collaborations across NCAR divisions and with the university and government communities and other laboratories both nationally and internationally. Within NCAR, ACD scientists and software engineers collaborate with the Climate and Global Dynamics (CGD) division on the relationships between atmospheric chemistry, biogeochemistry, and climate and contribute to the Community Climate System Model (CCSM). ACD also collaborates with the High Altitude Observatory (HAO) on the chemistry and dynamics of the upper atmosphere through the development of WACCM. ACD scientists and software engineers also work with the Mesoscale and Microscale Meteorology (MMM) division on air chemistry modules for the Weather and Research Forecasting (WRF) model coupled with chemistry (WRF-Chem.), and will also be collaborating with MMM and CGD scientists on studies of the UT/LS. ACD scientists and engineers work closely with the Atmospheric Technology Division (ATD) on the development of state-of-the-science instrumentation and in supporting community instrument developments and deployments. This activity will increase significantly as instruments are developed for the HIAPER aircraft platform. ACD is also planning collaborations with scientists from the Environmental and Societal Impacts Group (ESIG) on the societal implications of global change including urbanization, land use change, and pollution transport.

ACD scientists partner with many of our university and overseas colleagues on joint projects and field programs, on integrated field campaigns organized by ACD, and on measurement and model intercomparison exercises. ACD scientists also participate in programs organized by many of the other agencies engaged in environmental research such as the National Aeronautics and Space Administration (NASA), the National Oceanic and Atmospheric Administration (NOAA), and EPA.

In addition to the work of ACD that is supported by NSF's Atmospheric Sciences (ATM) division, many ACD scientists are engaged in collaborative research within other NSF programs. These programs include the polar program, the biocomplexity program, and the information technology research program, and the scientific questions examined are always pursued in collaboration with the university community. ACD activities are entirely consistent with NSF's "Outcome Goals" to invest in people, ideas, and tools (NSF GPRA Strategic Plan, FY 2001 – 2006) through our efforts to develop opportunities for young scientists and strengthen the scientific research potential of all scientific staff; to identify and contribute to the understanding of fundamental aspects of atmospheric chemistry; and to utilize and develop state-of-the-art instrumentation for use on ground-based, airborne, and satellite platforms.

The research outlined in the current ACD science plan enhances and supports the research efforts of other national and international programs, including NASA (www.earth.nasa.gov/visions/index.html), NOAA (www.osp.noaa.gov), IGAC, (www.igac.noaa.gov), and SPARC (www.aero.jussieu.fr/~sparc/initiatives.html), that address various aspects of atmospheric chemistry, dynamics, and chemistry/climate interactions.

For example, IGAC, a project of the IGPB and the Commission on Atmospheric Chemistry and Global Pollution (CACGP), focused primarily on tropospheric chemistry/climate, has developed three fundamental objectives that IGAC-II will pursue:

- To accurately determine global distributions of both short and long lived chemical species in the atmosphere and to document their changing concentrations over time.
- To provide a fundamental understanding of the processes controlling the distributions of chemical species in the atmosphere and their impact on global change and air quality.
- To improve our ability to predict the chemical composition of the atmosphere over the coming decades by integrating our understanding of atmospheric processes with the response and feedbacks of the Earth System.

ACD scientists are involved in various aspects of these national and international programs through a significant number of university and interagency collaborations. As seen below, the research goals of ACD augment and align with the goals of the above programs.

The following sections describe the ACD research plans for Regional and Global Air Quality (Section 2) and Chemistry in the Climate System (Section 3). Companion documents describe plans for the development of instrumentation, models, and remote sensing that will be required to achieve the goals outlined below.

2.0 Regional and Global Air Quality

2.1 Overview

The deterioration of air quality is a major environmental problem not only in urban areas, but also on regional and global scales. Satellite-, aircraft-, and ground-based observations throughout the global atmosphere are confirming that air pollution can be transported over large distances, e.g., from eastern Asia to the western U.S., from North America to Europe, and from mid-latitudes to the Arctic. Serious related concerns exist on continental scales for human respiratory health, cultivated and natural ecosystems damage, and visibility degradation, and on global scales for changes in radiative forcing and tropospheric oxidation (self-cleaning) capacity. Future emissions of primary pollutants and precursors of secondary pollutants are expected to increase as both population and economic development continue to increase.

Discussions of air quality generally center on issues related to atmospheric oxidants and particulates. Increases in tropospheric ozone are of particular concern as this compound is toxic to humans and to natural ecosystems, and is currently ranked as the third most important "greenhouse" gas. Thus, future trends in its concentration have strong links to both global air quality issues and to climate change. Potential global changes in hydroxyl radical (OH) concentrations are another major concern. OH is responsible for initiating the oxidation of many compounds emitted to the atmosphere into more soluble species that are removed from the atmosphere by wet and dry deposition or scavenged by aerosols in multiphase processes. These oxidative processes have been remarkably efficient in removing from the troposphere the enormous quantities of gaseous emissions (toxic gases, sulfur and nitrogen compounds, carbon monoxide [CO], CH_4, reactive carbon compounds, etc.) from anthropogenic activity (fossil fuel combustion, biomass burning, agricultural and industrial practice, and changes in land use) and from marine and terrestrial ecosystems, lightning-produced NO_x, and wildfires. Critical challenges within the context of global change will be to determine if the capacity of the atmosphere to remove these gaseous species will be reduced, and/or if climate change will affect the oxidation or emission processes and lead to significant change in the chemical composition of the troposphere.

The tropospheric ozone burden is dominated by non-linear photochemical processes involving the HO_x (OH, HO_2, and organic peroxy radicals) and NO_x (NO and NO_2) families, as well as CO, CH_4, and larger reactive carbon compounds. The overall process can be described as a set of photochemical reactions which cycle HO_x and NO_x between family members, consuming (oxidizing) carbon "fuel" while generating ozone and other secondary pollutants as by-products. The corresponding steady-state OH concentrations depend sensitively, and non-linearly, on the amounts of NO_x and VOC precursors.

Air quality continues to be a major source of concern in urban and regional environments. Furthermore, transport of ozone and some ozone precursors out of densely populated areas has led to increases in ozone on the global scale (estimated at 30% increase since the preindustrial era), and larger increases are expected with the demands of population growth. One of the major research themes within ACD in the coming years will be to investigate the influence of the export of urban pollution on regional and global air quality (see Section 2.2).

Reactive carbon species (CO and VOC) play a central role in determining tropospheric air quality. Primary VOC emissions are extremely diverse chemically, with both natural and anthropogenic sources, and range in complexity from simple gases such as methane to more complex chemical forms like the terpenes (naturally-occurring isomeric compounds of general formula $C_{10}H_{16}$). Once in the atmosphere, these gases are oxidized to more soluble forms (carbonyl compounds, organic nitrates, organic acids, multi-functional species, etc.) that are more readily removed from the atmosphere by deposition, or that can couple back into the HO_x and NO_x chemical cycles -- often at significant distances from the original source regions. The impact of the VOC on the troposphere is profound. First, CO and VOC oxidation generates the peroxy radicals that are a necessary component of ozone production chemistry. As the major reactants for OH, CO and VOC exert a controlling influence on the abundance of this radical and hence on the oxidative capacity of the troposphere. Some halogenated organic trace gases react slowly in the troposphere and are thus transported to the stratosphere, where their degradation releases active halogen that contributes to ozone loss. Finally, VOC can affect climate, as their oxidation can lead not only to the production of greenhouse gases (carbon dioxide [CO_2] and O_3), but also to highly soluble, low volatility compounds that contribute to the nucleation and/or growth of radiatively active aerosol and cloud condensation nuclei. The complex photochemical processes involved in the oxidation of VOC will continue to be a major topic of research within ACD, as outlined in Section 2.3.

Multiphase processes (gas-aerosol-cloud interactions) are increasingly recognized as being important to tropospheric air quality. High particulate concentrations, now common in and around urban centers but increasingly present on continental scales, pose a significant health risk. Many aerosols serve as cloud condensation nuclei and therefore influence cloud particle properties (e.g., albedo) and precipitation. They also directly scatter or absorb light, thus altering the atmospheric radiation field and photochemical rates, and reducing visibility. In addition, particles can act as sinks for some atmospheric oxidation products including sulfuric and nitric acid, ammonia, and many products of reactive carbon oxidation. The ability of aerosol particles to process gas phase compounds (in particular organics) remains largely unexplored, though such information could be important for understanding both gas and particle evolution. Clouds, too, influence both tropospheric air quality and climate through their impact on the hydrologic cycle, as transporters, processors, and scavengers of pollutants, and *via* their effects on the tropospheric radiation field. Deep convective clouds play a particularly important role as transporters of constituents from the polluted boundary layer to the upper troposphere, which enhances ozone production in the upper troposphere where changes in ozone have their largest radiative impact. Elucidation of the many complex physical/chemical processes involved in the multiphase chemistry of the troposphere - from particle nucleation and growth, to impacts of aerosols on gas phase composition, and the impacts of clouds as transporters and processors of trace gases - will be a major focus of ACD research activity (Section 2.4).

ACD will continue its lead role in improving our understanding of the complex photochemistry that governs air quality through 1) the organization of extensive ground-based and aircraft process studies; 2) instrumentation development for in situ measurements of “stable” and radical constituents, emission fluxes, and radiation fluxes during ground and aircraft programs; 3) laboratory studies of homogeneous and heterogeneous processes; 4) instrumentation development for satellite and other remote sensing measurements; 5) development and application of box, regional, and global scale models; and 6) participation in aircraft and ground-based process studies led by other agencies. Remarkable advances have been made over the last decade through the coordination of modeling efforts with larger-scale process studies conducted on the ground or on aircraft platforms. Particularly important has been the development of instrumentation for measurements of OH, HO_2, and peroxy radicals (RO_2), which together with instrumentation for in situ measurements of many of the precursors of ozone and HO_x have allowed detailed chemical closure experiments to be undertaken. Scientists in ACD will continue to apply this broad array of expertise to the study of important issues in tropospheric photochemistry/air quality in the coming years. The research will focus on the three themes that have been introduced in the preceding paragraphs (influence of urban pollution on regional and global scales; reactive carbon; and multi-phase chemistry), as described below.

2.2 Influence of Urban Pollution on Regional and Global Air Quality

GOAL: To characterize the chemical/physical transformations and the ultimate fate of pollutants exported from urban areas, and to assess the current and future impacts of these exported pollutants on regional and global air quality, ecosystems, and climate.

Urban areas are strong sources of pollutant gases and aerosols that can influence both regional and global environments. These pollutants include primary pollutants (e.g., VOC and NO_x) released into the urban atmosphere, as well as secondary pollutants produced in the atmosphere by photochemical processing (e.g., ozone, inorganic and organic nitrates, acids, peroxides, carbonyls, and other partly oxidized organics). Many of these secondary pollutants play an important role in the atmosphere far from source regions, for example as sources of HO_x and NO_x in the remote atmosphere. Aerosols may be both primary (emitted directly) and secondary, i.e., formed in the atmosphere by nucleation and condensation of gaseous compounds. The chemistry of this coupled gas-aerosol system is not well-understood, especially for the complex mixtures expected downwind of large urban areas. Many of the chemical and physical processes are non-linear, so it is not possible to apply simple scaling relationships (e.g., simple dilution) to estimate the impacts of current emissions and future urban growth on surrounding areas; therefore, detailed numerical model representations of the primary chemical and physical processes are required. Particularly complex behavior can occur near heavily polluted regions, where local pollution can be concentrated enough to saturate and suppress chemical reactivity. While this suppression may result in lower surface ozone concentrations locally, it shifts the reactive burden to larger geographic scales via the export of unreacted or partly reacted ozone precursors. Additional complex feedbacks can arise when urban environments modify the local meteorology (and therefore the export patterns) through changes in the surface heat, moisture, momentum, and alterations of boundary layer dynamics due to the absorption of radiation (both incoming and outgoing) by locally large concentrations of pollutant aerosols and gases.

ACD will focus its research towards a quantitative understanding of the chemical processes occurring during urban plume evolution, and the potential impacts on regional and global environments. Questions to be addressed include the following:

1. What is the chemical evolution of urban outflows (especially ozone, nitrogen oxides, VOCs, radicals, peroxides, acids)? Do hydrocarbon oxidation intermediates provide

substantial residual reactivity? How important are nighttime processes in the chemical processing of urban outflow?

2. What are the interactions between aerosol growth and gas phase chemistry? Are significant amounts of reactive gases being lost to aerosols? Is the relative importance of secondary aerosols increasing during export?

3. What are the effects of non-urban emissions (e.g., from vegetation, biomass burning, and lightning) when mixed with evolving urban plumes?

4. How does urban outflow impact the regional and global budgets of oxidants, HO_x radicals, NO_y reservoirs, and aerosols?

5. What determines the geographical and temporal extent of urban plumes? How are outflows affected by local, regional, and synoptic-scale circulations? How is local meteorology affected by urbanization (e.g., through changes in the surface heat, moisture, momentum, aerosol, and gas fluxes)?

6. How do gaseous and aerosol pollutants affect atmospheric and surface radiation on local, regional, and ultimately global scales? What are the consequences for surface and atmospheric energy budgets, photolysis processes, and visibility?

7. How are pollutants affecting downwind cloud formation, cloud reflectivity, and precipitation?

8. How is deposition of pollutants affecting downwind natural and agricultural ecosystems? What are the associated economic impacts?

Progress towards answering these questions will require a coordinated effort encompassing observations in the field and from satellites (e.g., monitoring urban CO plumes from MOPITT), modeling of chemical and transport processes, and quantitative characterization of key chemical transformations in controlled laboratory studies. ACD is in a unique position to lead such a program, based on its proven record of collaborative efforts with universities, government agencies and other research institutions, as well as through the expertise of its own scientific staff. Recognizing this, ACD scientists have initiated an integrated multidisciplinary program (MIRAGE), to study the export and transformations of pollutants from large urban areas to regional and global scales. For the next few years, the major activity under the MIRAGE umbrella will be the planning, preparation, and execution of a large field campaign to study pollution outflow from Mexico City (MIRAGE-Mex). Advantages associated with this particular megacity include the existence of an established urban pollution monitoring network (thus providing the necessary initial conditions for studying outflow chemistry), the existence of excellent logistic infrastructure and local collaborations, and the expectation of a high signal-to-noise for the strong urban plume relative to the regional background. The objectives are to examine the extent and the chemical composition of the urban outflow as it ages over several days, focusing on the interactions between gas phase photochemistry, physical and chemical evolution of aerosols, atmospheric radiation budgets, and local and regional meteorology. The field campaign is tentatively scheduled for early 2006, and will consist of several coordinated activities:

- ***Aircraft-based outflow measurements:*** *Flight paths to examine chemical composition of background air and of the plume as a function of downwind distance and altitude. To include* O_3 *(in-situ and remote), reactive nitrogen (*NO_x*,* NO_y*,* HNO_3*, PANs,* $RONO_2$*, HONO,* NO_3*,), CO,* CH_4*, VOC, oxygenated organics (*CH_2O*, other aldehydes, ketones, alcohols, peroxides),* SO_2*,* H_2SO_4*,* H_2O_2*,* CO_2*; aerosols (size distribution, chemical composition, physical and optical properties), standard state parameters (z, p, T, rh, global radiation, shortwave radiation) and UV actinic flux.*
- ***Ground-based measurements in Mexico City:*** *Characterize the initial chemical (gas and aerosol) composition. To include* O_3*,* NO_x*, speciated VOCs, aerosol size-resolved composition and solar radiation, and wind profilers for boundary layer evolution.*
- ***Ground-based measurements on mountain passes near Mexico City:*** *Examine early stages of the outflow. To include* O_3 *(in situ and remote),* NO_x*, speciated VOCs, aerosol size-resolved composition, solar radiation, and wind profilers.*
- ***Satellite-based observations:*** *Characterize the geographical location and extent of the plume, for flight planning and for interpretation of the results. To include measurements of cloud cover, aerosols, CO,* NO_2*,* CH_2O*,* SO_2*, and* O_3*.*
- ***Modeling:*** *In advance of the campaign, to design the overall flight plan strategy; during the campaign, to assist with specific flight planning; after the campaign, to interpret results and evaluate models. To include detailed photochemical process and radiation models; regional nested grid episodic chemistry-transport models; and global chemistry transport models.*

Participants will include scientists from several NCAR divisions as well as from U.S. and Mexican government agencies and universities. Simultaneous aircraft-, ground-, and satellite-based observations will be coordinated to provide a comprehensive picture of the extent and composition of the Mexico City outflow. A vigorous modeling activity will be required at all stages, from early planning through field campaign execution and continuing to analysis and interpretation of the results.

In parallel with the planning and execution of the Mexico City field campaign, ACD will continue a variety of activities that contribute to the understanding of regional and global air quality. These include participation in field campaigns led by other organizations (such as NASA's Intercontinental Chemical Transport Experiment [INTEX], NOAA's Northeast- North Atlantic 2004 [NENA], and a joint EPA and NSF study of the Chemical Emission, Loss, Transformation and Interactions within Canopies [CELTIC]). Additional activities consist of instrument development, including Chemical Ionization Mass Spectrometry (CIMS) techniques for reactive nitrogen and organic aerosol measurements, Proton Transfer Mass Spectrometry (PTR-MS) for measurement of oxygenated organics, and advanced laser techniques for detecting aldehydes. Furthermore, laboratory measurements of fundamental chemical processes (especially gas phase hydrocarbon oxidation and aerosol growth), and continued improvement of process models and chemistry-transport models (regional and global) are ongoing. Finally, satellite observations will play an increasing role in quantifying the export of urban pollution to larger geographical scales, both in combination with field campaigns such as that planned for Mexico City, and in extending the knowledge base to other megacities. Already, a joint Canadian-U.S. instrument, MOPITT, aboard NASA's Terra satellite, is making global measurements of CO and methane. ACD is responsible for the continued development of the data reduction algorithms, for operational processing, and for data delivery to NASA for use by the international science community. This is the first dataset of its kind, and represents a significant advance in satellite remote sensing of the troposphere, since CO and methane are among the few tropospheric trace gases that can be successfully monitored from space. CO is a good tracer of both natural and anthropogenic pollution since it is produced by incomplete combustion processes such as the burning of fossil fuels in urban and industrial areas, the use of biofuels in developing countries, biomass burning in the tropics, and wildfires.

Looking further into the future, the deployment of the HIAPER aircraft will enable us to study pollution outflow to the upper troposphere, simultaneously with measurements in the lower and middle troposphere (e.g., C-130-based). Such whole-troposphere studies should allow much more stringent closure on the regional budgets of chemical constituents from the urban outflow. Of particular importance will be the ability to study the effects of clouds on the transformation and vertical redistribution of pollutants (see also Section 2.4), as many megacities (including Mexico City) experience both dry and wet (deep-convective) seasons with distinctly different export patterns.

2.3 Reactive Carbon Research

GOAL: To characterize the atmospheric cycle of natural and anthropogenic reactive carbon compounds, to better quantify their central influence on tropospheric reactivity, and to assess the associated impacts on oxidant levels, regional air quality, and global climate.

As outlined in Section 2.1, the chemistry of reactive carbon compounds plays a central role in the determination of air quality. Thus, one of the major challenges in tropospheric chemistry over the next decade will be to understand and predict the fate and impacts of reactive carbon. Achieving this goal requires the study of the many complex chemical, physical, and biological processes that control the surface emissions of these species, their chemical transformations in the atmosphere (in both gas and condensed phases), and their eventual removal from the atmosphere via deposition. A number of activities in ACD, including field and laboratory observations, modeling activities, and instrument development have been focused on the study of reactive carbon over the past years. For example, observations by ACD scientists from airborne-, marine-, and ground-based platforms have expanded our understanding of the sources and distributions of primary and secondary reactive carbon products from urban sources, continental outflow, biogenic emissions, and marine surface exchange. Laboratory investigations have led to the discovery of novel processes which control the formation and atmospheric distribution of partially oxidized carbon compounds, and models that incorporate organic carbon emissions and chemistry have been developed and evaluated. Reactive carbon will remain a focus of the research conducted in ACD in the next decade. This research is closely linked with other ACD research themes presented elsewhere in this document. For example, the determination of the source strengths for biogenic VOC is a central part of research related to biogeochemical cycles (Section 3.3), and the reader is referred to that section for details. Within the MIRAGE-Mex studies (Section 2.2), there will be a focus on characterizing primary organic emissions and their evolution, including aerosol interactions. Studies related to the UT/LS region (Section 3.4) will examine reactive carbon species as sources and reservoirs of radical species and as tracers of air mass sources, while cloud-related research (Section 2.4) will examine water-soluble organic carbon and gas-aerosol partitioning of organic species.

Some of the basic scientific questions that will be addressed with the reactive carbon research theme include:

- *What are the products of the oxidation of complex biogenic and anthropogenic carbon compounds? What is the atmospheric distribution of these products? Can we understand and predict the evolution of the chemical composition of complex reactive carbon emissions from different source regions?*

The examination of these problems requires a fundamental knowledge of reaction rates and mechanisms and a theoretical model for predicting transformations. Basic laboratory investigations that include alkoxy/peroxy radical chemistry, examination of aromatic hydrocarbon oxidation, and product studies of biogenic organic gases will be conducted. Theoretical descriptions of these chemical mechanisms also need to be improved and expanded. For example, the NCAR Master Mechanism model is an explicit, detailed mechanism for tropospheric chemistry, with emphasis on the complexities of hydrocarbon oxidation. This model will be updated with new kinetic data, and extended to include gas-aerosol partitioning processes. Field investigations will range from small-scale process studies that will examine predicted versus measured products to larger survey studies that could evaluate chemical signatures from specific source regions (e.g., megacities, developing regions, land-use variations, etc.).

- *What are links between carbon oxidation and the nitrogen cycle?*

The carbon and nitrogen cycles in the atmosphere and biosphere are coupled. Deposition of labile nitrogen species from the atmosphere affects ecosystem productivity. Further, atmospheric reactions of NO_x with reactive carbon, e.g., to form organic nitrates, can impact oxidant formation as well as export of carbon and nitrogen from forest ecosystems and urban regions. Laboratory investigations of products and yields of various hydroxy and multifunctional organic nitrates and peroxynitrates will extend our understanding of the fundamental processes that act to couple the carbon and nitrogen cycles. Field studies, particularly in areas of strong emissions of reactive biogenic carbon, will examine the importance of complex organic nitrates to the reactive nitrogen and carbon budgets. In the upper troposphere, peroxyacetyl nitrate (PAN) can be the major reservoir of reactive nitrogen, and measurements of this species will be made to determine its distribution and role in this region.

- *How does reactive carbon oxidation and product formation affect atmospheric oxidant production and loss? How significant is this process in different regions of the atmosphere?*

Photochemical oxidant production involves reactions and cycling of radical species from the HO_x (OH, HO_2, and RO_2) and NO_x (NO and NO_2) families. Thus, a comprehensive description of photochemical oxidant production, especially in areas of strong VOC emissions, needs to include the effects of the many different organic peroxy radicals that are present. Chemical ionization mass spectrometer capabilities will be expanded to allow for speciated measurements of RO_2 radicals. Previous field programs have revealed serious measurement-model discrepancies for various oxygenated VOC (e.g., acetaldehyde, formaldehyde) in the free and upper troposphere, and further instrument development and measurement activities are planned to study this issue. Model investigations will examine the role of reactive carbon in radical cycling, and will compare coordinated field measurements of measured radical sources and sinks and rates of oxidant production to theoretical predictions.

- *How do reactive carbon oxidation products contribute to aerosol production, composition, and growth?*

An area of increasing interest in atmospheric chemistry is the role of organic compounds in aerosol processes. Studies to date have shown that organic species make up a surprisingly large fraction of the atmospheric aerosol. Limited data on the composition of the organic fraction suggests multiple sources: direct emission of biogenic, anthropogenic, and pyrogenic compounds; and secondary organics from precursor oxidation (e.g., dicarboxylic acids). The bulk of the organic fraction remains chemically uncharacterized, but its presence in the aerosol affects hygroscopic and nucleation properties. Research on the role of organics in aerosol nucleation and reactivity is needed, as is further chemical characterization of the aerosol organic fraction. ACD scientists will conduct basic laboratory investigations of organic acid formation, secondary product/aerosol reactions, and the role of organics in aerosol nucleation. Instrumentation will be developed to determine the principal organic components of the atmospheric aerosol and cloud water. Interactions between organic species and the aerosol phase will be incorporated into larger scale models to quantify the effects of organic aerosol on climate.

2.4 Multiphase Processes in the Troposphere

GOAL: To quantify the fundamental chemical and physical processes occurring on and in aerosols and cloud droplets, including their interactions with gas phase species, and to determine the impact of these processes on cloud and aerosol radiative properties, on atmospheric oxidant levels, and on air quality.

2.4.1 Aerosols

It is a worthy challenge to the analytical and computational skills in ACD to quantify the chemical and physical gas- and condensed-phase processes that control the number density, size distribution, chemical composition, and physical and optical properties of aerosols and to represent these processes realistically in chemistry/climate models. While progress has been made in understanding, at the molecular level, the processes involved in the nucleation and growth of sulfate aerosol, the study of the role of low volatility organic compounds in these processes is in its infancy. While it is likely that aerosols act as scavengers and/or processors of many gas-phase species (e.g., reactive radicals and multi-functional organic compounds), the quantitative aspects of these processes and their impacts on tropospheric air quality have not been fully determined. ACD will address the following aerosol-related questions.

- *What are the gas-phase concentrations and distributions of the principal secondary aerosol precursors?*

ACD scientists have been leaders in the ambient measurement of aerosol precursors through the development of state-of-the-art instruments. Measurements of ambient sulfuric acid (a major precursor of particle nucleation and growth) and of atmospheric ions and ion clusters (that are responsible for ion-induced nucleation events) are an essential contribution to our ability to understand and predict the gas-to-particle production source terms for both urban and remote regions. The important role of low volatility organic compounds in aerosol nucleation and growth will drive the development of faster and more sensitive techniques for measuring these types of compounds. Concurrent with these ambient measurements, laboratory studies examining the first steps in aerosol formation (i.e., the formation of molecular clusters) will provide unique insights into aerosol nucleation processes, while studies of gas-phase oxidation mechanisms for VOC (e.g., terpenes and aromatics) will provide important information on the sources of aerosol precursors.

- *What is the chemical composition of ultrafine particles in various regions of the atmosphere?*

ACD also has unique expertise and instrumentation capabilities to measure the chemical composition of ultrafine particles. The ultra-high sensitivity that has been achieved and the ability to apply the measurements to non-soluble molecular aerosol components have provided a foundation for aerosol growth studies in the field. ACD scientists are poised to make major advances in this science with the development of fast, efficient, and sensitive methods to measure trace biogenic and anthropogenic organic oxidation products in particles. These methods will include state-of-the-art ion sources/ion drift tube sources coupled to tandem mass spectrometers or high throughput ion trap mass spectrometers. The development of these new instruments and research techniques will ensure an appropriate leadership role for ACD scientists in ground- and aircraft-based aerosol measurements.

- *Can models be developed to predict the chemical composition of secondary aerosol (especially organics)?*

ACD scientists and their university collaborators have developed a highly detailed mechanism for the gas-phase oxidation of hydrocarbons (the NCAR Master Mechanism) that accounts explicitly for formation and destruction of thousands of intermediate species. Many of these organic intermediates are estimated to have low volatility and should therefore partition to the aerosol phase, but previous studies - based on much less detailed chemical mechanisms - have only been able to account for a small fraction of the organic species observed in aerosols. We plan to take advantage of recent increases in computational power to develop an explicit, fully coupled, gas-aerosol process model, to predict size-resolved, detailed, chemical composition profiles of aerosols under different conditions (e.g., urban, forest), and to evaluate this model using measurements obtained by the advanced instrumentation described in the previous paragraphs.

2.4.2 Clouds

Interactions between clouds, aerosols, and trace gases are complex and varied. For example, clouds modify radiative properties, which influence photochemical rates and emission rates of biogenic organic compounds. Cloud chemistry, which includes both aqueous and ice chemistry and also leads to separation of soluble and non-soluble species, affects air quality, photochemistry, and aerosol composition. Storms, especially convective systems, play a key role in redistributing chemical species through transport, wet deposition, and as a source of NO_x from lightning. The uncertainties associated with the cloud parameterizations in large-scale models are regarded as crucial impediments to further progress in the development of reliable predictive capabilities for global atmospheric composition. ACD will address the following cloud-related questions.

- *How do convective systems influence photochemically important chemical species and multiphase chemistry?*

Analysis of data from the STERAO field campaign (in which mixing ratios of several chemical species in the inflow of thunderstorms and in anvils were determined) will continue. Although a better understanding of lightning characteristics in mid-latitude convection and of the relation between lightning discharges and NO_x production has already been obtained from these data, further analysis and modeling of these data will provide a more complete understanding of the convective transport of reactive and soluble chemical species and their influence on HO_x chemistry in the upper troposphere. Analysis of data from the recent NASA CRYSTAL-FACE (Cirrus Regional Study of Tropical Anvils and Cirrus Layers - Florida Area Cirrus Experiment) study and from satellites will focus on the uptake of nitric acid on ice crystals and on the importance of lightning as a source of NO_x in the atmosphere, particularly near the tropopause. Furthermore, to assess the effect of convection on ozone chemistry in the upper troposphere, a field experiment focused on the role of convection as a source of NO_x and HO_x species in this region is planned (see UT/LS research theme later in this document). Finally, improved knowledge will allow for better parameterizations of these convective events in global climate and chemistry models.

- *What are the quantifiable effects of cloud chemistry on photochemistry and on aerosols?*

ACD scientists are also investigating the effects of clouds on photochemistry through analysis of data acquired during recent field experiments (e.g., TRACE-P [Transport and Chemical Evolution over the Pacific]) coupled with modeling studies, and through improvements in the calculation of photolysis frequencies in ACD large-scale models. These studies will be extended to show the direct interaction between the radiative effect of clouds and photochemistry, and to examine the long-term climate impacts of cloud radiative effects and chemical constituents.

The importance of cloud chemistry on photochemistry, particularly O_3 concentrations, will also be investigated with the regional model, WRF (Weather Research and Forecast)-Chem. Because WRF-Chem has the capability of predicting the concentrations of constituents in concert with the meteorology, important processes like wet deposition will be represented much more accurately than in previous studies that simulated chemistry separately from the meteorology. This feature, combined with a model that is capable of resolving clouds both temporally and spatially and is capable of simulating regional-scale domains for integration periods of days, will allow us to examine the impact of clouds on photochemistry in a more comprehensive way.

Finally, ACD scientists will study the importance of aqueous chemistry on aerosol composition and size distribution using detailed cloud chemistry parcel models and through analysis of field measurements of cloud condensation nuclei (CCN) properties. Model studies will focus on organic aqueous chemistry forming carboxylic and dicarboxylic acids, the latter directly becoming part of the CCN and affecting their properties. Organic aqueous chemistry is emerging as a topic of study in the context of organic aerosols and their importance on aerosol-cloud-climate effects.

3.0 Chemistry in the Climate System

3.1 Overview

The global climate system is a composite of local, regional, hemispheric, and interhemispheric processes that occur from the surface to the upper atmosphere on time scales from minutes to centuries. The role of chemistry in this complex system involves multiple interconnected components with a range of temporal and spatial scales. The direct influence of chemistry on the climate system occurs mainly through the absorption and scattering of radiation by trace gases and aerosols. Therefore, understanding the abundances and distributions of these trace species and the processes that control them, both spatially and temporally, are key scientific objectives. Of particular importance is understanding how these abundances and distributions will evolve and impact future climate and how climate change will impact chemistry. In this section we describe the major research themes in ACD that relate to the role of chemistry in the climate system.

A primary focus of the chemistry-climate modeling studies in ACD is to evaluate direct anthropogenic and biogenic emissions both spatially and temporally, to determine the influence of transport processes on the distribution of those emissions, and to examine the impacts of the emissions on atmospheric chemistry. Data from several satellite sensors, including MOPITT, and from in situ measurements will be used to evaluate natural and anthropogenic emissions and the resultant chemical processing in the models. In addition, the modeling studies also examine aerosol distributions, formation processes, influence on chemical species, and radiative properties and impacts including indirect aerosol and cloud effects. These studies, based on the current climate system, additionally provide a foundation for model simulations designed to study the influence and feedbacks of climate and global change on chemistry of past and, most importantly, future climate regimes (Section 3.2).

Focused studies of biogenic emissions are a key aspect of ACD research on biogeochemical cycles. These studies include measurements of emissions and vertical flux of many species, including VOCs, NO_y, O_3, and CO. These measurements have been collected on a broad range of spatial scales from leaf, plant, and canopy, through to regional scales. The implications of these flux determinations on the local, regional, and global atmosphere (Section 3.3) are evaluated through the incorporation of empirically-based flux parameterizations in numerical model simulations.

The UT/LS region of the atmosphere plays a crucial role in the climate system because of the radiative impacts of water vapor, ozone, and aerosols in that region. ACD research in the UT/LS region is focused on understanding the distributions of ozone and water vapor and how photochemistry, multiphase chemistry, convection, and stratosphere-troposphere exchange influence those distributions (Section 3.4).

The role of the middle atmosphere (the region between the lower stratosphere and the lower thermosphere) in the climate system is not well-characterized. ACD research in this area is focused on understanding the broad interactions between chemistry, radiation, and transport using a combination of models and measurements/calculations of chemical constituents and energy budgets (Section 3.5). The observations from the TIMED (Thermosphere, Ionosphere, Mesosphere, Energetics and Dynamics) mission and the HIRDLS instrument will contribute to the understanding of this region of the atmosphere.

3.2 Chemistry-Climate Modeling Studies

GOAL: *To understand the interactions between the Earth's chemical, biogeochemical and climate systems in the present, past, and possible future climates.*

The distribution and abundance of radiatively active gases and aerosols are important determinants in the Earth's radiation budget and the state of the climate system. The most important radiatively active trace gases in the atmosphere are water, CO_2, CH_4, ozone, halocarbons, and N_2O. Atmospheric chemistry and transport are key factors in determining the abundance and distribution of these trace gases and aerosols.

The atmospheric chemical system is forced by the physical climate system together with anthropogenic and biogenic emissions. Changes in the climate will impact trace gas distributions via alterations in chemical reaction rates (e.g., from changes in temperature), photolysis rates (e.g., from changes in aerosols), emissions (e.g., from changes in lightning NO_x emissions), and transport characteristics. Changes in the chemistry-climate-biogeochemistry system are expected to be strongly coupled with important, but as yet not well-quantified, feedbacks. Particularly important changes include potential alterations to the tropospheric oxidizing capacity as well as to the stratospheric ozone budget.

An understanding of the current climate-chemistry-biogeochemistry system is a prerequisite to understanding the system under different climate regimes. In particular, understanding current inter-annual variability in chemical constituents provides a methodology to predict future global change with improved confidence. An examination of interannual variability in the current climate will allow us to 1) assess and improve our ability to simulate chemical changes over the recent historical record by ongoing evaluation of models against measurements obtained from satellite-, space shuttle-, aircraft-, balloon-, and ground-based platforms; 2) identify mechanisms that drive inter-annual variability; 3) identify chemical sensitivities to these mechanisms; and 4) identify those processes, interactions, and feedbacks most important for predicting future global change.

Several models are developed or under development that will enable examination of various aspects of the climate-chemistry-biogeochemistry system. Existing models include the MOZART-2 (Model for Ozone and Related Chemical Tracers, second generation) and MOZART-3 Chemical Transport Models for the troposphere and middle atmosphere, respectively. These models can be run using imported meteorological or Global Climate Model (GCM)-generated data, but do not incorporate feedbacks between meteorology, chemistry, and the biosphere. However, models are being developed, including an Earth System Transport Model (ESTM) and an Earth System Climate Model (ESCM), that will simulate the interactions between atmospheric chemistry, aerosols, transport and the carbon and nitrogen cycles in the present-day climate, future climates and past climates. The ESCM will be an unconstrained climate model incorporating all the important feedbacks between the components of the Earth system while the ESTM will be constrained to follow a particular dynamical evolution representing actual weather patterns or simulations from a conventional climate model.

To follow are some outstanding issues and questions that must be addressed to gain a fuller understanding of the coupled atmospheric chemistry-climate-biogeochemical systems. Research activities will be focused on three areas: a study of the present-day climate system and its inter-annual variability, studies of past climate systems, and simulations of future climates states based on a range of global change scenarios.

3.2.1 The Present-Day Climate System

Initially we will examine the sensitivity of atmospheric chemical composition to four key factors -- emissions, aerosols, transport and the biosphere -- in a series of multi-year present day simulations (e.g., 1960-2000). The processes that influence the atmospheric chemical forcing of the system will be quantified and isolated to the extent possible. These simulations will be evaluated with respect to remotely sensed and in situ measurements. In addition to the concentrations of chemical species, information on the fractionation of carbon and oxygen isotopes will be considered. We will advance our understanding of the atmosphere and related Earth system components by addressing the following questions.

- *What are the magnitudes and spatial distributions of present anthropogenic, biomass burning, and lightning emissions of chemically important compounds and how do they vary seasonally and inter-annually?*

Present anthropogenic, biomass burning, lightning, and biogenic emissions of chemically important trace gases are not well-quantified in magnitude, spatial distribution, and seasonal and inter-annual variation. Uncertainties are even larger under different climate scenarios. Changes in climate will impact these emissions through changes in the magnitude and variability of precipitation and convection, through alterations in land use, and through behavioral response to climate change. Accurate emission estimates are needed to adequately constrain and evaluate chemical-climate simulations in the present climate, and to be able to simulate past and future climates.

Multi-year present day simulations will be used to evaluate the magnitude, spatial distributions, and temporal variability of emissions, as well as the effect of their interannual variability on tropospheric composition and chemistry. The emissions from biomass burning will be constrained by satellite observations of fires. The interannual variation of lightning in the simulations will be compared with satellite observations of lightning flashes. Additional satellite observations, from the wealth of Earth system remote sensing data now being derived routinely, is currently being integrated into a self-consistent form that can be used for quantitative analysis and prediction. Comparisons of model results and new satellite data will help both the data and model validation efforts. For example, the combination of global satellite measurements and inverse modeling procedures will be employed to verify or constrain emissions inventories for CO using MOPITT data, and for aerosols using MODIS and AVHRR (Advanced Very High Resolution Radiometer) data.

Because our emphasis is on the analysis of present-day tropospheric composition, these simulations will be performed using MOZART-2. The use of analyzed winds will enable the direct comparison of model results with observations.

- *What determines the distributions of radiatively and chemically active species? What are the impacts on the distribution of chemical species from intercontinental transport, convection, synoptic transport, local circulation (land-sea breezes), inter-hemispheric transport, cross-tropopause transport, North Atlantic Oscillation/Arctic Oscillation (NAO/AO), and El Niño-Southern Oscillation (ENSO)?*

Transport significantly influences the distributions and concentrations of many atmospheric chemical species. Transport processes in the troposphere and in the lowermost stratosphere are not well-quantified and also may be altered by changes in the physical climate system. Current model transport schemes parameterize many sub-grid scale transport processes such as horizontal mixing, the effect of gravity waves, and convective and boundary layer transport, and the accuracy of these parameterizations, particularly under changing climate conditions, must be evaluated.

Complex and poorly understood interactions between transport and cloud microphysics govern the transport of water vapor across the tropopause. Water vapor plays a crucial role in radiative processes near the tropopause while the nature of the chemistry in the stratosphere depends on the magnitude of water transported across the tropopause. Interactions between chemistry and transport that govern the O_3 balance in the UT/LS (the region where the radiative response to ozone is most sensitive to its distribution) are also not well-understood.

Multi-year present day simulations will be used to isolate the effect of meteorological variability (including variability in transport, variability in temperature fields, changes in photolysis rates due to changes in cloudiness, changes in wet and dry deposition, and changes in lightning NO_x emissions) on the distributions of radiatively active trace species. Convective and boundary layer parameterizations developed for the Community Climate System Model (CCSM) will be evaluated in the chemical atmospheric models by comparison with concentrations of observed trace species. Influence of stratospheric/tropospheric exchange on chemistry and climate will be investigated in a fully coupled model (i.e., the ESCM) with emphasis on chemical radiative transport processes.

- *What are the fundamental processes that control the formation, growth, and spatial distribution of aerosols, and hence their impacts on radiation? What are the impacts of aerosols on distributions of chemical species? What are the effects of the formation of aerosols on the tropospheric oxidant balance? What radiative-dynamical feedbacks are governed by the distribution and composition of aerosols?*

Although sea salt, mineral aerosols, smoke and other particles are released directly into the atmosphere, the formation, composition, growth, and removal of many aerosols, including most CCN, is governed by chemical processes in the atmosphere. Our understanding of fundamental aerosol processes and how they are represented in numerical models is still in its infancy. Many aerosol processes need to be further elucidated, including those controlling aerosol formation and growth, chemical composition, hygroscopicity, and removal rates. Furthermore, the reactive, radiative, and microphysical properties of aerosol depend on the multi-component nature (sulfate, nitrate, sea salt, mineral dust, biogenic carbon, black carbon, ice, etc.) and segregation (internally or externally mixed, agglomerated) of the aerosol. The global distributions of aerosols and the processes which control these distributions are not well-quantified, nor are the effects of aerosol formation on the tropospheric oxidant balance and the concentration of aerosol precursors, such as SO_2, NH_3, H_2SO_4, HNO_3, VOC and their degradation products.

Interannual variability of the formation, composition, and radiative impact of aerosols will be studied using the multi-year present day simulations. The interactions and feedbacks among aerosols, dynamics, chemistry, and water cycle in the present climate will be examined in coupled chemistry-climate simulations.

To take full advantage of the aerosol development work conducted in NCAR's CGD Division (especially the aerosol-radiation feedback), this work will be performed in the ESCM/ESTM framework after inclusion of the MOZART-2 aerosol package.

- *What are the responses of biogenic emissions to changes in temperature, the water cycle and atmospheric composition? What are the impacts of atmospheric composition on the carbon cycle and climate through nitrogen fertilization? What are the impacts and resultant feedbacks of surface ozone and other pollutants on vegetation growth, terrestrial carbon storage, and ecosystem dynamics?*

The nature and magnitude of the interactions between atmospheric composition and the biogeochemical system, and their influence on the climate system, is highly uncertain. The importance of these interactions and possible feedbacks between the biosphere and atmospheric chemistry will be quantified under present, future, and past climates. Impacts on the water, energy, carbon, and nitrogen cycles as well as biogenic emissions will be considered. Processes that will be studied include the response of biogenic emissions to changes in temperature and the water cycle; the impact of atmospheric composition on the carbon cycle and climate through nitrogen fertilization; and the impact of surface ozone and other pollutants on vegetation growth and dynamics. All of these studies will require simulations that incorporate interactive biosphere models. Adding to the complexity of the climate system, these impacts may feedback through the climate system onto the biosphere.

Since the goal is to identify the feedback of biogenic emissions on climate variables, the ESCM will be used to fully explore the coupled nature of this problem.

3.2.2 Simulations of Past and Future Climates

Accurate understanding of past and future climate changes requires assessment of potential impacts of various emissions scenarios and possible feedback mechanisms. Simulations of past climates provide an opportunity to test our models under dramatically different chemical climate regimes to identify and understand potential non-linear feedbacks, thus providing more confidence in simulations of future climate.

- *What are the chemistry-climate interactions and their influences on tropospheric oxidizing capacity through geologic time, including interactions amongst aerosols, biogenic emissions, and biogeochemistry?*

ACD scientists will study the chemistry and climate over time periods characterized by dramatically different atmospheric composition, climate, solar forcing, and anthropogenic and natural emissions. Methane concentrations will be simulated on paleo timescales using the ESCM. Short simulations not requiring coupling between chemistry and climate will make use of the ESTM driven by meteorological fields simulated by the CCSM for the relevant period. Methane abundances have been determined from ice-cores over 400,000 years before present and play a central role as an indicator of the tropospheric oxidizing capacity.

- *How will simulations using IPCC scenarios of future emissions differ from those using current emission estimates? What will be the impact on the carbon cycle of changes in nitrogen deposition and ozone stress? What will be the effect of changing climate on lightning* NO_x *emissions (through changes in convection)?*

Model simulations of future climates will be made using coupled chemistry-climate models, which will include aerosols, and will be capable of simulating the biogenic, land use, and ecological responses to climate change. Feedbacks will be identified that are likely to result in amplification of chemical changes, including dynamical and biological interactions. Future studies will use chemistry inline in the ESCM, allowing detailed chemical coupling between tropospheric chemistry, the biosphere, aerosols, and the stratosphere. Particular attention will be given to the radiatively active species and the tropospheric oxidation capacity. The uncertainty of our prediction will be estimated based on studies of the present and past climates.

3.3 Biogeochemical Cycles

GOAL: To understand the exchange of trace gases and aerosols between the Earth and atmosphere, to quantify the controlling processes, and the feedbacks of these processes to climate change.

The bi-directional exchanges of trace gases and aerosols between the Earth surface and the atmosphere are controlling factors in the determination of tropospheric chemical composition. Accurate predictions of future atmospheric chemical distributions require a quantitative understanding of these controlling factors. Fluxes of reactive chemicals are impacted directly by anthropogenic activity as well as indirectly by human influences on terrestrial and marine ecosystems. Terrestrial ecosystem fluxes, including snow and ice-covered surfaces, are very sensitive to climate and land management change and a better understanding of their controls is needed for assessments of the total environmental impact of global change. Marine ecosystem fluxes may also be sensitive to climate change through perturbations of the interactions between physical, chemical, and biological processes occurring in the oceans and the atmosphere.

Biogenic emissions may directly or indirectly influence the distribution of radiatively active gases and aerosol, resulting in a global warming or cooling that will impact the biosphere through non-linear relationships with the ecological and physiological processes controlling emissions. This interaction could result in a global feedback involving the chemical and physical climate system and could operate over a wide range of temporal and spatial scales. ACD will continue multidisciplinary studies that address the interactions among the carbon, nitrogen, water, and aerosol cycles. The goals of this research are

1. to quantify the major factors controlling spatial and temporal (diurnal, seasonal and interannual) variability of reactive gas and aerosol fluxes between the atmosphere and terrestrial biosphere;
2. to estimate the influence of biosphere-atmosphere exchange of trace gases and aerosols on climate, air quality, radiative forcing, and ecosystem function on regional to global scales;
3. to understand how biogeochemical cycles respond to changing climate conditions, and identify the feedbacks and interactions among global and climate change, land management, urbanization, technological development, economics, and political and individual decision-making; and
4. to identify and quantify the key factors controlling variation in pyrogenic emissions and to understand how biosphere-atmosphere trace gas and aerosol exchange is modified by fire frequency and intensity.

Progress in this area will come from the development of instruments and models to measure and simulate trace gas and aerosol exchange at the process level, as well as on canopy, regional and global scales. Systems for measuring vertical turbulent fluxes of isoprene and other VOC, NO_y, ozone, ammonia, particles, and CO have been or are being developed for tower and aircraft platforms. ACD will continue to organize and lead community field campaigns to address key questions related to biosphere-atmosphere chemical exchange and transformations. Empirical model parameterizations that are valid under changed climate conditions will be developed from biogenic emissions measurements made in controlled-environment growth chamber studies. Numerical modeling studies on several spatial scales will be conducted; trace gas and aerosol exchanges will be incorporated into the coupled CCSM framework, the impact of future land management and climate on air quality will be investigated with regional models, and numerical studies of biological, chemical, and physical processes and interactions occurring in and above the forest canopy will be conducted. ACD research efforts will address the following questions.

- *What is the response of terrestrial gas and aerosol exchange to land management and climate change?*

Studies of terpenoid compound emissions will be expanded to include other VOC, CO, NO_y, NH_3 and particles. A greater emphasis will be placed on growth chamber studies and regional flux measurement studies using aircraft turbulent flux measurement systems. In addition to studies in the U.S., we will continue our investigations of the tropical landscapes (Africa, Americas, and Asia), that dominate global fluxes and are rapidly changing yet are the least well-understood.

- *What are the reactive biogenic carbon and nitrogen interactions and impacts on oxidants and aerosols within and above forest canopies?*

ACD scientists will continue to lead studies with substantial university participation that will simultaneously measure fluxes and concentrations of isoprene, monoterpenes, sesquiterpenes and other VOC, CO_2, H_2O, O_3, CO, SO_2, NO_y, organic nitrogen, PAN, MPAN, NH_3 and particle size distribution, numbers, and chemical compositions at multiple heights within and above vegetation canopies. The relative roles of soil and canopy fluxes in controlling oxidant and aerosol formation and growth will be investigated using observations during the CELTIC field campaign and one-dimensional canopy model simulations. The improved understanding of these processes will be used to parameterize regional and global three-dimensional models.

- *Can the significant sources (and sinks) of reactive carbon be more accurately quantified? What are the variations in surface exchange rates and controlling variables?*

To even begin to evaluate the role of reactive carbon in the atmosphere requires the accurate prediction of the rates of surface exchange (emission and deposition) of reactive carbon species and an understanding of the processes that control these exchanges. ACD has established a leading role in developing and applying methods to measure and model fluxes of reactive carbon species, especially those of biogenic origin. Laboratory investigations of leaf and branch level emissions will continue with improved temporal resolution to provide information on transient responses of plants to environmental factors. Models will incorporate updated emissions algorithms and better flux parameterizations. Field investigations will continue to evaluate emission and deposition rates from different environments, with an emphasis on improved estimation of speciated VOC emissions and oxidation products.

- *How can urban emissions be characterized and what are the impacts of urban plumes on the regional biosphere?*

To understand the impact of megacities on the regional environment, regional exchange measurement systems (tower turbulent flux and tethered balloon profiling) will be used to quantify fluxes of VOC, CO, CO_2, O_3, and aerosols from Mexico City. The effect of chemical deposition from this large urban plume on downwind biogenic emissions will be determined by measuring trace gas exchange from two towers situated in similar ecosystems, one influenced by the urban plume and the other in relatively clean air uninfluenced by urban emissions.

- *What are the global responses to changes in the land/atmosphere chemical coupling system?*

The interacting emissions and deposition of biogenic VOC, reactive nitrogen, and aerosols will be investigated with the ESTM. The components of the global model are derived from the results of field and process model studies. The global response to land management and climate change, coastal zone and marine boundary layer phenomena, and the impact of megacities on the regional and global environment will be studied.

- *What is the magnitude of emissions from pyrogenic processes, including wildfires and other biomass burning?*

Accurate assessments of the impact of fires on regional air quality require an improved understanding of direct pyrogenic emissions and secondary production of oxygenated volatile organic compounds (OVOC) and their influence on oxidants and aerosols in an aging smoke plume. Biomass burning emissions will be characterized from the results of controlled laboratory studies. Secondary OVOC production will be characterized from aircraft-based measurements of aging smoke plumes. These observational data will be incorporated into regional and global scale models to evaluate the impact of biomass burning and wildfires on atmospheric chemistry.

- *What is the influence of biogenic marine and coastal emissions on gas and aerosol distributions?*

As a net source of numerous gases (including reduced sulfur species, halogenated organic compounds, and organic nitrates), the oceans have an important influence on local air quality and global distributions of trace gases. For example, the oxidation of short-lived organic iodine and sulfur species leads to new particle formation in the Marine Boundary Level (MBL), and can also influence MBL oxidant levels. Organic nitrates can be transported into the free troposphere, where they may provide a source of reactive NO_x. Longer-lived, ocean-derived halocarbons such as methyl bromide may be transported to the stratosphere where their degradation liberates reactive halogens that contribute to stratospheric ozone depletion. Finally, many of these species have unique oceanic sources, and thus their detection in the free/upper troposphere can be used as an indicator of marine convective influence..

ACD will contribute to studies of the role of a wide range of organic compounds found in the marine boundary layer through measurement of mixing ratios and distributions in several maritime environments. In addition, we will investigate the contribution of marine biogenic iodine and sulfur emissions to aerosol formation and growth in coastal regions. Coastal sites will also be used to characterize regional terrestrial exchange of moderately stable gases (e.g., methanol and acetone) using a mass balance approach that uses clean marine air for boundary conditions.

- *What processes are involved in the oxidation of ocean-derived sulfur species during the daytime and the nighttime?*

Under daytime tropical and mid-latitude conditions, dimethylsulfide (DMS) is readily oxidized to gas-phase compounds such as sulfuric (H_2SO_4) and methanesulfonic (MSA) acidand the corresponding aqueous phase products, sulfate and methane sulfonate. At night in remote marine environments, NO_x and thus nighttime NO_3 are typically very low as is OH, so little oxidation is expected. While this is often the case, some exceptions have been observed. For example, in the tropics in an area of high DMS production, dimethylsulfoxide (DMSO), an oxidation product of DMS thought only to be produced during the day, appeared to also have a nighttime source. In another instance, gas-phase H_2SO_4 and MSA, which typically have atmospheric lifetimes of an hour or less, were observed at relatively high concentrations throughout much of the night in a remote mid-latitude marine environment. Both of these observations suggest one or several as yet unidentified nighttime oxidation processes in the remote marine environment. Such processes could be important if widespread, but are largely unstudied due to a lack of night flights in the remote MBL. ACD scientists plan to conduct further investigations of these nighttime oxidative phenomena to the extent possible, as components of upcoming field campaigns such as the Antarctic Tropospheric Chemistry Investigation (ANTCI) (see below) and INTEX.

- *What are the major processes controlling atmospheric levels of reactive radicals, photochemical oxidants and sulfur species over the Antarctic continent? What are the physico-chemical factors* *that control the exchange of trace gases (e.g., reactive carbon and nitrogen species) between the snowpack and the atmosphere? How do these exchange processes influence oxidant formation in areas covered by snowpack, and perhaps on larger scales?*

One of the more fascinating recent advances in atmospheric chemistry research has been the recognition of the central role of photochemical processing within snowpack on the chemistry of polar plateau boundary layer air. The most dramatic effects of the snowpack emissions appear to exist in Antarctica where, as part of the ISCAT experiments, ACD scientists and colleagues from Georgia Tech have shown that large fluxes of NO_x from the snowpack into a relatively shallow boundary layer leads to elevated OH levels, and hence to the existence of a surprisingly active oxidative environment at the South Pole. There are also indications that enhanced NO and OH concentrations may extend above this layer into the free troposphere where they result in reduced lifetimes for species such as DMS as it is transported from the coast to the plateau. Similar boundary layer processes have also been observed in polar regions of the northern hemisphere (NH) (Alert, Canada; Summit, Greenland), and may also have an impact on mid-latitude, snow-covered areas in springtime. Further studies of this snowpack chemistry are planned in the upcoming ANTCI field experiments, which serve as a continuation and extension of the ISCAT and SCATE (Sulfur Chemistry in the Antarctic Troposphere Experiment) missions that have been carried out at the South Pole and Palmer Station respectively over the past decade. Among the major objectives of these missions will be to evaluate the detailed dynamical and chemical processes controlling spring/summer levels and partitioning of HO_x and reactive nitrogen species at the South Pole, and to assess the impact of oxidative processes in controlling the distribution of sulfur species across the transition from coastal source regions to the inland plateau.

Emissions of trace gases from snowpack have been shown to be driven by photochemistry and there is now a growing need to further characterize the radiation field within the snowpack. Thus, measurements of actinic flux within snowpack will be made at various locations (Greenland; Antarctica; Niwot Ridge, Colorado), and comparisons of these measurements with various radiative transfer models (including one developed within ACD) are planned. Concurrent with the actinic flux measurements, the levels of various pollutants (e.g., nitrate ion), the emission rates of various HO_x/NO_x precursors, and deposition fluxes of various reservoir species (e.g., HO_2NO_2) will be measured. Overall, these studies will identify the major factors controlling solar penetration into the snowpack (e.g., snowpack morphology, soot content), determine the key photochemical steps involved in the release of trace gases from the snowpack, and allow for the incorporation of these snowpack processes into regional/global models. One of the key questions to be addressed is whether these snowpack emissions affect only the boundary layer, or whether NO_x emissions in particular also influence the remote free troposphere.

3.4 Integrated Study of Dynamics, Chemistry, Clouds, and Radiation of the Upper Troposphere and Lower Stratosphere

GOAL: To understand and quantify the physical and chemical processes that maintain the chemical, radiative and dynamical environment of the upper troposphere and lower stratosphere, and to develop the ability to simulate the relevant processes in global-scale models that are used for global forecasts or sensitivity studies.

The UT/LS region (the tropopause ± 2-3 km) is of critical importance for understanding long term global changes and their impact on climate. The UT/LS is a region where ozone is an effective greenhouse gas, and where water vapor, cirrus clouds, and aerosols each make significant contributions to the radiation budget. The UT/LS is also a region where transport processes that couple the stratosphere and troposphere occur on a multitude of scales, which when combined with the strong vertical gradients in many chemical constituents, present a challenge to observational techniques and numerical models. Chemically, the UT/LS region represents a transition in the nature of the mechanisms of ozone production and loss. For example, the effect of anthropogenic and natural emissions on the net rate of production of O_3 is usually positive in the UT and negative in the LS. The UT/LS region has not been examined as extensively as the lower-middle troposphere or the middle stratosphere; consequently, there are several outstanding issues regarding chemical behavior in this region.

a) Distributions of ozone and water vapor: Ozone and water vapor are the most important greenhouse gases in the UT/LS region, yet the processes that control their variability are not fully understood. For example, contributions of chemical processes and transport to the seasonal variation of UT ozone have not yet been quantified. Similarly, the transport of water vapor from the UT to the LS is not well-understood but is essential to understanding the water vapor content of the UT/LS and to the trend of water vapor in the stratosphere. In turn, the trend in stratospheric water vapor may have a significant impact on the ozone layer and on the Earth's radiation budget.

b) Stratosphere-troposphere exchange (STE): Bi-directional STE has a primary impact on the distributions of trace gases in the UT/LS. The mechanisms of exchange and the extent, seasonality, and inter-hemispheric differences require additional quantification and understanding before they can be reliably incorporated into chemical transport models.

c) Convective Influence: Convective transport influences the distributions of a large number of trace gases, including water vapor and ozone. For example, it is unclear how frequently deep convection reaches or exceeds the thermal tropopause and whether such events are associated with significant irreversible transport of tropospheric constituents into the lower stratosphere. Furthermore, the impact of convective transport of boundary layer or lower tropospheric constituents on UT/LS chemistry has not been fully characterized. The magnitude and vertical distribution of lightning produced NO_x is one of the largest sources of uncertainty in global models. In addition, the nature and variability of convective systems themselves requires further characterization for improved parameterization in models.

d) Oxidizing capacity: The oxidizing capacity of the atmosphere is a measure of the ability of the atmosphere to remove primary pollutants through oxidation and ultimately wet or dry deposition. A number of processes related to the oxidizing capacity are not fully understood, including the impact of convective transport of reactive chemical constituents, direct injection from aircraft, production and direct injection of constituents by lightning, gas-particle interactions resulting from in situ or anvil-outflow cirrus formation or from other aerosol formation processes. It is important to observe and verify chemical processing in the background UT/LS region in order to quantify the impact of STE, aircraft emissions, or convectively transported constituents from the surface biosphere or polluted regions.

e) Multiphase chemistry associated with aerosols and cloud particles: Substantial gaps remain in understanding the nature and impact of heterogeneous/multiphase chemistry in the UT/LS, particularly at mid and low latitudes. Of particular interest is cloud processing of chemical species, especially in convective systems. Gas-liquid or gas-ice interactions combined with large particle sedimentation may also have a significant impact on UT chemistry.

f) Cloud microphysics: Significant advances in measurements, models, and process studies are required to adequately address the nature, magnitude, and variability of cloud microphysical processes in determining the water vapor content of the UT/LS. Cirrus layers and ice crystals in the tropopause region have significant impact on local and regional, chemical and radiative balance. Characterization of these impacts is currently in initial stages.

Several new capabilities are coming on-line which significantly enhance our capacity to investigate the UT/LS, including the HIRDLS satellite instrument, the HIAPER aircraft, and WACCM and WRF-Chem numerical models. HIRDLS is an infrared limb-scanning radiometer designed to sound the upper troposphere, stratosphere, and mesosphere to determine temperature, the concentrations of O_3, H_2O, CH_4, N_2O, NO_2, HNO_3, N_2O_5, CFC11, CFC12, and aerosols; as well as the locations of polar stratospheric clouds and cloud tops. HIRDLS will be capable of higher vertical and horizontal resolution than has previously been possible.

A new high altitude research aircraft, HIAPER, will be available to the community within the next few years. HIAPER offers exceptional opportunities for photochemistry and transport research in the UT and at mid- to northern latitudes in the LS. To achieve the full potential of the HIAPER platform will require a significant effort from the atmospheric science community including ACD. ACD will develop instrumentation to characterize the chemical composition of near tropopause air masses, including instrumentation for the measurement of long-lived trace gases, reactive VOCs, radicals (HO_x, RO_2), PANs, NO, NO_y, CO, CO_2, O_3, actinic flux, and fine aerosol composition.

WACCM, as described in the Middle Atmosphere Science section, and WRF-Chem, as described below, will be especially valuable tools for studying global and regional aspects of chemistry and transport in the UT/LS region.

The primary scientific issues to be addressed in ACD's UT/LS research represent two main topics: 1) the structure and variability of the UT/LS, and 2) the processes that control this structure and variability, including multi-scale transport and STE, and chemical, microphysical, and radiative processes. Specific issues to be addressed are as follows.

- *How is air that enters the stratosphere in the tropics dehydrated? What do the seasonal and interannual variations in temperature, ozone, water vapor and cirrus tell us about physical processes in the tropical tropopause layer? How does the NH summer monsoon contribute to troposphere-stratosphere exchange at low latitudes?*

ACD has focused on analysis of satellite data and models to study processes that control dehydration and cirrus formation near the tropical tropopause. Satellite observations show a strong coupling between water vapor, cirrus, and temperatures in the tropics, and idealized model calculations show the importance of including ice microphysics (i.e., growth, fallout, and re-evaporation) in explaining the observed large-scale variability. ACD's goals will be to more accurately understand the influence of convection (by including water vapor isotopes in large-scale models), and to quantify the influence of the NH summer monsoon on transport within the UT/LS.

- *What are the large and small-scale spatial and temporal variabilities of temperature, ozone, water vapor, cirrus and other constituents in the midlatitude tropopause region?*

Variability of the mid-latitude UT/LS region spans a range of space and time scales with strong mixing in association with synoptic weather systems. In ACD, aircraft studies of constituent measurements and high resolution model calculations are being used to quantify mixing ratio variability, and transport and mixing associated with frontal systems and breaks in the tropopause. These measurements will be used to evaluate tropopause definitions. Satellite measurements of UT/LS ozone, water vapor, and other constituents will provide a global (lower resolution) perspective complementing aircraft measurements, and allow a focus on seasonal and interannual time scales (and comparison with global models).

- *How is UT chemistry affected by transport, especially convective transport of constituents from the lower troposphere? What processes control the production and loss of radical species (HO_x, RO_2, NO_x, ClO_x, BrO_x) in the UT? What is the effect of temporal and spatial variability of radical species on ozone production and loss in the UT/LS? What are the concentrations and impact of VOCs transported to the UT/LS?*

A number of ACD groups have participated in the NASA TRACE-P program at mid-latitudes and the NASA ACCENT (Atmospheric Chemistry of Combustion Emissions Near the Tropopause), and CRYSTAL-FACE programs in the tropics and sub-tropics. These programs have demonstrated the importance of convection in distributing reactive constituents to the tropopause region. Model simulations will be conducted to assess the impact on radical and ozone budgets. Unique capabilities developed by ACD staff to measure tracer distributions have allowed the identification of the origin of convective outflow from maritime or continental boundary layers. To support research into the UT/LS region, the WRF regional model will be enhanced with chemical transport capabilities, WRF-Chem. Simulations of deep convection will be used to investigate the influx of tropospheric constituents to the UT/LS region with consideration of transport, multiphase chemistry, and deposition of soluble species. These simulations will also be used to examine dehydration of the UT by cirrus anvils.

- *What is the impact of multiphase chemistry in the UT region? What chemical constituents are taken up on/in cirrus particles?*

ACD measurements made during the recent NASA CRYSTAL-FACE program have provided measurements of the uptake of NO_y constituents on cirrus clouds formed either in situ or in deep convective outflow. Comparisons with expectations from laboratory studies are currently being made. By comparison with similar results for HNO_3 measured by the NOAA

Aeronomy Laboratory, an assessment of the uptake of constituents of odd nitrogen other than HNO_3 will also be possible. Modeling studies will be carried out to assess the importance of denitrification by sedimentation of large ice particles in the UT.

- *What is the impact of NO_x production by lightning in deep convection on the HO_x and ozone balance in the UT/LS region?*

Results from the CRYSTAL-FACE program in Florida and from some previous ACD-led campaigns (STERAO) have led to the conclusion that a major fraction of lightning-produced NO_x appears in the anvil outflow (10 km to the tropopause). Particularly large mixing ratios (~8 ppbv) were found in Florida storms, which will greatly perturb local HO_x and ozone budgets. Several models, including MOZART, have been used to evaluate the sensitivity to total amount and the vertical distribution of lightning-produced NO_2. Future comparisons of model results with data from the Florida region will help to improve the lightning parameterization used in chemical transport models and determine the effects on radical and ozone budgets.

- *What are the budgets of organic halogen species in the UT/LS region and how do they vary with time and location? What are the characteristics of the distributions and variability of organic compounds across the tropopause? What are the long term trends in inorganic species in the stratosphere?*

ACD participation in several NASA sponsored aircraft campaigns has allowed detailed evaluation of organic halogen budgets in the mid- to high-latitude northern hemisphere over North America and Northern Europe. These budgets are required to fully characterize ozone photochemistry in the UT/LS. These measurements are also being used to determine trends and losses of anthropogenic organic halogens such as CFCs, hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) in the lower stratosphere as well as in evaluations of the characteristics of the age spectra in the LS. Mixing ratio gradients of organic constituents across the tropopause will be used in model evaluations of chemistry and dynamics in the UT/LS. ACD is also involved in the Network for the Detection for Stratospheric Change (NDSC), which is a network of remote-sounding research stations for observing and understanding the physical and chemical state of the stratosphere. Long term high resolution spectrometer measurements of columns and profiles of a number of gases, including HBr, HCl, HNO_3, HF, N_2O, and H_2O isotopes, are being used to evaluate seasonal variations, long term trends, and the relationships between chemical transformations, dynamics, and aerosols in the stratosphere.

3.5 Middle Atmosphere Science

GOAL: To describe the chemical, radiative, and dynamical environment between the lower stratosphere and the lower thermosphere, to quantify the physical and chemical processes responsible for defining the environment, and to develop the ability to simulate the relevant processes in global-scale models.

Although there have been rapid advances in our understanding of the middle atmosphere, much remains to be discovered. A range of new phenomena, such as mesospheric thermal inversions, a tertiary ozone maximum, and a rich spectrum of tides and atmospheric normal modes that interact with chemical trace species have been observed but are not well-understood. In the stratosphere, the growth of water vapor above that expected from the increase in methane is an indicator of climate change and has important implications for stratospheric chemistry. Furthermore, the apparent link between the state of the winter stratosphere and the tropospheric Arctic oscillation has important implications for tropospheric and stratospheric chemistry.

ACD is conducting research on many of these issues. ACD personnel have developed a hierarchy of middle atmosphere numerical models, and are participating in current and projected space-borne observation programs. ACD scientists are PIs or co-PIs on NASA's TIMED and HIRDLS satellite instruments, among others. Numerical modeling work also benefits from observational and laboratory studies carried out in the division. Following are several questions and brief summaries of current and planned middle atmosphere research activities.

- *What are the interactions and coupling between stratospheric dynamics and chemistry?*

Although the mechanisms that control stratospheric ozone depletion are understood in principle, the future behavior of the ozone layer is uncertain because of increasing concentrations of greenhouse gases. These gases are predicted to cool the middle atmosphere while they warm the troposphere, leading to changes in the climate of both regions. Thus, the climate of the stratosphere is expected to change even as anthropogenic chlorine emissions are reduced. In addition, the processes that have contributed to ozone depletion over the last two decades, in particular the role of dynamics in northern winter and spring, are incompletely understood. ACD will seek to refine our understanding of ozone changes in the last two decades, and will employ this knowledge to predict future interactions between greenhouse gases, atmospheric circulation, and ozone.

- *What are the effects of solar variability on the atmosphere and climate system*?

Although total solar irradiance varies by only 0.1% over the 11-year solar cycle, the middle atmosphere is affected much more strongly. There is also a strong modulation of energetic particle precipitation, leading to enhanced auroral production of NO_x during solar maximum. These changes in energy input affect heating rates both directlyand indirectly via changes in the abundance of minor species, especially ozone. The influence of solar variability on the middle atmosphere is beyond doubt and well-documented by observations. In addition, statistical evidence has emerged over the last two decades that suggests that changes in solar input affect the lower stratosphere and even the troposphere. A fully interactive version of WACCM is being developed by ACD staff, in collaboration with CGD and HAO, to attack these problems. WACCM incorporates physical and chemical processes required to investigate the upper mesosphere and lower thermosphere, and couplings between atmospheric regions between the surface and 140 km.

- *What are the dynamical connections between the winter stratosphere and the troposphere?*

Recent studies show an apparent connection between the state of the winter stratosphere and the behavior of the tropospheric Arctic oscillations. Although plausible mechanisms linking the two regions have been proposed, the explanation of such a link remains speculative. Work with WACCM suggests that extreme winter stratospheric states (unusually undisturbed polar vortices, or major sudden warmings) do influence the subsequent behavior of the Arctic oscillation. ACD will seek to establish a physical basis for this apparent relationship through detailed diagnosis of multi-year numerical model simulations.

- *What are the characteristics of middle atmosphere circulation systems and how do they influence photochemistry?*

The upper reaches of the middle atmosphere – the mesosphere and lower thermosphere – are among the least well-observed and understood regions of the atmosphere. Outstanding issues will be addressed through interpretation of new data from NASA's TIMED mission and from the HIRDLS instrument onboard EOS (Earth Observing System). The goal of NASA’s TIMED program is to elucidate the circulation, photochemistry and energy budget of this region; the EOS /HIRDLS program will also provide valuable data throughout the middle atmosphere. Through their participation in these programs and access to numerical models, ACD scientists will study tides and normal modes, energetics and the mean meridional circulation, and the interactions between circulation systems and mesospheric photochemistry.

4.0 References

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