

IV. Our Research: The Chemistry, Radiation, and Dynamics of Climate

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

Aeronomy Laboratory research on the topic of the chemistry, radiation, and dynamics of climate focuses on two aspects of "aeronomy": (i) field and laboratory measurements of the key chemical processes that influence radiative forcing by a range of trace gases and aerosols, and (ii) the use and interpretation of radar measurements of dynamical variables, especially in key regions in the tropics.

It has long been known that a variety of gases can influence atmospheric dynamics and climate. Most notably, water vapor plays a central role in the formation of clouds, while natural and human-induced changes in carbon dioxide are a key factor in studies of long-term (e.g., paleo and post-industrial) climate change. More recently, it has become clear that aerosols can strongly influence the propagation and absorption of solar radiation and hence the climate system. In particular, over the past century a number of greenhouse gases such as carbon dioxide and methane have increased, causing a positive radiative forcing of the climate system, but changes in aerosols have also affected the radiative balance. Increases in tropospheric ozone due to human-made pollution produce a positive radiative forcing that is also significant on hemispheric scales, while the depletion of stratospheric ozone produces a negative forcing. Obtaining a better understanding of the Earth's climate system requires evaluation of the nature and magnitude of each of these radiative agents, their changes, and, most importantly, the degree to which positive and negative terms may offset one another both locally and globally.

Lower stratospheric and tropospheric ozone are a major focus of both field and laboratory studies within the Aeronomy Laboratory. Kinetic and field measurements have helped to identify the key chemical processes controlling ozone and their relation to anthropogenic emissions of precursors such as CO, NO_x, and nonmethane hydrocarbons.

As chlorofluorocarbons have been phased out because of their role in depleting stratospheric ozone, other new chemicals have been introduced as substitutes. A hallmark of Aeronomy Laboratory research has been the careful evaluation of the environmental roles of such compounds, including detailed studies of chemical lifetimes and greenhouse warming potentials (GWPs). Laboratory research has recently shown that the perfluorocarbons and SF₆ have atmospheric residence times of several millennia, which is important to consideration of emissions and uses of these nearly-immortal gases.

A new area of laboratory research has been the development of instrumentation to measure the composition of single aerosol particles. This unique instrument has been used, for example, to evaluate the extent to which sulfate and organic material is found within the same particle, which strongly affects the radiative forcing resulting from emissions of sulfur compounds. In related laboratory studies, the chemical mechanisms controlling the oxidation of sulfur gases have also been examined in detail, allowing a better understanding of the influence of sulfur gases in leading to radiative forcing. Another new area of emphasis is the use of visible spectroscopy to examine the radiative forcing of clouds. This long-standing area of central importance to atmospheric dynamics has recently been the subject of increased scrutiny because of the possibility of 'anomalous' absorption in clouds. The same instrumentation and techniques that Aeronomy Laboratory researchers developed to obtain the first measurements of very weakly absorbing stratospheric trace gases such as chlorine dioxide are providing new insights into clouds and their role in the radiative budget.

The radiative forcings due to trace gases, aerosols, and clouds are among the factors that influence atmospheric dynamics but must be studied in concert with other processes that control dynamical structure and variability. Of particular importance to the global dynamical system is tropical climate, for it is here that the 'furnace' of the global circulation resides. Tropical convection is driven by evaporation from the warm ocean surface, so that variations in sea surface temperatures and their coupling to clouds and circulation are key to understanding global climate. Deep convection is particularly prevalent over the warm waters of the western tropical Pacific. The outflow from deep convection drives the Walker and Hadley circulations, so that variations in tropical sea surface temperatures are coupled to the major circulation patterns that characterize the climate on hemispheric scales. The Aeronomy Laboratory has shown that such processes not only affect dynamics, but also influence tropospheric ozone variability on decadal scales and the distribution of water vapor in the region near the tropopause. Aeronomy Laboratory research focuses on radar measurements of wind, temperature, and precipitation, which are critical to understanding the dynamics of the El Niño – Southern Oscillation (ENSO). Recent work is aimed at the distribution of tropical clouds, convection, and precipitation.

Through these studies of dynamics, chemistry, and radiation, the Aeronomy Laboratory maintains a focus on high-quality and unique measurements in the laboratory and in the field, with the goal of furthering the understanding of key processes affecting the climate system.

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

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

1. Radiatively important gases: Lifetimes, chemical processes, radiative forcing, and budgets

- **Fully fluorinated compounds: The ultimate greenhouse gases**

The starting point: Molecular properties. In 1993, Aeronomy Laboratory researchers carried out a detailed study of the chemistry of fully-fluorinated compounds such as CF₄, SF₆, C₅F₁₂, etc. The work was motivated in part by the suggestion that such molecules could serve as useful substitutes for the chlorofluorocarbons. In addition, SF₆ was used to produce cushions in certain athletic shoes and CF₄ is an inadvertent by-product of aluminum manufacture.

Nearly immortal molecules: While these gases contain no chlorine or bromine and hence are not ozone depletors, the research demonstrated that their extreme chemical inertness led to atmospheric lifetimes in excess of 2000 years. In addition, these gases are effective absorbers of infrared radiation. Their long lifetimes and strong infrared absorption bands lead to extremely large global warming potentials, making them the most effective greenhouse gases discovered to date. Aeronomy Laboratory research played a pivotal role in the inclusion of these gases along with CO₂ and CH₄ in the Kyoto Protocol on climate change.

No magic bullets: In a collaborative study with scientists at the Phillips Laboratory, Aeronomy Laboratory scientists probed the possibility of high-altitude ionic mechanisms for

removal of these gases. It was shown that removal by ions was not a mechanism to significantly shorten the lifetimes of these gases. In another collaborative study with scientists involved in remote sensing from the space shuttle, Aeronomy Laboratory researchers used simultaneous stratospheric observations of CF₄ and N₂O to demonstrate that the lifetime of CF₄ must be in excess of 2300 years.

Ravishankara, A. R., S. Solomon, A. A. Turnipseed, and R. F. Warren, Atmospheric lifetimes of long-lived species, *Science*, 259, 194-199, 1993.

Morris, R. A., T. M. Miller, A. A. Viggiano, J. F. Paulson, S. Solomon, and G. C. Reid, Effects of electron and ion reactions on atmospheric lifetimes of fully fluorinated compounds, *J. Geophys. Res.*, 100, 1287-1294, 1995.

Zander, R., S. Solomon, E. Mahieu, A. Goldman, C. P. Rinsland, M. R. Gunson, M. C. Abrams, A. Y. Chang, R. J. Salawitch, H. A. Michelsen, M. J. Newchurch, and G. P. Stiller, Increase of stratospheric carbon tetrafluoride (CF₄) based on ATMOS observations from space, *Geophys. Res. Lett.*, 23, 2353-2356, 1996.

- **Environmental acceptability of substitutes for phased out compounds.**

From one gas to another: CFCs and halons, which are now phased out, had a multitude of uses. No one compound or single family of compounds can replace the CFCs; a large variety of substitutes are needed. In addition, while the substitutes may be safe for the ozone layer, their impact on other environmental concerns such as greenhouse forcing and local air pollution must be considered.

Back to the laboratory: Many substitutes were tested in the laboratory by measuring parameters needed to assess their atmospheric lifetimes and, in some cases, evaluating new ways in which they can affect the abundance of stratospheric ozone.

Identification of environmentally safe alternatives: The results of these studies showed that CF₃I, if released at the Earth's surface, would be an environmentally acceptable substitute for CH₃Br because only a very small fraction of the emission would reach the stratosphere. The global warming potentials of two proposed halon substitutes (HFC-236ea and fa) were also evaluated, providing a better basis for choices between the two.

Solomon, S., J. B. Burkholder, A. R. Ravishankara, and R. R. Garcia, On the ozone depletion and global warming potentials of CF₃I, *J. Geophys. Res.*, 99, 20929-20935, 1994.

Gierczak, T., R. K. Talukdar, J. B. Burkholder, R. W. Portmann, J. S. Daniel, S. Solomon, and A. R. Ravishankara, Atmospheric fate and greenhouse warming potentials of HFC 236fa and HFC 236ea, *J. Geophys. Res.*, 101, 12905-12911, 1996.

- **Sources of methane and use of isotopes**

Isotopic chemistry of a key greenhouse gas: Methane is one of the most abundant organic compounds in the atmosphere and a major greenhouse gas. Identification of its sources is a key issue for regulation of emissions. Methane is removed from the atmosphere mainly via its reaction with OH radical (with some contribution from reactions with Cl in the stratosphere). The total flux of methane in the atmosphere is reasonably well established. However, because of the diffuse nature of the sources, whose emissions are individually small and variable in time, quantification of the strengths of individual sources is difficult. Isotopic signatures of various emissions and the isotopic composition of atmospheric methane can constrain the source strengths, if their atmospheric fractionation is known.

Accurate measurements of the primary loss processes: We have measured the rate coefficients of OH reactions with CH₄, CH₃D, CH₂D₂, CHD₃, and CD₄ as a function of

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temperature relevant to the atmosphere. These detailed measurements together with measurements of the corresponding Cl atom reactions are needed to allow field observations of deuterated methanes to be used to quantify the sources.

Gierczak, T., R.K. Talukdar, S.C. Herndon, G.L. Vaghjiani, and A.R. Ravishankara, Rate coefficients for the reaction of hydroxyl radical with methane and deuterated methanes, *J. Phys. Chem. A.*, *101*, 3125-3134, 1997.

- **HO_x production in the atmosphere is better quantified.**

A key tropospheric radical: OH plays a critical role in the removal of many greenhouse gases, such as methane and HFCs. The OH radical is also involved in the chemistry of ozone in the troposphere and hence in its role in radiative forcing.

Quantifying its chemistry in the laboratory: The O(¹D) quantum yields in photolysis of O₃ were measured between 203 and 320 K, and 289 to 329 nm. A significant fraction of the measured O(¹D) yields at wavelengths greater than 310 nm is attributed to the spin-forbidden production of O(¹D) and O₂(³S) and a large part of the temperature dependence in the quantum yields has been attributed to the photodissociation of vibrationally and rotationally excited O₃. The OH production rates were calculated for various atmospheric conditions. Quantum yields for photodissociation of acetone were also measured in the 290-320 nm wavelength regions as functions of pressures and temperatures. It was shown that acetone photolysis could be a very significant source of HO_x in the upper troposphere.

From the laboratory to the field: Recent airborne measurements have provided unique data sets that include simultaneous *in situ* observations of NO, NO_y, OH and HO₂ (OH + HO₂ = HO_x) in the upper troposphere (UT). NO and NO_y are measured with the an Aeronomy Laboratory instrument on board the NASA ER-2 aircraft. In model simulations of this data set, a HO_x source in addition to the standard O(¹D) + H₂O source is often required to match the HO_x observations. The addition of acetone to the model using concentrations inferred from observed carbon monoxide (CO) improves the HO_x model agreement in most cases. The convection of peroxides from the lower atmosphere is also a potential HO_x source for the UT. Because of the elevated HO_x values, the production rate of ozone from the HO₂ reaction with NO is larger in the sampled UT air parcels than standard model predictions. This implies that ozone in the UT will be more sensitive to the input of NO_x from biomass burning and aviation emissions than previously expected.

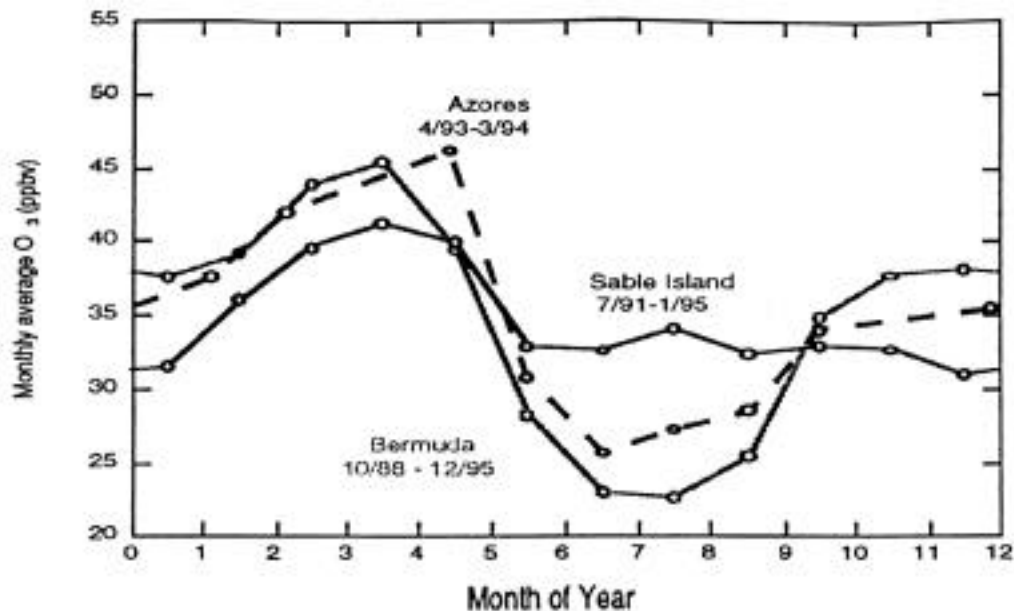
Talukdar, R.K., C.A. Longfellow, M.K. Gilles, and A.R. Ravishankara, Quantum yields of O(¹D) in the photolysis of ozone between 289 and 329 nm as a function of temperature, *Geophys. Res. Lett.*, *25*, 143 -146, 1998.

McKeen et al., The photochemistry of acetone in the upper troposphere: A source of odd-hydrogen radicals, *Geophys. Res. Lett.*, *24*, 3177 - 3180, 1997.

Keim, E. R., *et al.*, NO_y partitioning from measurements of nitrogen and hydrogen radicals in the upper troposphere, *Geophys. Res. Lett.*, submitted, 1998.

- **Export of ozone to the North Atlantic**

Observations of the seasonal cycle of ozone: As part of the North Atlantic Regional Experiment (NARE), measurements of O₃ and CO were carried out at surface sites from July 1991 to January 1995. The figure on the next page indicates that the highest monthly average O₃ levels occur in the springtime. At least three causes have been proposed for this annual maximum. First, it has been attributed to the annual maximum in natural ozone input to the troposphere from the stratosphere; second, it has been argued that substantial amounts of



Seasonal Cycles of Ozone in the North Atlantic

anthropogenic O₃, both transported from the continent and produced during transport, contribute to the springtime maximum; and third, photochemical production of O₃ in the spring from pollutants that build up at high northern latitudes during the winter may also contribute. The third process is expected to be stronger at northern latitudes, adjacent to the wintertime reservoir of anthropogenic pollution, while the continental contribution is expected to be stronger at southern latitudes, since the transport from North America to the North Atlantic is preferentially to the southeast in the spring.

An improved understanding of the origin of ozone: The higher springtime peaks observed at Bermuda (32°N) and the Azores (39°N) than at Sable Island (44°N) suggest that the first two of the proposed causes must dominate. A significant role for transport of anthropogenic pollution at the Azores is indicated by the strong O₃-CO correlations in the spring at that site. This signature of O₃ produced from anthropogenic precursors is clearest in the spring at the Azores and in the summer at Sable Island. The influence of the natural stratospheric source is apparent at Sable Island in the spring. The springtime O₃ peak as shown in the figure occurs in April when there is little correlation with CO and the minimum in the variability in CO indicates that episodes of pollution transport to Sable Island are at a minimum in frequency. The O₃ variability is at a maximum at Sable Island in the spring, which likely indicates the increasing frequency of stratospherically influenced air masses.

Parrish, D. D., M. Trainer, J. S. Holloway, J. E. Yee, M. S. Warshawsky, F. C. Fehsenfeld, G. L. Forbest, and J. L. Moody, Relationships between ozone and carbon monoxide at surface sites in the North Atlantic region, *J. Geophys. Res.*, 103, 13357-13376, 1998.

- **ENSO effects on tropospheric ozone at midlatitudes**

Long-term trends in tropospheric ozone. The importance of tropospheric ozone as a radiatively important trace species has intensified interest in identifying any changes induced by human activities. Our current knowledge of possible long-term trends is based largely on balloon soundings that are made 1 - 2 times per week at a number of stations worldwide. Several sites now have records extending over more than 20 years with more than 2000 soundings.

However, ozonesondes are impractical for repetitive measurements and each individual sounding represents a “snapshot” that may deviate significantly from the climatological mean because of short-term variations in the ozone mixing ratios. Superposition of this “noise” on records based on 1-2 soundings per week may also obscure smaller variations that occur on interannual timescales and confound the determination of trends that are expected to be on the order of 1%/year or less.

Differential Absorption Lidar (DIAL) at Fritz Peak Observatory. The influence of short-term variations in ozone can be minimized by averaging multiple profiles measured using the differential absorption lidar (DIAL) technique. The Aeronomy Laboratory DIAL system at Fritz Peak Observatory (FPO) is optimized for day or night profiling of ozone throughout the free troposphere with an absolute accuracy of at least 10% for a 2-minute integration time and a 1-km vertical resolution. The system has been fully operational since mid-1993 and more than 25,000 ozone profiles were acquired on 489 days during the 5-year period from July 1, 1993 to June 30, 1998. This unique dataset is being used to characterize the variability of tropospheric ozone on timescales ranging from minutes to years. An analysis of daily profiles that were time averaged to dampen the short-term variations revealed a small, but significant 6-month lagged correlation between free tropospheric ozone above FPO and the El Niño/Southern Oscillation (ENSO) that had not been previously identified.

Impact for long-term trend analyses. The observed relationships between variations in tropospheric ozone above FPO and key indicators of ENSO were used to estimate the possible influence of ENSO on long-term trends. It was found that these variations alone can induce apparent trends ranging from -0.1 to +0.8%/year for 10-year intervals that include large El Niño or La Niña events. Further work is underway to better understand the causal relationship and hence the possible impact for other sites.

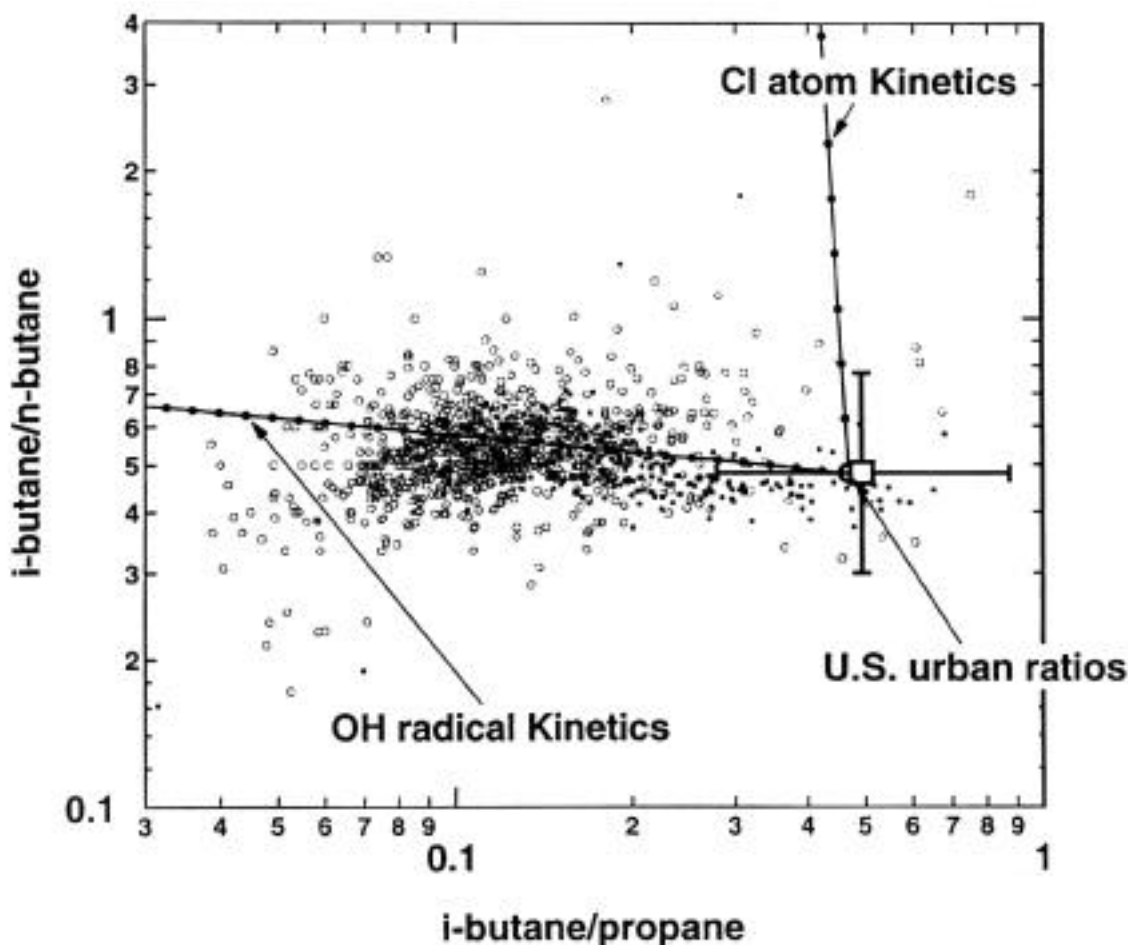
Langford, A.O., T.J. O'Leary, C.D. Masters, K.C. Aikin, and M.H. Proffitt, Modulation of middle and upper tropospheric ozone at northern midlatitudes by the El Niño/Southern Oscillation, *Geophys. Res. Lett.*, 25, 2667-2670, 1998.

- **Sinks for non-methane hydrocarbons in the marine boundary layer: Relative importance of OH versus Cl**

Oxidation mechanisms. The hydroxyl radical is generally believed to be the primary oxidant in the troposphere. However, it has been suggested that in the polluted marine boundary layer Cl atoms may compete with OH as the predominant sink for non-methane hydrocarbons. Such processes play an important role in the chemistry of tropospheric ozone and hence in radiative forcing.

Observations of the hydrocarbons provide clues to mechanisms. Correlation plots of alkane concentration ratios give direct information regarding the relative contributions of Cl atom and OH radical reactions to alkane removal. Kinetic data (obtained in part through key Aeronomy Laboratory kinetic studies) indicate that Cl reacts with the two isomers of butane at different rates, but react with i-butane and propane at nearly the same rate. In contrast, OH reacts with the butane isomers at nearly the same rate, but with i-butane and propane at different rates. Thus, a plot of the ratio of i-butane to n-butane versus i-butane to propane provides two approximately orthogonal axes that will separate the Cl and OH contributions to alkane removal.

A dominant role for OH oxidation. The figure on the next page compares experimental data with the behavior expected from the reaction kinetics for Cl and OH reactions. The data include aircraft and surface station data collected in the North Atlantic field studies in 1993, 1996, and 1997. These data represent urban emissions from North America transported to the North Atlantic where they resided for varying periods of time. These marine data are compared to data collected in Boulder, Colorado. The OH reaction provides a mechanism for the evolution of the ratios characteristic of the urban emission source areas to the ratios observed in aged



Observations of Hydrocarbon Ratios and Their Implications for Chemistry

marine (Atlantic data) as well as the continental (Boulder data) areas. In contrast, the Cl reaction would tend to move the ratios perpendicular to the trend of the data. The close fit of the data to the OH kinetic line and the agreement between marine and continental data clearly establish that there is no evidence for a significant contribution of Cl atoms to the oxidizing capacity of the temperate marine boundary layer.

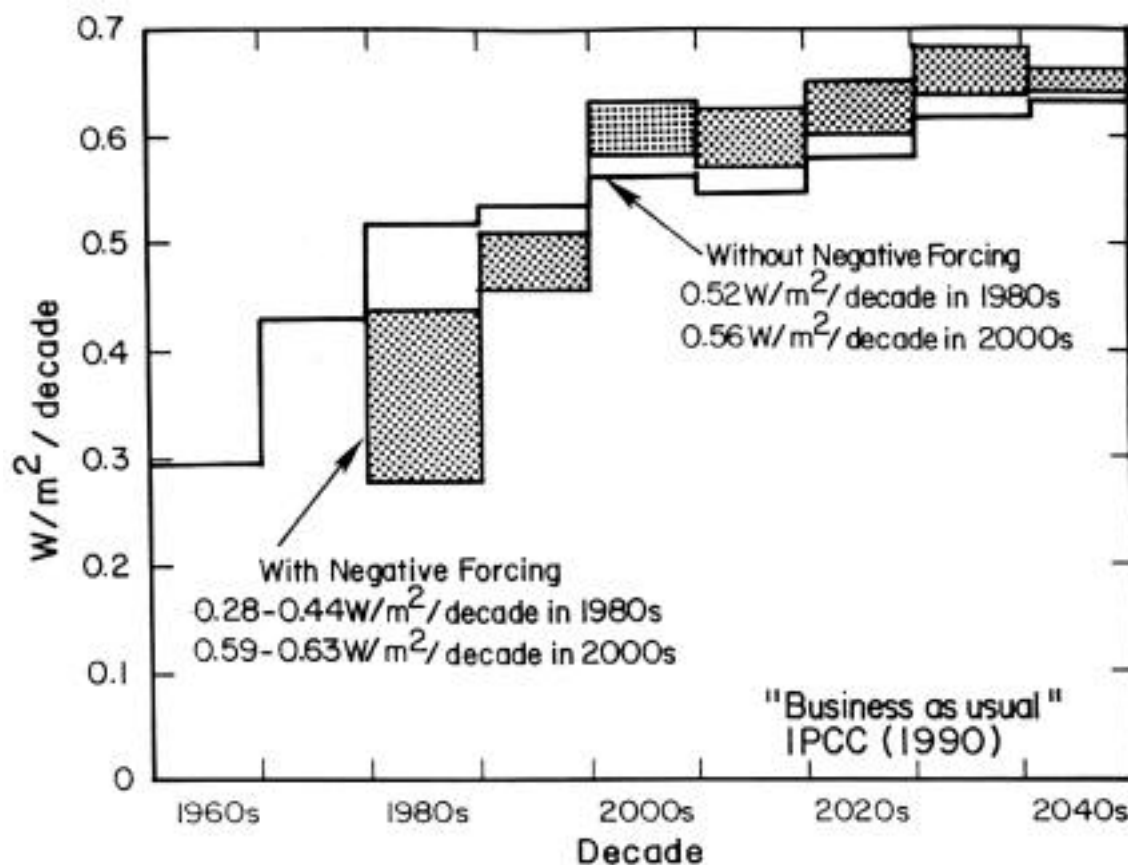
Parrish, D. D., C. J. Hahn, E. J. Williams, R. B. Norton, F. C. Fehsenfeld, H. B. Singh, J. D. Shetter, B. W. Gandrud, and B. A. Ridley, Reply, *J. Geophys. Res.*, 98, 14995-14997, 1993.

Talukdar, R. K., A. Mellouki, T. Gierczak, S. Barone, S. Y. Chiang, and A. R. Ravishankara, Kinetics of the reactions of OH with alkanes, *Int. J. Chem. Kin.*, 26, 973-990, 1994.

- **Ozone and the radiative forcing of recent and future decades: A critical coupling**

Role of ozone in climate change. Increases in chlorinated and brominated halocarbons are believed to be responsible for the depletion of stratospheric ozone observed over much of the globe in the past decade or so. Ozone depletion is in turn believed to lead to a negative radiative forcing, tending to cool the stratosphere and the surface.

Big changes in a short time. A detailed study of the time behavior of ozone depletion was carried out, and the implications for radiative forcing of the climate system were evaluated.



Radiative Forcing Decadal Change With and Without Indirect Effects of Ozone Depletion

The rapid onset of the ozone losses in the 1980s are particularly important and can be contrasted with the much slower buildup of carbon dioxide since the late 1800s or so.

A better understanding of the radiative forcing of recent decades, and a new view of the future. This works shows that ozone led to a negative forcing of the climate system in the 1980s that slowed significantly the rate of change of total anthropogenic radiative forcing due to the combined effect of all greenhouse gases over that decade. As much as half of the heating due to CO₂ was probably offset by ozone depletion during the 1980s, when ozone depletion grew rapidly. As the emissions of ozone-depleting gases are reduced and eventually phased out, the rate of ozone depletion is expected to decrease and eventually reverse, implying that the ozone forcing will become positive in the first decade of the 21st century. This change from deepening ozone depletion in the 1980s to ozone increases in the future should lead to a pronounced increase in the decadal rate of change of anthropogenic greenhouse forcing of the next few decades, perhaps to levels unprecedented in this century.

Solomon, S., and J. S. Daniel, Impact of the Montreal Protocol and its amendments on the rate of change of global radiative forcing, *Climatic Change*, 32, 7-17, 1996.

2. Aerosols, Water Vapor, and Clouds: Formation, Composition, and Radiative Effects

- **New insights to sulfur chemistry: DMS and NO₃ as an oxidant in the condensed phase.**

Sulfur is a key actor on the greenhouse stage. Sulfate aerosols provide a mechanism to reflect sunlight back to space, thereby offsetting to some degree the warming influence of carbon dioxide and other greenhouse gases. Hence, understanding the chemistry of sulfur has become a topic of extremely high priority, including evaluating oxidation mechanisms and the role of the natural sulfur source, dimethyl sulfide (DMS).

New chemistry. The NO₃ radical, an important nighttime oxidant, can also initiate the oxidation of S(IV) species dissolved in liquid matter in the atmosphere, e.g., cloud, marine aerosol, and fog. We measured the uptake of NO₃ on solutions containing atmospheric reactants and deduced the relevant physico-chemical parameters. It was shown that NO₃ uptake at night into marine aerosol and cloud droplets can (i) oxidize sulfur dioxide, (ii) suppress ambient NO₃ concentrations, (iii) reduce atmospheric lifetime of various species, and (iv) liberate halogens from marine sea-salt aerosol. In addition, laboratory studies of the DMS oxidation mechanisms and rates were carried out using various techniques. It was found that sulfur containing free radicals and molecules, such as CH₃S, can weakly bind to the abundant O₂, and other species, and thus alter the rates of reactions and identity of the products. A simplified oxidation mechanism was developed to follow the course of sulfur atom in this process.

Sulfur is better understood: This work helps better understand the role of natural sulfur compounds in past, present, and future atmospheres and its oxidation mechanisms. These studies allow calculation of SO₂ yield (i.e., new particle formation rate) and also help explain some of the observed variation in the concentration of sulfur compounds in ice cores. The latter may also be applied to the use of the measured ratios of methane sulfonic acid to non-sea salt sulfate ratios in the ice cores as “thermometers” of the past.

Rudich, Y., R.K. Talukdar, R.W. Fox, and A.R. Ravishankara, Reactive uptake of NO₃ on pure water and ionic solutions, *J. Geophys. Res.*, 101, 21023-21031, 1996a.

Ravishankara, A. R., Y. Rudich, R. Talukdar, and S. B. Barone, Oxidation of atmospheric reduced sulphur compounds: Perspective from laboratory studies, *Phil. Trans. Royal Soc. London, B*, 352, 171-180, 1997.

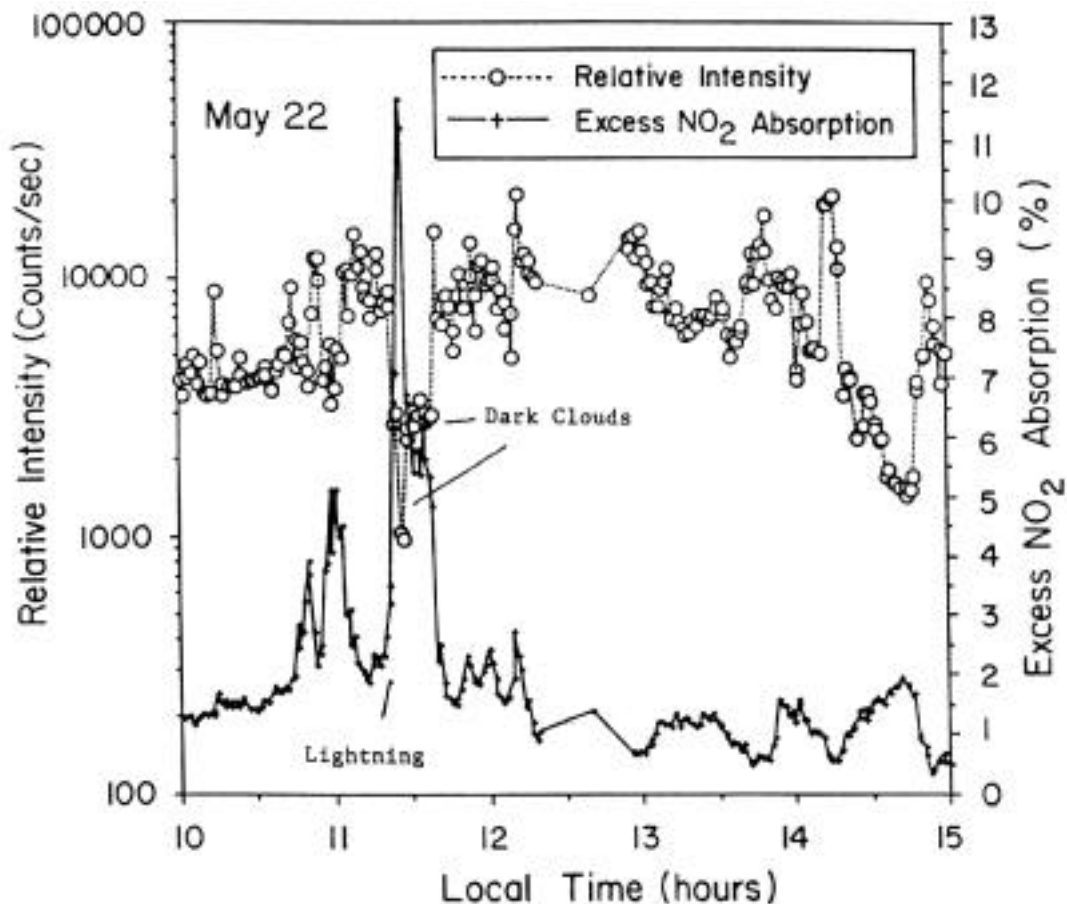
- **Anomalous absorption: What it may be, and what it isn't**

Clouds and radiation: Recent studies of the radiation budget by a variety of authors have suggested a remarkable imbalance, particularly under cloudy conditions. These studies have suggested that there is 'anomalous absorption' of perhaps as much as 50-100 W/m² at some times, and that much of the anomaly occurs in the visible part of the spectrum. Anomalous absorbers with such impacts on the radiative budget would have very great impacts on both regional and global climate. Indeed, some recent work suggests that ENSO modelling may require consideration of anomalous absorption, since some research suggests that the Pacific warm pool is a region where absorption anomalies exceed 30 W/m² on average. A major new emphasis for the Aeronomy Laboratory's visible spectroscopy group is that of bringing to bear their extensive experience in visible spectroscopy relating to observations of trace chemicals (e.g., BrO, OClO, NO₃) on this key climate-relevant problem.

Observations of an important "new" absorber: Direct measurements of the absorption of downwelling visible radiation by nitrogen dioxide show that it can contribute significantly to radiative forcing under certain conditions. Enhanced nitrogen dioxide is due to pollution and to

production by lightning in convective clouds. Case studies of several days of observations in Colorado reveal peak absorption of downwelling radiation by NO_2 of up to 5-12% in dark clouds (figure below), corresponding to an estimated radiative forcing that is likely to be in the range of $5\text{-}20\text{ W/m}^2$, although values as low as about 3 W/m^2 may be obtained in the unlikely event that all of the NO_2 resided in the bottom of the cloud. On the other hand, radiative forcing as high as $15\text{-}30\text{ W/m}^2$ may be obtained if the NO_2 resided near the cloud top, depending upon the cloud particle size and liquid water path. These case studies suggest that NO_2 can play a significant role in the anomalous (or enhanced) absorption of radiation under polluted conditions or when electrically active storms are considered. The estimates presented in this paper likely do not represent upper limits for this role, since the storms studied were not particularly intense nor were the sites particularly polluted.

Searching for other anomalies. Atmospheric measurements in clear and cloudy skies in the 610 - 680 nm and 400 - 450 nm regions were also examined in detail in a search for 'anomalies'. The observed wavelength dependence of water vapor absorption in the bands near 442 and 650 nm were shown to agree well with their expected spectral structure under both clear and cloudy-sky conditions for the instrumental resolution employed, implying that large errors in understanding of the spectroscopy of water vapor at these wavelengths are not a factor in



Observations of Large NO_2 Absorption in a Boulder Thunderstorm

anomalous absorption. The observations also rule out the possibility of significant unknown absorbers displaying structured features under either clear or cloudy conditions at these wavelengths. However, the possibility of anomalous broad continuum or quasi-continuum absorption cannot be ruled out.

Solomon, S., R. W. Portmann, R. W. Sanders, J. S. Daniel, W. Madsen, B. Bartram, and E. G. Dutton, On the role of nitrogen dioxide in the absorption of solar radiation, submitted to *J. Geophys. Res.*, 1998.

Solomon, S., R. W. Portmann, R. W. Sanders, and J. S. Daniel, Absorption of solar radiation by water vapor, oxygen, and related collision pairs in the Earth's atmosphere, *J. Geophys. Res.*, 103, 3847-3858, 1998.

- **Aerosol chemistry: Measuring the composition of single particles**

New capabilities for analyzing aerosols. A new instrument, Particle Analysis by Laser Mass Spectrometry or PALMS, has been developed to measure the composition of single aerosol particles. Some new capabilities are: good sensitivity to organics, in situ analysis which avoids artifact problems in taking samples back to the laboratory, and single particle analysis to distinguish internal mixing (species present on the same particles) from external mixing (on different particles).

First field studies. The first field deployment of PALMS was at Idaho Hill, Colorado, in September 1993 as part of the OH Photochemistry Experiment. These were the first field measurements ever made of the composition of single aerosol particles. Organics were found to be important constituents of aerosols at this remote continental site. New to this study was evidence that organics are present on many aerosols instead of being concentrated only in a few pure organic particles. Aerosol organics were correlated with ozone but anticorrelated with gas phase organics. This suggests that the condensed organics were mostly the result of secondary photochemistry rather than primary emissions.

A second field deployment of PALMS was to Cape Grim, Tasmania, in November 1995 as part of the First Aerosol Characterization Experiment (ACE-1), where aerosols were measured in a clean marine atmosphere. Small amounts of sea salt were present in most particles down to the smallest measurable sizes (0.16 μm). Sulfate was present on the same particles as sea salt. Small amounts of organic material were found on most of the sea salt particles, forming an estimated 5 to 50% of the aerosol mass. Correlations with other species in the particles indicated two sources for these organics: the ocean surface and condensation of secondary organics from the gas phase.

A global role for organics in aerosols. Observations of organics at both remote continental and marine sites show that organics must be considered in aerosol budgets and chemistry in all areas of the globe. An important portion of the global climate forcing from aerosols is most likely due to organics.

Single particle analysis shows linkages between chemical cycles. At Idaho Hill, sulfates and secondary organics were often present in the same particles. This means that efforts to improve visibility and reduce haze by reducing sulfur emissions are linked, probably in a non-linear fashion, with the secondary photochemistry of organics. At Cape Grim, sulfates and sea salt were often in the same particles. The idea that sulfate from DMS oxidation is adding to submicron sea salt particles rather than forming new particles will change calculations of the radiative impact of marine aerosols.

D. M. Murphy, and D. S. Thomson, Chemical composition of single aerosol particles at Idaho Hill: Negative ion measurements, *J. Geophys. Res.* 102, 6353-6368, 1997.

D. M. Murphy, J. R. Anderson, P. K. Quinn, L. M. McInnes, F. J. Brechtel, S. M. Kreidenwies, A. M. Middlebrook, M. Pósfai, D. S. Thomson, and P. R. Buseck, Influence of sea salt on aerosol radiative properties in the Southern Ocean marine boundary layer, *Nature*, 392, 62-65, 1998.

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Middlebrook, A. M., D. M. Murphy, and D. S. Thomson, Observations of organic material in individual marine particles at Cape Grim during the First Aerosol Characterization Experiment (ACE1), *J. Geophys. Res.*, 103, 16475-16483, 1998.

- **Stratospheric/upper tropospheric water vapor distribution and radiative forcing**

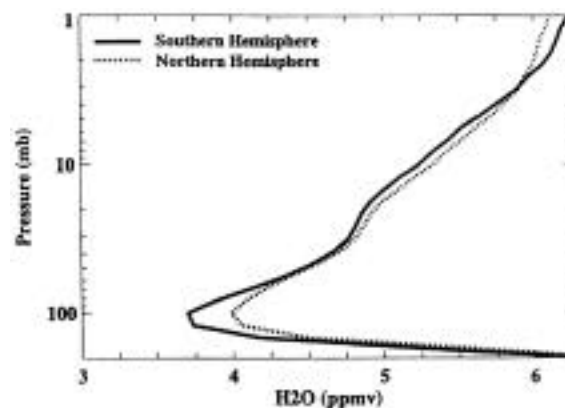
Water vapor in the tropopause region. Past aircraft observations indicated the Southern Hemisphere lower stratospheric and upper tropospheric air was drier than in the north. It had been suggested that polar dehydration during Antarctic winter could be a major player in the middle and low latitude water budget in the lower stratosphere. A thorough study of the lower stratospheric water vapor budget with new satellite data was undertaken to address these issues.

Mechanisms controlling hemispheric differences. As shown in the figure, several years of zonally averaged global water data show the Southern Hemisphere is drier than in the Northern Hemisphere when considering an annual average. Several factors contribute to this asymmetry. Antarctic polar vortex dehydration plays a role at high latitudes during late winter and spring. Equatorward of $\sim 50^{\circ}\text{S}$, the tropical seasonal cycle in water vapor coupled with the seasonal cycle in extratropical descent controls the water vapor hemispheric asymmetries. Additionally, during the tropical wet period, air ascending in the Indian monsoon region influences the north more than the south, again moistening the Northern Hemisphere lower stratosphere and upper troposphere. This combination of local processes and advection by the zonally averaged circulation act together to produce a drier Southern Hemisphere lower stratosphere and uppermost troposphere as compared to that in the north. This study also underscores the importance of understanding the transport of chemical species relating to tropical circulation.

A better understanding of radiative forcing: Using satellite data to examine seasonal cycles of water vapor in the vertical has given new information on transport characteristics and the global distribution of water vapor near the tropopause, where it plays a key role in radiative forcing.

Rosenlof, K. H., Seasonal cycle of the residual mean meridional circulation in the stratosphere, *J. Geophys. Res.*, 100, 5173-5191, 1995.

Rosenlof, K. H., A. F. Tuck, K.K. Kelly, J. M. Russell III, M. P. McCormick, Hemispheric asymmetries in water vapor and inferences about transport in the lower stratosphere, *J. Geophys. Res.*, 102, 13213-13234, 1997.



Averaged HALOE H₂O: 30° - 90° Latitudes

3. Dynamical Measurements and Theory

- **Internal Gravity Waves**

Gravity waves and atmospheric dynamics: Gravity waves strongly influence global circulation by their efficient vertical transport of energy and horizontal momentum. In order to parameterize the effects of gravity waves in GCMs, we have undertaken studies to describe and understand the gravity wave field.

Towards a better understanding: We derived spectra of temperature and horizontal wind versus vertical waves from a few hundred radiosonde balloon ascents launched from near the Flatland Atmospheric Observatory (FAO) in Illinois. We hypothesized that the discrepancy we found between the observed mean ratio of these spectra and the prediction of standard gravity-wave theory was due to enhancement of gravity-wave energy near the inertial period (which is 18.4 hours at FAO). We found strong evidence for such an enhancement in the five-year database of horizontal winds obtained by the White Sands wind-profiling radar. On one occasion a large-amplitude inertial oscillation remained in phase for about 11 inertial oscillations (10 days!). The redistribution of total gravity-wave energy implied by these observations will influence the parameterization of gravity waves in GCMs.

Fritts, D.C., and T.E. VanZandt, Spectral estimates of gravity-wave energy and momentum fluxes, I: Energy dissipation, acceleration and constraints. *J. Atmos. Sci.*, 50, 3685-3694, 1993.

Nastrom, G. D., T. E. VanZandt, and J. M. Warnock, Vertical wavenumber spectra from high-resolution balloon soundings in the lower atmosphere over Illinois, *J. Geophys. Res.*, 102, 6685-6701, 1997.

- **Theory and prediction of wind variations in the troposphere**

Wind measurements from commercial aircraft. In the early 1980's a campaign to measure the horizontal (both zonal and meridional) variations of the spectra of wind speed in the troposphere was conducted as part of the Global Atmospheric Sampling Program (GASP). Wind measurements were made from international commercial aircraft fitted with measuring equipment. The data gathered was thereby global and covered all seasons. The principal experimental finding was that wind speed variations were wave-like with speeds increasing as $L^{5/3}$ for $L < 200$ km and increasing as L^3 for $L > 200$, where L is the wavelength. The data were published in 1984 and up until now has defied a quantitative explanation.

Theory of horizontal wind spectra in the free troposphere. In order to explain the observed variations, it was necessary to extend the theory of turbulence so as to include buoyancy forces typical of the atmosphere. A key element recognized for the first time, was that the pressure-strain rate term (a velocity-pressure correlation) converted vertical buoyancy forcing to buoyancy forcing along the horizontal. It is this pressure-strain rate effect which causes enhanced wind motion along the horizontal, and is responsible for the hitherto unexplained L^3 behavior observed at L exceeding 200 km. Physically, the theory establishes that the horizontal variability is caused by gravity waves and vortical modes. The identity of these variations had been controversial.

More accurate prediction of decadal and longer climate variations. This theory will, for the first time, allow horizontal wave fluctuations, 200 km and less, to be accounted for in global circulation and climate models by a sub-grid scale parameterization. This parameterization will improve the predictive reliability of the models. Related horizontal wave fluctuation phenomena also occurs in oceans currents and can now be parameterized in ocean models as well.

Weinstock, J., Lagrangian coordinates and their application to gravity wave spectra, in Coupling Processes in the Lower and Middle Atmosphere, *edited by:* Thrane, Blix, and Fritts, Kluwer Acad. Publishers, Dordrech, 1993, p. 241-260.

Weinstock, J., Spectral closure for stratified turbulence, *J. Geophys. Res.*, 103, in press., 1998.

- **Diagnosis and classification of precipitating cloud systems using profilers**

Tropical convection and diabatic heating. Tropical convection is the major source of tropospheric heating that drives the large-scale atmospheric circulation. The vertical diabatic heating profiles are quite different for stratiform and convective precipitation. Profilers are ideal tools for observing the vertical structure of convective systems, for classifying the convection, and for determining the diurnal cycles of convection.

AL profilers classify precipitating cloud systems in the tropics. During the Tropical Ocean Global Atmosphere Coupled Ocean-Atmospheric Response Experiment (TOGA COARE) a network of 915 MHz profilers were deployed as part of Integrated Sounding Systems (ISS) to measure the winds in the lower troposphere. The profilers simultaneously observed the vertical structure of precipitating cloud systems. These data have been used to classify precipitation into convective and stratiform components. The profiler classification reveals that close to 40% of the precipitation over the Pacific warm pool is stratiform in nature. In addition, in a detailed study at Manus Island, Papua New Guinea, observations reveal that deep cloud systems occur as much as 25% of the time over the warm pool region when it is not raining at the surface. In contrast, rain occurs at the surface about 7% of the time. These deep anvil structures are the remnants of active mesoscale convective systems. They impact the global heat budget by intercepting the Earth's long wave radiation and reflecting incoming short wave radiation back to space. A detailed profiler-derived precipitation data set has been prepared for distribution to the COARE research community. Several studies have been made in collaboration with NASA Tropical Rain Measuring Mission (TRMM) scientists to intercompare classification of precipitation by the profilers with other methods and to estimate evaporation rates using the detailed information on vertical structure provided by the profilers.

An improved representation of convection in numerical models. One of the major challenges in contemporary atmospheric sciences is to improve the simulation of the hydrological cycle in atmospheric models. One approach to improve convective parameterization is to simulate convection in cloud resolving models. Observations of the time-height structure of hydrometeors such as were obtained by profilers during COARE, are an important resource for validating these models. In addition the profilers are an important component of the TRMM ground validation program contributing to the calibration and validation of the TRMM satellite products.

Gage, K.S., C.R. Williams, and W.L. Ecklund. UHF wind profilers: A new tool for diagnosing convective cloud systems. *Bull. Amer. Meteorol. Soc.*, 75, 2289-2294, 1994.

Williams, C.R., W.L. Ecklund and K.S. Gage. Classification of precipitating clouds in the tropics using 915 MHz wind profilers. *J. Atmos. And Oceanic Technol.*, 12, 996-1012, 1995.

- **Organization of deep tropical convection by atmospheric equatorial waves**

Tropical convection and large-scale circulation. Tropical convection tends to be organized into "cloud clusters", which occur over a broad range of temporal and spatial scales. Much of this convection tends to be embedded within large-scale wave disturbances. A major objective of the TOGA COARE project was to gain a better understanding of the processes that organize convection over the tropical oceans.

The dynamical link between deep tropical convection and atmospheric equatorial waves. Research at the Aeronomy Laboratory has exploited a 25-year-long record of satellite-observed cloudiness to link tropical convective variability to the fundamental dynamics of atmospheric wave activity in the tropics. A space-time spectral analysis of the satellite cloudiness reveals that a substantial fraction of deep tropical convection is modulated by trapped wave disturbances moving parallel to the equator. Using NCEP/NCAR reanalysis data, these modes have been shown to exhibit spatial structures and propagation characteristics consistent with so-called "shallow water" theory of equatorial waves. The modes are observed to propagate vertically,

and appear to provide an important energy source for driving middle atmosphere motions. Thus the shallow-water theory has been shown to provide a relatively simple framework for the understanding of the organization of deep tropical convection by the large-scale circulation.

Improved representation of tropical variability in models. A similar space-time spectral analysis of cloudiness and rainfall produced by some general circulation models reveals shortcomings in the variability of model tropical convection. While most models are able to simulate some of the observed equatorially-trapped modes, their propagation speeds are universally too fast. This points to a fundamental shortcoming in the way deep tropical convection is represented in such models. A better understanding of the dynamical causes for the observed phase speeds is a prerequisite for improved simulation and prediction of tropical variability. Ultimately, improvements in the convective parameterization schemes will be required for better simulations of both the tropics and extratropics. The space-time analysis methodology developed at the Aeronomy Laboratory will serve as a benchmark in diagnosing and evaluating the quality of newly developed convective parameterization schemes.

Kiladis, G., Observations of Rossby waves linked to convection over the eastern tropical Pacific, *J. Atmos. Sci.*, 55, 321-339, 1998.

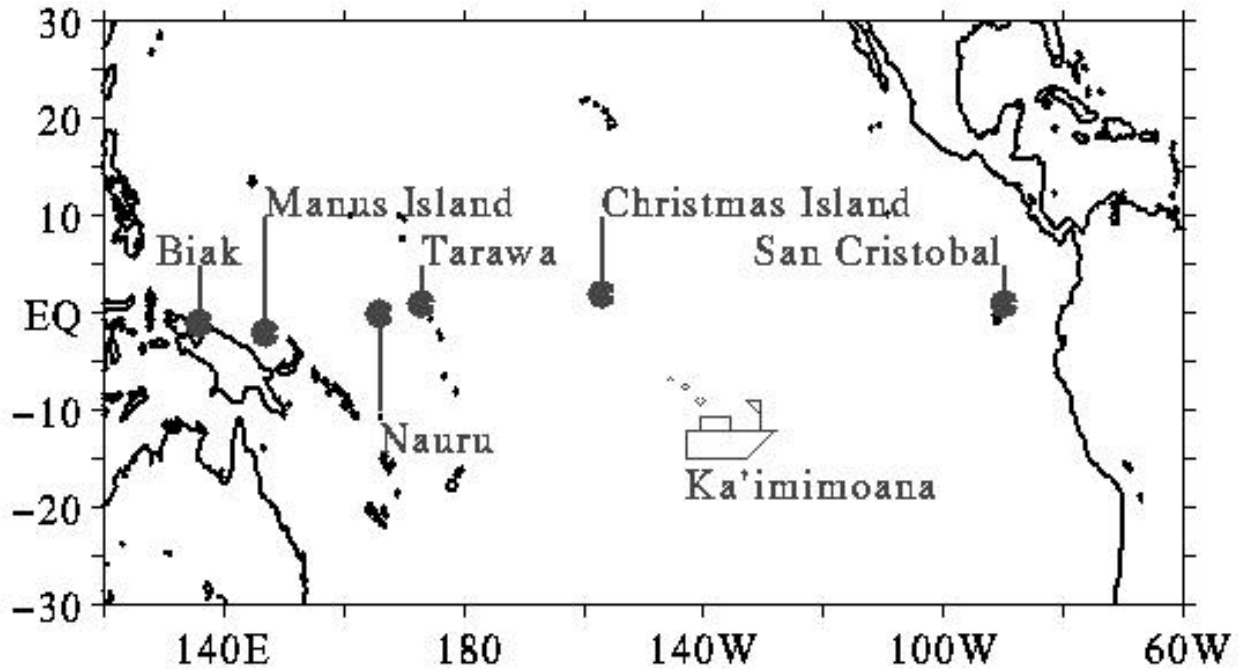
Wheeler, M. and G. N. Kiladis, Convectively-coupled equatorial waves: Analysis of clouds and temperature in the wavenumber-frequency domain, *J. Atmos. Sci.*, in press, 1998.

- **NOAA/CU Trans-Pacific Profiler Network records changes in tropospheric circulation over the central equatorial Pacific**

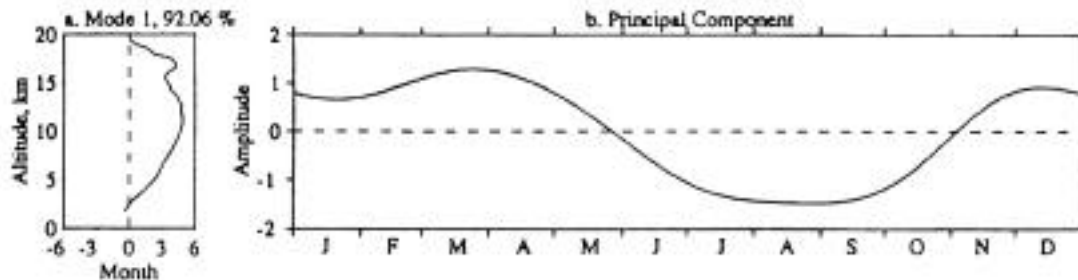
Wind observations are very sparse over the tropical Pacific equatorial zone. Wind is an essential variable in any model that simulates or predicts the atmosphere. While wind is observed routinely by a dense rawinsonde network over much of the developed world, reliable observations are lacking over the global oceans. Wind data are sparse to non-existent over much of the tropics and southern hemisphere. The now-mature technology of wind profiling Doppler radar pioneered at the NOAA Aeronomy Laboratory has enabled the deployment of a network of island-based wind profilers that now spans the equatorial Pacific (figure on next page).

The Trans-Pacific Profiler Network monitors seasonal, interannual, and decadal variations in tropospheric circulation. The NOAA/CU Trans-Pacific Profiler Network (TPPN) provides a cost-effective means to obtain high resolution wind measurements from the data sparse tropical Pacific. Completed in 1994, the TPPN is comprised of a combination of UHF and VHF wind profilers at seven sites: Piura, Peru; San Cristóbal, Ecuador; Christmas Island, Kiribati; Tarawa, Kiribati; Nauru, Manus Island, Papua New Guinea; and Biak, Indonesia. A robust feature of these observations is the pronounced annual cycle of mean zonal winds in the upper troposphere (figure on next page). Upper tropospheric mean zonal westerlies are observed during northern winter when deep equatorial convection is most intense over the western Pacific warm pool region. The annual cycle in zonal winds is significantly modulated by the El Niño/Southern Oscillation (ENSO) phenomenon, being strongest during La Niña and weakest during El Niño. The wind record is now long enough to reveal a decadal time scale variation in circulation that accompanied the persistent El Niño episode of the 1991-1994 period.

TPPN observations validate model output and contribute to an increased quality of analysis products. The TPPN wind observations from Christmas Island were the first profiler observations to be distributed on the Global Telecommunication System (GTS). Comparisons of TPPN observations with ECMWF and NCEP analyses show that the analyses capture most of the variability in the zonal wind field. However, the observations from Christmas Island reveal an unexpected secondary maximum in northerly flow in the middle troposphere that is only weakly reflected in the NCEP/NCAR reanalysis product. This feature is being investigated in connection with the vertical structure of ITCZ convection which lies to the north of Christmas Island.



Trans-Pacific Profiler Network (TPPN)



Zonal Low Pass Wind, Christmas Island, 1986 - 1995

Gage, K.S., J.R. McAfee, and C.R. Williams. On the annual variation of tropospheric zonal winds observed above Christmas Island in the central equatorial Pacific, *J. Geophys. Res.*, 101, 15061-15070, 1996.

Gage, K.S., J.R. McAfee, and C.R. Williams. Recent changes in tropospheric circulation over the central equatorial Pacific. *Geophys. Res. Lett.*, 23, 2149-2152, 1996.

C. Future Plans: What's Next?

Ground-Based Investigations

Aeronomy Laboratory researchers are engaged in ongoing efforts to improve the reliability and quality of Pacific profiler observations and to make the data broadly available to the scientific community. New sites are also being considered, and one possibility is the expansion of the profiler network into the Indian Ocean. Further, profilers are rapidly becoming established as important tools for precipitation research. Laboratory researchers are involved in intercomparison and calibration activities relating to the TRMM satellite precipitation system,

and are examining the potential of profilers for measurement of the distribution of drop-sizes in precipitating cloud systems, which is of central importance in numerical cloud resolving models. Ground-based visible spectroscopy measurements are currently focussing on observations of absorption by oxygen and oxygen complexes in clouds and clear sky. Since the amount of oxygen in the atmosphere is well known, changes in oxygen absorption within clouds provide unique information on the effective optical depth of clouds. The optical depth or optical path may play a role in anomalous absorption, and is of intrinsic interest for radiative transfer studies. These measurements are being carried out as part of a "collaboratory" involving Aeronomy Laboratory, Environmental Technology Laboratory, and Climate Monitoring and Diagnostics Laboratory scientists to obtain a unique combined dataset of cloud vertical extent and liquid water path, surface irradiance, aerosol distributions, and effective optical depths.

Modeling and Analysis

Changes in water vapor and their links to dynamics are an area of focus. There is evidence of a long-term trend in water vapor in the stratosphere and in the tropopause region that may be linked to changes in dynamics, particularly changes in tropopause heights. Future analysis work relating to the lidar ozone dataset will examine the causal mechanisms for linkages between tropospheric ozone over Colorado and ENSO. An intriguing result relating to sources and sinks of tropospheric ozone was obtained on the NOAA P-3 flights during September 1997 (which covered the western North Atlantic), in which CO was shown to be reasonably well mixed in the lower troposphere, while ozone exhibited a strong and unexpected vertical gradient in the marine boundary layer. This gradient must be driven by loss processes in the boundary layer. The longer-term surface data from Sable Island indicate an even more pronounced effect, with higher median CO and significantly lower ozone. Future work will involve investigating the NARE 1996 and 1997 data sets in the context of photochemical model calculations to illuminate the systematics of the ozone sinks in the marine boundary layer. Further, Aeronomy Laboratory researchers are developing a global ozone climatology and working with scientists at NCAR to examine the role of changes in ozone, aerosol, and other trace gases in influencing global climate over the past century using a coupled atmosphere/ocean general circulation model.

Airborne Studies

The PALMS instrument will be deployed on airborne platforms to examine the composition of particles in the upper troposphere. Better understanding of upper tropospheric particle chemistry is likely to lead to significant changes in our picture of radiative forcing, just as the surface measurements with this unique system already have done. A key question is the mix of sulfates and organics on upper tropospheric aerosol, and the possible role of mineral dust.

Laboratory Investigations

Laboratory studies will continue to focus on topics of highest relevance for climate change. One area of emphasis includes the measurement of reaction kinetics for isotopic CO. CO plays a key role in the photochemical production of tropospheric ozone, but its sources are not well understood (e.g., industrial emissions, biomass burning, etc.). With detailed measurements of the kinetic rates of removal of various isotopes of CO, measurements of the CO isotopic ratios can be used to provide insight into the balance of sources. Measurements of the key kinetics rates for isotopic methane with Cl are also planned, in order to provide the complete database needed to interpret observations of isotopic methane abundances. Liquid phase chemistry will also be an area of emphasis, with a near-term goal of examining the liquid phase oxidation of various compounds by NO₃ in sulfuric acid solutions, which can play an important role in aerosol chemistry and radiative forcing.