

## II. Our Research: The Stratospheric Ozone Layer

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

The change in the abundance of stratospheric ozone ( $O_3$ ), as well as alterations in its vertical distribution, due to human-induced emissions is a major environmental issue. This concern is primarily because the ultraviolet radiation at the Earth's surface will increase, with deleterious effects, when ozone in the stratosphere is depleted. Ozone changes will also affect the climate system, because  $O_3$  itself is an important greenhouse gas and because changes in its stratospheric abundance alter the composition of the troposphere.

Measurements of ozone and other chemicals during the Antarctic ozone hole formation and the subsequent analyses have now clearly shown that the basic hypothesis proposed by Aeronomy Laboratory scientists in 1986 – that reactions on condensed matter liberate active chlorine and allow rampant depletion of ozone – is indeed correct. Over the past few years, our understanding has improved further in the face of more-numerous and better observations. The most important among those changes is the discovery that stratospheric sulfate aerosol can also do what polar stratospheric clouds (PSCs) do, as long as the temperatures are low. Aeronomy Laboratory scientists have pioneered in this discovery through modeling, laboratory studies, and field measurements. Work done at the Aeronomy Laboratory and elsewhere during the past few years has shown that the contribution of polar-processed air to the midlatitude lower stratosphere (~18 to ~25 km) ozone depletion is small. The Arctic springtime ozone depletions have waxed and waned, but overall have increased during the past decade. Perturbed composition in the Arctic winter/spring lower stratosphere has been observed via in situ observations and remote sensing. The lessons learned from the analysis of the Antarctic vortex have been applied to the Arctic case: it is clear that halogens are causing the ozone depletion in this region. Again, research by the Aeronomy Laboratory has contributed greatly to this work.

Ozone depletion at midlatitudes, largely in the lower stratosphere, has been the other major focus of Aeronomy Laboratory research in the past few years. Based on the observed sulfuric acid aerosol loading and the laboratory-measured rates of various multiphase and gas phase reactions, the modeling studies carried out in the Aeronomy Laboratory clearly showed that we can account for the observed midlatitude ozone trends, which have changed from year to year. It also clearly showed that midlatitude ozone changes are strongly controlled by multiphase reactions, much like the case of the polar regions. At midlatitudes, however, the reactions were shown to take place in liquid sulfuric acid aerosol and at warmer temperatures. These studies also showed that the signature in the ozone trend due to volcanoes could be mistaken for solar cycles. All this research has made it clear that halogens are responsible for the observed depletion of lower stratospheric ozone; this depletion takes place due to chemistry in this region and the impact of polar processes on midlatitude ozone depletions is not very significant.

The occurrence of the hydrolysis of  $N_2O_5$  in sulfuric acid aerosol was clearly demonstrated by Aeronomy Laboratory scientists and bolstered our confidence in the role of heterogeneous or multiphase reactions in the lower stratosphere. The importance of reactions in liquid sulfuric acid in converting inactive chlorine compounds into active forms, and the subsequent large ozone depletions, was clearly indicated. This was based on many Aeronomy Laboratory studies on the reactivities in sulfuric acid. The ability to quantitatively include multiphase reactions in models was developed in the Aeronomy Laboratory, and pertinent data on the most important stratospheric reactions on condensed matter were also obtained here. The impact of temperature fluctuations on the highly non-linear rates of heterogeneous/multiphase reactions was assessed, and a simple method to include them in models was put forth. Measurements in the Aeronomy Laboratory quantified the rates of many important free radical reactions and photochemical parameters.

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Laboratory studies here have shown that the  $\text{HO}_x$  production rates during high solar zenith angles are larger, due to a large yield of electronically excited O atoms from ozone photolysis and due to the multiphase hydrolysis of  $\text{BrONO}_2$ . They have helped deduce the efficiency of bromine in destroying ozone and partitioning in the many chemical families.

One of the major advances for identification, and possibly quantification, of ozone changes has been the use of tracer correlation methods. This method has been greatly improved and quantified by the work done in the Aeronomy Laboratory and has anchored  $\text{N}_2\text{O}$  as a “chemical” coordinate with respect to which changes in ozone or  $\text{NO}_y$ , or other species, can be calculated. This method originally relied on the in situ measurements carried out from the ER-2 aircraft and was made possible by the highly precise measurements of  $\text{N}_2\text{O}$ ,  $\text{O}_3$ , and  $\text{NO}_y$ . The latter two of these species were measured by Aeronomy Laboratory scientists and a majority of the correlation studies were carried out by Aeronomy Laboratory scientists in collaboration with other colleagues from the National Aeronautics and Space Administration (NASA), the National Center for Atmospheric Research (NCAR), and universities.

In addition to the winter/spring polar regions, studies of the summer lower stratosphere were carried out in the Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) mission in which the mission scientist and several principal investigators were from the Aeronomy Laboratory. The results from the POLARIS mission are currently being analyzed and, already there are a few surprises: the photochemistry of the nitrogen oxides is not what it was assumed to be. Now, laboratory research carried out in the past few months combined with the field observations show that the partitioning of  $\text{NO}_y$  between active and inactive forms is different: there is more  $\text{NO}_x$  for a given amount of  $\text{NO}_y$  and we understand the reasons for it.

In addition to understanding the processes responsible for determining the ozone abundance in the stratosphere, “testing” of chemicals to ascertain their ozone friendly nature has continued in the Aeronomy Laboratory. This work, initiated immediately after the London Amendment to the Montreal Protocol that phased out CFCs, has been extended to many new substitutes. This work has separated the acceptable substitutes from the unacceptable in terms of their ozone depletion and global warming potentials.

All the above work has been done via close interactions between field measurements, laboratory determinations, and modeling: this is a research paradigm that is well rooted in the Aeronomy Laboratory and has been highly successful. The following pages give a partial list of the significant findings by Aeronomy Laboratory scientists during 1993 – 1998.

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

We give here *examples* of Aeronomy Laboratory research endeavors that address the stratospheric ozone layer. 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 stratospheric ozone layer. 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. Reactive Chemical Species as Tracers in the Stratosphere

Reactive nitrogen ( $\text{NO}_y$ ) and ozone ( $\text{O}_3$ ) are produced mostly in the upper tropical stratosphere and the circulation in the stratosphere moves recent tropospheric air upwards in the tropics and poleward and downward into the lower stratosphere. The common stratospheric production regions and relatively long lifetimes of  $\text{NO}_y$  and  $\text{O}_3$ , combined with horizontal mixing, leave their abundances well correlated throughout the lower stratosphere at mid- to high-latitudes. Deviations from these correlations indicate occurrence of other processes, such as chemical ozone depletion or denitrification in the polar regions. The correlations and the deviations from the correlations are powerful tools for estimating abundances and diagnosing concentration changes in the stratosphere. Such correlations have been developed over the past decade by lower stratospheric observations of  $\text{NO}_y$ ,  $\text{O}_3$ , and  $\text{N}_2\text{O}$  made aboard the NASA ER-2 aircraft. In these missions,  $\text{NO}_y$  and  $\text{O}_3$  (in most missions) were measured by Aeronomy Laboratory scientists. Some selected accomplishments follow.

- **Characterizing ozone abundance using a conserved tracer**

*$\text{O}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_y$  correlation.* When transport and chemistry are highly coupled, it is hard to isolate changes due to chemistry. Correlations lead to one approach for the separation.

*Analysis of  $\text{O}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_y$  data from ER-2 flights.*  $\text{O}_3$  data gathered during eight ER-2 missions on more than 260 flights have been correlated with simultaneous measurements of  $\text{NO}_y$  and  $\text{N}_2\text{O}$ , the conserved tracers. These correlations have revealed clear signatures of high latitude  $\text{O}_3$  loss in both hemispheres, tropical  $\text{O}_3$  production, and transport into high latitudes that were not previously detected. Data gathered during the 1997 POLARIS mission have given us a first look at these correlations at high latitudes during the summer months and have provided new insights into  $\text{O}_3$  loss and transport in this region.

*Measurements of  $\text{O}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_y$  have provided a sensitive indicator of net  $\text{O}_3$  production, loss and transport.* Chemical ozone depletion can be now identified.

M. H. Proffitt, K. Aikin, J. J. Margitan, M. Loewenstein, J. R. Podolske, A. Weaver, K. R. Chan, H. Fast and J. W. Elkins, Ozone loss inside the northern polar vortex during the 1991-1992 Winter, *Science*, 261, 1150-1154, 1993.

- **$\text{NO}_y/\text{O}_3$  ratio as a constraint on transport and flux in the lower stratosphere**

*Characterizing stratospheric transport from aircraft data.* The common stratospheric production regions and relatively long lifetimes of  $\text{NO}_y$  and  $\text{O}_3$ , combined with horizontal mixing, leave their abundances well correlated throughout the lower stratosphere at mid- to high latitudes. Interpretation of this data yields valuable information about transport in the stratosphere.

*Interpretation of the variation of  $\text{NO}_y$  with  $\text{O}_3$ .* In the ER-2 data sets, a striking feature of the correlation ratio is the sharp decrease that occurs between the extratropics and tropical regions in the lower stratosphere. Ratios are lower in the tropics because of increased *in situ*  $\text{O}_3$  production there and because the strong isentropic mixing that is present at midlatitudes does not penetrate into the tropics. Most 2-D atmospheric models fail to simulate the low tropical ratios because diffusive transport across the gradient region is too large. When the simulation is improved to represent this decreased transport, the lifetime of long-lived stratospheric species decreases in some models because transport from midlatitudes into the upwelling region in the tropics is reduced. In addition, improvements change the sensitivity of model ozone values to perturbations from aircraft and other anthropogenic emissions.

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*NO<sub>y</sub>/O<sub>3</sub> ratios constrain transport and flux calculations in the lower stratosphere.* Strong features found in atmospheric observations of long-lived species offer important constraints and guidance to modeling the present and future state of the lower atmosphere and calculation of fluxes of species in the stratosphere.

Murphy, D. M., and D. W. Fahey, An estimate of the flux of stratospheric reactive nitrogen and ozone into the troposphere, *J. Geophys. Res.*, *99*, 5325-5332, 1994.

Murphy, D. M., *et al.*, Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, *98*, 8751-8773, 1993.

- **NO<sub>y</sub>/N<sub>2</sub>O correlation and interpretation**

*Understanding differences between the two hemispheres.* NO<sub>y</sub> and N<sub>2</sub>O are two long-lived species in the stratosphere and are intimately related because the photochemical decomposition of N<sub>2</sub>O in the stratosphere is the principal source of stratospheric NO<sub>y</sub>. Their variations provide information about stratospheric processes.

*Interpretation of ER-2 data on NO<sub>y</sub> and N<sub>2</sub>O.* 1994 NASA Airborne Southern Hemisphere Ozone Expedition / Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) and 1995-96 Stratospheric Tracers of Atmospheric Transport (STRAT) missions extended the NO<sub>y</sub> and N<sub>2</sub>O measurements to a broader range of latitudes in several seasons. The correlation of measurements of NO<sub>y</sub> with N<sub>2</sub>O in the lower stratosphere reveal compact, near-linear relationships throughout the data sets. The slope of the correlation is proportional to the conversion efficiency of N<sub>2</sub>O to produce NO<sub>y</sub> in the stratosphere and, hence, is a key parameter in the global budget of both species. Data taken in the Southern Hemisphere (SH) exhibit a much larger seasonal variation in the slope during this time period than was observed in the Northern Hemisphere (NH). The increase in the slope of nearly 30% over the fall to late winter/early spring period suggests that significant changes occur in the NO<sub>y</sub> budget in the SH and that comparable changes do not occur in the NH. Comparisons with two-dimensional model results show that the slope decreases in the SH when the denitrified Antarctic vortex is diluted into mid latitudes upon vortex breakup in late spring and that through descent of stratospheric air, the slope recovers during the following fall/winter period as observed. Because of the lack of intense denitrification in the NH winter vortex, the seasonal cycle there is small. Differences in stratospheric circulation may also play a role in the hemispheric seasonal cycles.

*The observed NO<sub>y</sub>/N<sub>2</sub>O correlation and their interpretation shows the difference between the Arctic and Antarctic.* Understanding the large differences in the hemispheric seasonal cycles of NO<sub>y</sub> and N<sub>2</sub>O in the lower stratosphere is important to explain present changes in stratospheric ozone, its sensitivity to future perturbations of the NO<sub>y</sub>, and N<sub>2</sub>O global budgets.

Keim, E. R., M. Loewenstein, J. R. Podolske, D. W. Fahey, R. S. Gao, E. L. Woodbridge, R. C. Wamsley, S. G. Donnelly, L. A. Del Negro, C. D. Nevison, S. Solomon, K. H. Rosenlof, C. J. Scott, M. K. W. Ko, D. Weisenstein, and K. R. Chan, Measurements of the NO<sub>y</sub>-N<sub>2</sub>O correlation in the lower stratosphere: Latitudinal and seasonal changes and model comparisons, *J. Geophys. Res.*, *102*, 13193-13212, 1997.

Nevison, C. D., S. Solomon, R. R. Garcia, D. W. Fahey, E. R. Keim, M. Loewenstein, J. R. Podolske, R. S. Gao, R. C. Wamsley, S. G. Donnelly, and L. A. Del Negro, Influence of Antarctic denitrification on two-dimensional model NO<sub>y</sub>/N<sub>2</sub>O correlations in the lower stratosphere, *J. Geophys. Res.*, *102*, 13183-13192, 1997.

## 2. Dynamics in the Stratosphere

Transport of species in the stratosphere between various regions within it and between the stratosphere and the troposphere determine the distribution of the ozone abundance in the stratosphere. Transport and chemistry, sometimes separable in time scales and at other times closely coupled, are major components needed to understand the present and past ozone distributions and for predicting the future levels. The understanding of the dynamics of the stratosphere has been improved through measurements of many chemical species from aircraft missions involving an Aeronomy Laboratory scientist.

### • **The Brewer-Dobson circulation in the light of in situ aircraft observations**

*Brewer-Dobson circulation.* In Brewer-Dobson circulation (long-term zonal and temporal means) air rises from the tropical tropopause and sinks at the poles. Smaller-scale variations in this circulation are important for stratospheric ozone chemistry and need to be assessed.

*Analysis of aircraft data reveals some details.* ER2 data taken at latitudes ranging from 60°N to 70°S at longitudes from 115°W to 150°E were used to investigate the features of circulation patterns. Many new insights were obtained:

- o Evidence for recirculation of air between the upper troposphere and lower stratosphere, particularly in the tropics, was obtained. Some air in the upper troposphere and lower stratosphere of the tropics contained depleted layers of tracers and near isothermal temperature profiles characteristic of the mid latitude lower stratosphere. Such advection would allow deeper convection than temperature inversions otherwise found in the lower tropical stratosphere.
- o The possible formation of new particles near the tropical tropopause, as a consequence of the dehydration process, was indicated.
- o Interhemispheric asymmetries in CO, condensation nuclei, and NO<sub>y</sub> suggested that the stratosphere in each hemisphere receives a dominant fraction of its air from its own troposphere. The Inter Tropical Convergence Zone (ITCZ) is thus not a completely efficient mixer of tropospheric air from the two hemispheres.
- o Evidence was found for an extensive fraction (1/4 - 3/5) of air recently coming from the lower stratosphere of midlatitudes from the inner tropical tropopause up to potential temperature 500 K.
- o The layer between the tropopause and potential temperature 400 K was shown to consist of air descended through the polar vortex mixed with air recently from the upper extratropical troposphere and from the lower tropical stratosphere.
- o There was a difference of ~ 0.5 ppmv in the mixing ratios of 2CH<sub>4</sub> + H<sub>2</sub>O at ER2 cruise altitudes (potential temperature 470 K) between the “younger” air in the tropics and the “older” air elsewhere, in both hemispheres in both March and October. The H<sub>2</sub> was essentially flat at 0.5 ppmv. These observations suggested a positive trend in stratospheric water of ~ 0.15 ppmv year<sup>-1</sup> for the period 1990 - 1994, a period coincident with the most protracted El Niño on record.
- o The transport of PSC - processed air with low tracer mixing ratios to austral midlatitudes was very evident in early June, a period when minimum vortex temperatures had dropped below 195K but when the polar night jet had attained only about half to two thirds its eventual strength.
- o There was midwinter ozone loss in the outer vortex of up to 25% which had developed between early June and early August. Low-ozone air was observed outside the vortex in mid October.
- o Meridional gradients of tracers, such as CFC-11, methane and nitrous oxide, NO<sub>y</sub>, H<sub>2</sub>O and HCl suggested that there is a 10° latitude-wide mixing zone centered on the Antarctic jet core between 16 and 20 km altitude; it contains about as much mass as the cap poleward

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of it. The effects of such mixing were evident out to about 40°S in the S. America sector in 1987, and out to about 50°S in the New Zealand sector in 1994.

- o Vertical profiles in the outer vortex of tracers, wind speed and wind direction showed layered structures both at the edge of and inside the vortex which are ubiquitous over the southern ocean thousands of kilometers from land. They are likely to cause irreversible mixing across the polar night jet stream.

*Further details of the Brewer-Dobson circulation were obtained from in situ aircraft observations.* The presence of detectable stratospheric air in the upper troposphere, including the tropics, raises the possibility that the chemical production from the stratosphere, including its particle loading, could be involved in cirrus cloud formation in the upper troposphere and hence in climate. The lower stratospheric asymmetry in particle number density between the hemispheres may have important implications for the chemistry associated with CFCs and high flying aircraft, particularly if the asymmetry extends to aerosol composition as well as number. The combined radiative effects of ozone loss between the tropopause and potential temperature 400 K, with the presence there of water vapor of midlatitude tropospheric origin, raises the question of the stability of the tropopause under CFC and greenhouse forcing. The water vapor ranges from 5 to 50 ppmv between 400 K and the extratropical tropopause; the values at the tropopause are variable and in the high end of the range, and are radiatively significant, particularly at cold tropopauses.

Tuck, A. F., D. Baumgardner, K.R. Chan, J.E. Dye, J.W. Elkins, S.J. Hovde, K.K. Kelly, M. Loewenstein, J.J. Margitan, R.D. May, J.R. Podolske, M.H. Proffitt, K.H. Rosenlof, W.L. Smith, C.R. Webster, and J.C. Wilson, The Brewer-Dobson Circulation in the light of high altitude *in situ* Aircraft observations (1995 Symons Memorial Lecture), *Q. J. R. Meteorol. Soc.*, 123, 1-69, 1997.

- **Mass fluxes and their role in the O<sub>3</sub> budget of the upper troposphere/lower stratosphere**

*Mass transport and ozone budget.* A quantitative estimate of the mass transport circulation is needed to describe the ozone budget.

*Analysis of satellite data.* Using satellite-observed temperature and constituent profiles as input to a radiative heating rate calculation, the zonally averaged meridional circulation was estimated over a multi-year period. A strong annual cycle exists, with maximum upwelling into the stratosphere in the tropics during Northern Hemisphere winter. The estimated circulation has been shown to control the observed zonally averaged temperature distribution in the stratosphere, and deviations between dynamical and radiative estimates of the circulation has been used to show the importance of small scale processes in driving the circulation in the middle and lower stratosphere.

*Average mass fluxes of O<sub>3</sub> between the upper troposphere/lower stratosphere is better quantified.* Using the calculated zonally averaged circulation in conjunction with satellite constituent measurements, the globally averaged O<sub>3</sub> flux out of the photochemically active portion of the stratosphere was estimated to be 5 - 10 Tg/year. The seasonal cycle of the O<sub>3</sub> mass flux into the upper troposphere is complicated by the fact that the mass of the lower stratosphere varies with season. In the Northern Hemisphere the mass (and likely ozone) flux into the troposphere is a maximum in late spring. In the Southern hemisphere the flux into the troposphere is a maximum in winter.

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

Gettelman, A, J. R. Holton, and K. H. Rosenlof, Mass fluxes of O<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O and CF<sub>2</sub>Cl<sub>2</sub> in the lower stratosphere calculated from observational data, *J. Geophys. Res.*, 102, 19149-19159, 1997.

- **Radiative cooling rates over Antarctica in the stratosphere**

*Rate of cooling in Antarctic Spring.* Understanding the rate of cooling in Antarctica is essential for describing the past ozone holes and predicting the future.

*Cooling rate calculation and their dependence on input.* Calculations of infrared cooling rates over Antarctica from fall through spring have been carried out using a variety of data sources. In clear air, High-resolution Infrared Sounder (HIS) results from aircraft led to somewhat larger cooling rates compared to those calculated from operational meteorological analyses due to warmer HIS temperatures. The coupling of tropospheric phenomena, such as clouds, to the stratosphere via the 9.6  $\mu\text{m}$  ozone band was shown to be an important process. The insertion of tropospheric clouds increased instantaneous cooling rates by 0.5 K/day in potential temperature (50% - 100%) compared to clear air calculations, with the net effect to increase the diabatic downwelling flow through the vortex by 40% - 60% in the monthly mean. Calculations using observed balloon profiles of ozone and water vapor from McMurdo showed that the midwinter dehydration slows the cooling rate by about 30%, so preventing an even colder and stronger vortex than actually occurs. Once chlorine chemistry has removed the ozone between 40 and 150 hPa in September/October, the vortex there is stabilized by the loss of ozone heating and so lasts longer than before CFCs were in the atmosphere; above 40 hPa more heating occurs, destabilizing the vortex.

*Radiative cooling-rate calculations over Antarctica show the importance of inputs.* The sensitivity to the actual measured ozone and water profiles suggests that calculations made with climatological data may be significantly in error. A previously undiscovered minimum in the cooling rate at the edge of the vortex in late winter and early spring occurs as a result of gradients of inputs important to the cooling rate calculation.

Hicke, J., and A.F. Tuck, Tropospheric clouds and lower stratospheric heating rates: Results from late winter in the southern hemisphere, *J. Geophys. Res.*, submitted, 1998.

### 3. Elucidating the Role of Stratospheric Aerosols: What Are They and What Do They Do?

The critical role of heterogeneous chemistry in depleting Antarctic ozone was proposed by Aeronomy Laboratory researchers in 1986. At that time, it was thought that such processes were confined to solid polar stratospheric cloud surfaces. Laboratory studies carried out at the Aeronomy Laboratory, and elsewhere, later suggested that similar processes may also occur on liquid sulfuric acid aerosols, even at warmer temperatures. The abrupt changes in ozone abundances following the eruption of Mt. Pinatubo provided further evidence for this role of sulfate aerosol. Since then, a concerted effort involving field measurements, laboratory studies and model calculations have shown the crucial nature of the role played by reactions in sulfuric acid aerosols in determining the ozone abundance in the midlatitude lower stratosphere.

- **How to deal with reactions in sulfate aerosols and the effects of temperature fluctuations.**

*Reactions in sulfate aerosol must be included in models.* Calculating the rate of reaction in a condensed medium where two or more reactants come from the gas phase is difficult, especially in forms suitable for including in atmospheric models. Temperature in the stratosphere fluctuates a great deal and its consequence has to be well represented in models.

*A framework for reactions in liquid aerosols.* A framework was developed where the rate of the multiphase reaction can be calculated using laboratory measured basic physico-chemical parameters and which also takes into account the changes in the reactivity with the size of the droplet. This framework is now universally adopted for stratospheric modeling. Further, this method identified the parameters that need to be measured in the laboratory to derive the rates of multiphase reactions in the atmosphere. The rates of reactions in sulfuric acid aerosol vary greatly

with temperature. It was shown that rate of chlorine activation calculated when the temperature fluctuations are included is faster than that calculated for the mean temperature.

*A framework for modeling reactions in sulfate aerosol was developed and the importance of including the effects of temperature fluctuations was illustrated.* The framework for including reactions in liquid aerosol has enabled easy incorporation of such processes in models. It also helped identify the parameters that need to be measured in the laboratory. The enhanced rates for the reactions important in the midlatitude stratosphere due to temperature fluctuations were calculated as enhancement factor and they can now be used in models.

Hanson, D. R., A. R. Ravishankara, and S. Solomon, Heterogeneous reaction in sulfuric aerosols: A framework for model calculations, *J. Geophys. Res.*, 99, 3615-3629, 1994.

Murphy, D. M. and A. R. Ravishankara, Temperature averages and rates of stratospheric reactions, *Geophys. Res. Lett.*, 21, 2471-2474, 1994.

- **Multiphase reactions in the stratosphere**

*Rates of multiphase reactions.* To quantify the rates of multiphase reactions needed for modeling the stratosphere and to explore the importance of new processes, physico-chemical parameters (such as the Henry's law solubility constants and liquid phase reaction rate constants) are needed.

*Laboratory measurements of multiphase reaction rates.* Solubility constants and rates of reactions were measured using a coated-wall flow tube equipped with chemical ionization mass spectrometry for detecting reactants and products. More accurate parameters were obtained for the reactions of ClONO<sub>2</sub> and HOCl with HCl, and the hydrolysis of N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub>. The potentially important reaction of HONO with HCl was also quantified and shown to be insignificant under lower stratospheric conditions. Several important atmospheric reactions exhibit surface specific reactivity (e.g., the ClONO<sub>2</sub> + HCl reaction) and size dependent reaction probabilities (e.g., the ClONO<sub>2</sub> + H<sub>2</sub>O reaction). Surface specific reactions and the variation of reaction probabilities with particle size were investigated using chemical ionization mass spectrometry (CIMS) with liquid-coated flow reactors and an aerosol flow reactor, respectively. A theoretical framework was developed to quantify these phenomena.

*Rates of many multiphase reactions in the stratosphere are quantified.* The rate of chlorine activation in the lower stratosphere can be accurately calculated, if the aerosol abundance is known.

Hanson, D.R. and A. R. Ravishankara, Reactive uptake of ClONO<sub>2</sub> onto sulfuric acid due to reaction with HCl and H<sub>2</sub>O, *J. Phys. Chem.*, 98, 5728-5735, 1994.

Hanson, D.R. and E. R. Lovejoy, Heterogeneous reactions in liquid sulfuric acid: HOCl + HCl as a model system, *J. Phys. Chem.*, 100, 6397-6405, 1996.

- **Multiphase hydrolysis of BrONO<sub>2</sub> and the role of bromine in the stratosphere**

*Reactions of bromine compound in the stratosphere.* Multiphase reactions of chlorine containing compounds important in the stratosphere were extensively studied. However, such studies on bromine species are lacking.

*Reactive uptake of BrONO<sub>2</sub>.* It was shown that bromine reservoir species in the stratosphere, such as BrONO<sub>2</sub>, also efficiently undergo multiphase reactions. Unlike the hydrolysis of ClONO<sub>2</sub>, which is highly dependent on the water content of the sulfate aerosol, BrONO<sub>2</sub> hydrolysis proceeds very rapidly for almost all the compositions encountered in the lower

stratosphere and produces HOBr. To assess the rate of photolysis of HOBr, its absorption cross section was also measured.

*Multiphase hydrolysis of BrONO<sub>2</sub> was shown to be a significant process.* Based on these results, it is now accepted that the hydrolysis of BrONO<sub>2</sub> is an important multiphase reaction in the stratosphere and a source of HO<sub>x</sub> at high solar zenith angles. This work also showed bromine to be a more potent ozone destroyer than previously believed. Hydrolysis of BrONO<sub>2</sub> was identified as the source of the hitherto unexplained early morning OH observed in some field measurements of the lower stratosphere.

Hanson, D. R., A. R. Ravishankara, and E. R. Lovejoy, Reaction of BrONO<sub>2</sub> with H<sub>2</sub>O on submicron sulfuric acid aerosol and the implications for the lower stratosphere, *J. Geophys. Res.*, *101*, 9063-9069, 1996.

- **What determines the upper bound to the sulfate aerosol layer?**

*Sulfate aerosol formation and loss.* Gas phase H<sub>2</sub>SO<sub>4</sub>, formed in the stratosphere through the reaction of SO<sub>3</sub> with H<sub>2</sub>O, leads to sulfate aerosol. The abundance of sulfate aerosol is determined by the balance between the H<sub>2</sub>SO<sub>4</sub> formation and loss processes. The rate of formation of H<sub>2</sub>SO<sub>4</sub> is controlled by the abundance and loss processes of its precursors. Therefore, these two processes have to be quantified.

*Measurements of SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> loss processes.* In conjunction with the laboratory studies of the rate coefficient and mechanism of the SO<sub>3</sub> + H<sub>2</sub>O reaction, the gas phase absorption cross sections for SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> were also determined. Atmospheric calculations of the sulfate formation were carried out using a one-dimensional model.

*Factors that determine the upper bound to the sulfate aerosol layer were elucidated.* Our results show that the decrease in H<sub>2</sub>SO<sub>4</sub> formation coupled with the increased photolysis of SO<sub>3</sub> with increasing altitude leads to a sharp drop off in sulfate aerosols near 40 km.

Burkholder, J.B. and S. McKeen, UV absorption cross sections for SO<sub>3</sub>, *Geophys. Res. Lett.*, *24*, 3201-3204, 1997.

Lovejoy, E.R., D.R. Hanson, and L.G. Huey, Kinetics and products of the gas-phase reaction of SO<sub>3</sub> with water, *J. Phys. Chem.*, *100*, 19911-19916, 1996.

- **Aerosol chemistry: New results in the stratosphere**

*Heterogeneous chemistry and PSCs merit further study.* Sulfate aerosols, in addition to their participation in multiphase chemistry, also play a crucial role as nuclei for polar stratospheric clouds (PSCs). Yet, few measurements have been made to assess how trace or volatile species in stratospheric aerosols might affect their heterogeneous or nucleation behavior.

*The WB57F Aerosol Mission (WAM).* To investigate the composition of the sulfate aerosol, a WB57F aircraft fitted with instruments to make measurements of aerosol composition, aerosol size and refractive index, water, long-lived tracer molecules, and temperature profiles was flown in April and May of 1998. Key to this payload were the first *in-situ* measurements of the composition of aerosol particles in the stratosphere made by the Aeronomy Laboratory's new Particle Analysis by Laser Mass Spectrometry (PALMS) instrument.

*Possible role of minor sulfate aerosol constituents indicated.* A preliminary analysis of the data has already shown that a large number of aerosols in the lower stratosphere contain Fe, Mg, and other meteoritic material. Small amounts of organics, nitrogen species, and mercury are also present in many stratospheric aerosols. One possible implication of this finding is that debris from the ablation of meteorites in the mesosphere may affect the way new sulfate particles nucleate in the stratosphere.

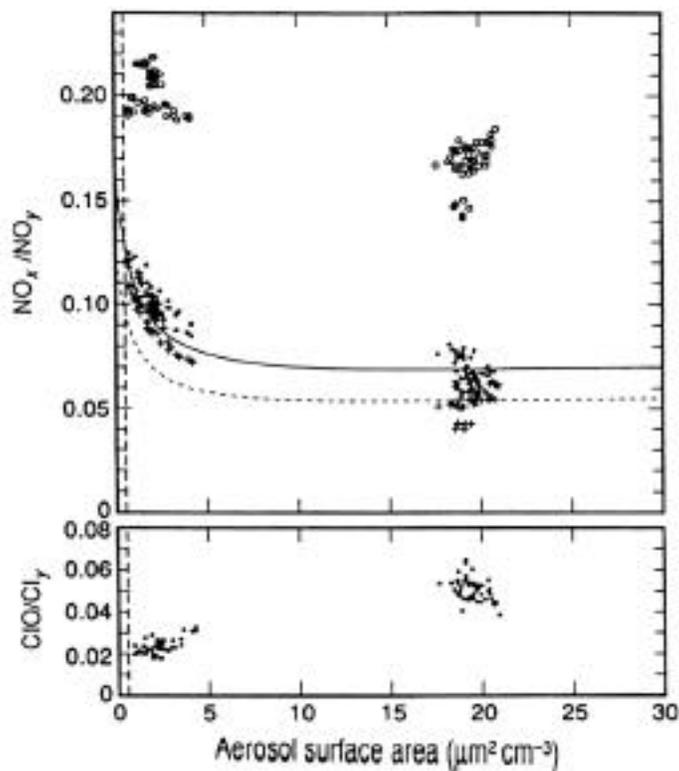
- **Field evidence for reactions in sulfuric acid**

*Background.* Even though modeling calculations, coupled with laboratory measurements, can show the importance of specific reactions, it is mandatory to find evidence that such chemistry does indeed take place in the atmosphere. Some of the earliest and most-significant such findings came from studies carried out by Aeronomy Laboratory scientists and colleagues. Two examples follow:

(a)  $\text{NO}_x/\text{NO}_y$  ratio and the role of heterogeneous reactions

*Hydrolysis of  $\text{N}_2\text{O}_5$ .* Laboratory data on the multiphase hydrolysis of  $\text{N}_2\text{O}_5$  in sulfate aerosol combined with photochemical model simulations of the stratosphere indicate that this reaction significantly reduces  $\text{NO}_x$  within the  $\text{NO}_y$  reservoir. Experimental confirmation of the role of this reaction came in part from mid- and high-latitude measurements of reactive and reservoir species and aerosols made on board the NASA ER-2 aircraft.

*ER-2 based measurements of  $\text{NO}/\text{NO}_y$  ratio.* The measured  $\text{NO}/\text{NO}_y$  ratios were used to estimate the  $\text{NO}_x/\text{NO}_y$  ratio in air parcels containing a range of sulfate aerosol surface area between background and volcanically enhanced values. The resulting  $\text{NO}_x/\text{NO}_y$  ratios were significantly less than model simulations using only gas-phase reactions and in good agreement when the  $\text{N}_2\text{O}_5$  hydrolysis reaction was included. The abundance of  $\text{ClO}$  increased with sulfate aerosol as a result of the reduced formation rates of  $\text{ClONO}_2$  in reaction with  $\text{NO}_2$ . The observations also indicated that the changes in  $\text{NO}_x/\text{NO}_y$  with increased aerosol reach a limit because the rate of conversion is controlled at high aerosol loading by the gas-phase reaction of  $\text{NO}_2$  with  $\text{O}_3$ . Thus, catastrophic increases in  $\text{ClO}$  and associated ozone loss rates do not occur in volcanic periods.



$\text{N}_2\text{O}_5$  Hydrolysis Suppresses  $\text{NO}_x$ -to- $\text{NO}_y$  Ratio

*N<sub>2</sub>O<sub>5</sub> hydrolysis impacts ozone loss rates.* This chemistry is now considered part of the standard photochemical reaction set needed to simulate ozone production and loss in the stratosphere. An important example of the effect of including the N<sub>2</sub>O<sub>5</sub> hydrolysis reaction in models is the reduced response of global ozone to the emissions of a future fleet of supersonic aircraft.

Fahey, D. W., *et al.*, *In situ* measurements constraining the role of sulfate aerosols in mid-latitude ozone depletion, *Nature*, 363, 509-514, 1993.

#### (b) Evidence for chlorine activation

*Chlorine activation on sulfate aerosol.* Based on laboratory measurements, sulfate aerosol is expected to directly activate chlorine in the stratosphere and its detection in the atmosphere is necessary.

*Ground-based measurements of OCIO.* Aeronomy Laboratory measurements of OCIO in Antarctica provided the first observational evidence in support of multiphase reactions in sulfuric acid aerosol. Unprecedented amounts of sulfuric acid aerosols were injected into the stratosphere by the eruption of Mt. Pinatubo, providing an opportunity to observe their chemistry in detail. Aeronomy Laboratory researchers have measured springtime (September - October) OCIO for more than a decade. Following Pinatubo, they observed substantial OCIO in autumn (April), at a time when temperatures were too warm for the formation of solid PSCs.

*Direct chlorine activation in sulfate aerosol seen.* These data provided key direct evidence for enhancements in reactive chlorine due to processing in liquid sulfuric acid at temperatures above 200K.

Solomon, S., R. W. Sanders, R. R. Garcia, and J. G. Keys, Enhanced chlorine dioxide and ozone depletion in Antarctica due to volcanic aerosols, *Nature*, 363, 245-248, 1993.

- **Measurements in aircraft exhaust plumes and their interpretation**

*Role of exhaust from supersonic aircraft.* There is an increasing concern about the effect of aircraft emissions on the global atmosphere because of the growing subsonic aircraft fleet and a proposed fleet of new supersonic aircraft. The accumulation of emissions in the upper troposphere and lower stratosphere is expected to perturb the chemical and radiative budgets in those regions in important ways. Understanding the perturbations of aircraft emissions requires an understanding of the nature of the aerosol and gas-phase emissions of aircraft and the interaction of these emissions with ambient air in the aircraft exhaust plume and in the background atmosphere.

*Chasing a Concorde's plume.* Reactive nitrogen species (Aeronomy Laboratory data), particles, and carbon dioxide were measured with the NASA ER-2 aircraft in the exhaust plume of the Concorde operating at supersonic speeds in the lower stratosphere and the data were extensively analyzed.

*Aircraft-generated particles are important.* The results showed that the emission index and partitioning of reactive nitrogen species were consistent with test-bed measurements on engines, thereby increasing confidence in aircraft scenario emission estimates. The large number of small volatile particles observed are thought to contain sulfuric acid derived from fuel sulfur while the smaller number of non-volatile particles are assumed to be soot. If a large fleet of aircraft had similar emissions of sulfur-containing particles, models show that the background aerosol layer would be increased significantly in surface area and number and that stratospheric ozone levels would be decreased as a result. The decrease would augment that from the accumulation of nitrogen oxide emissions. The soot particle and ozone measurements in the exhaust plume were also used to show that ozone is sufficiently unreactive on aircraft soot surfaces and that reactions on accumulated soot in the background stratosphere will not significantly perturb global ozone levels.

## OZONE LAYER

Gao, R. -S., B. Kärcher, E. R. Keim, D. W. Fahey, Constraining the heterogeneous loss of O<sub>3</sub> on soot particles with observations in jet exhaust plumes, *Geophys. Res. Lett.*, In press, 1998.

Fahey, D. W., *et al.*, Emission measurements of the Concorde supersonic aircraft in the lower stratosphere, *Science*, 270, 70-74, 1995.

### 4. Better Understanding of Chemistry in the Polar Regions: From Antarctica to the Arctic

The discovery of the Antarctic ozone hole in the 1980s was a spectacular scientific finding. Observations not just of ozone but also of the chemicals that affect it revealed the primary cause of this dramatic seasonal depletion: the human-produced chlorine present in today's stratosphere, coupled with reactions on polar stratospheric cloud (PSC) surfaces lead to massive Antarctic ozone losses. This laid the scientific foundation for regulation of the chlorofluorocarbons and related gases. However, the Antarctic ozone hole "opened" up extremely rapidly (mainly between 1980 and 1985) and the mystery of this onset was a key challenge to scientific understanding for about a decade.

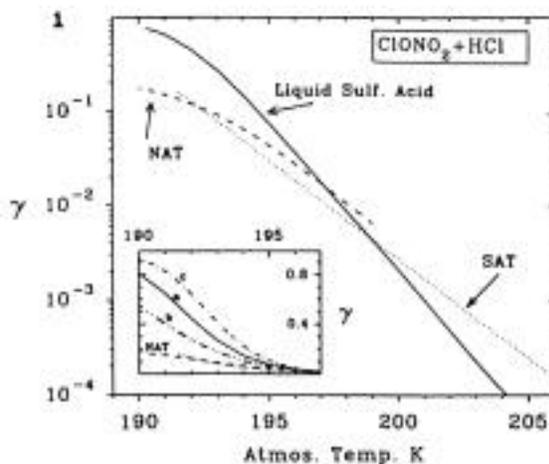
Unlike the Antarctic, the Arctic stratosphere did not experience large ozone depletions in the late 1970s and 1980s, when the atmospheric chlorine loading was increasing rapidly. However, there have been large springtime losses in most of the 1990s, when the chlorine loading has been fairly constant. Accounting for these recent Arctic depletions, understanding the difference (and similarities) between the Arctic and Antarctica, and predicting the future of polar ozone changes are key challenges to atmospheric scientists. Many studies carried out by Aeronomy Laboratory scientists have contributed towards achieving this goal.

- **Do the phase and composition of PSCs matter?**

*Reactivity of different surfaces.* It has been assumed that PSCs (both Type I and Type II) are solids. The Type II PSCs could be many different kinds of solids (nitric acid trihydrate, nitric acid dihydrate, etc.) that contain HNO<sub>3</sub> and H<sub>2</sub>O. Recently, it was shown that Type II PSCs could be liquids. It is, therefore, critical to know if the rate of chlorine activation is dependent on the phase and composition of the condensed matter.

*Rates of chlorine activation on stratospheric surfaces.* Many laboratory measurements were carried out on different types of solid PSC-like substrates. Based on the results on solids, as well as liquid sulfate aerosol, it was shown that to a first approximation, the composition and the phase of the condensed matter does not impact the rate of chlorine processing.

*The phase and composition of PSCs were shown to be of secondary concern for chlorine activation.* The important parameters were shown to be temperature and water vapor pressure. This finding has completely changed the paradigm for polar processing and helped simplify our understanding of chlorine activation in the polar region.



Phase and Composition Are Not Crucial

Ravishankara, A. R. and D. R. Hanson, Differences in the reactivity of Type I PSCs depending on their phase, *J. Geophys. Res.*, 101, 3885-3890, 1996.

- **Antarctic polar photochemistry: Absence of polar night**

*Chlorine activation in the winter polar regions.* The Aeronomy Laboratory's near UV/Visible remote sensing instruments provided the first ground-based measurements of OCIO in 1986, pointing towards chlorine as the cause of the ozone hole. Information regarding the mechanism of activation of chlorine and its timing during the winter season is needed.

*Groundbased observation of stratospheric constituents.* The needed information was obtained through the first ground-based observations of winter polar chemistry using the moon. Observations of NO<sub>2</sub>, NO<sub>3</sub>, and OCIO showed that air parcels over McMurdo Station, Antarctica, did not experience prolonged periods of polar night. Rather, it was demonstrated that the air parcels undergo frequent excursions to the sunlit atmosphere. Interpretation of the 1991 moon measurements revealed that OCIO rose to high levels in June, implying extensive conversion of chlorine to active forms and some exposure to sunlight.

*Antarctic polar photochemistry can occur during polar night.* These data showed that some midwinter Antarctic ozone depletion is likely to occur (about 50 Dobson Units). Such occurrences are also likely in the Arctic, where the vortex is further off the pole.

Solomon, S., J. P. Smith, R. W. Sanders, L. Perliski, H. L. Miller, G. H. Mount, J. G. Keys, and A. L. Schmeltekopf, Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica, 8. Observations of nighttime NO<sub>2</sub> and NO<sub>3</sub> from April-October, 1991, *J. Geophys. Res.*, 98, 993-1000, 1993.

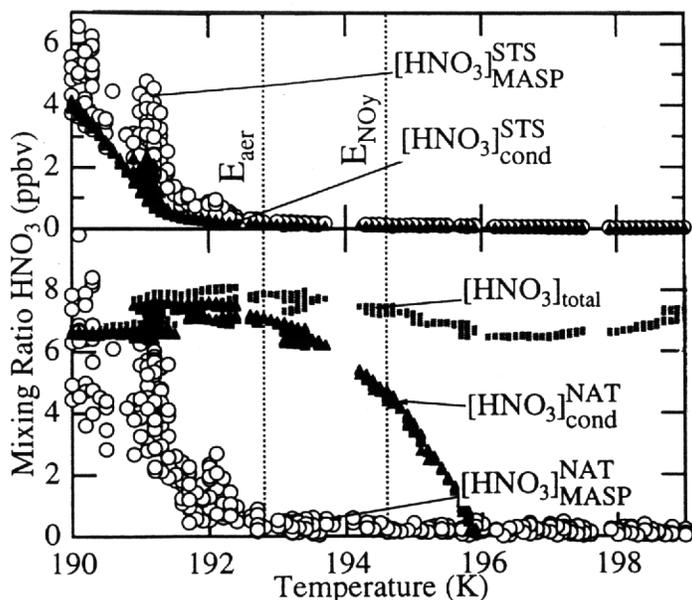
Sanders, R. W., S. Solomon, J. P. Smith, L. Perliski, H. L. Miller, G. H. Mount, J. G. Keys, and A. L. Schmeltekopf, Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica, 9. Observations of OCIO from April-October, 1991, *J. Geophys. Res.*, 98, 7219-7228, 1993.

- **Polar stratospheric clouds and polar chemistry: Observations and interpretation**

*Nitric acid trihydrate or supercooled ternary solution?* Few field observations of the chemical composition of PSCs are available because of instrumental and sampling limitations. The most extensive chemical PSC observations come from measurements from the ER-2 aircraft in both polar regions.

*ASHOE/MAESA mission.* The most recent measurements in the Antarctic region were part of the combined NASA Airborne Southern Hemisphere Ozone Experiment / Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign in late July 1994. Measurements of total reactive nitrogen (NO<sub>y</sub>) (from the Aeronomy Laboratory), aerosol particles, and long-lived tracers were combined with aerosol models to evaluate the composition of PSC particles observed near the edge of the Antarctic vortex (68°S). The interpretation of the results (figure on next page) show that the supercooled ternary solution (STS) composed of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>O is much more consistent with the observations of the onset and intensity of the PSC than either the solid nitric acid trihydrate (NAT) or nitric acid dihydrate (NAD) phases.

*Observations and interpretation of polar stratospheric clouds shed light on their composition.* These and other results strongly suggest that STS are important in both polar regions. Using estimated emissions of a fleet of supersonic aircraft, calculations show that accumulated emissions in polar regions will cause a greater increase in the abundance of STS than of the other solid phases. These results have improved our understanding of PSC formation in polar regions while strengthening the requirement that STS aerosols be included in studies of polar ozone loss and the effects of aircraft emissions.



### Field Observations Show Existence of Supercooled Ternary Solutions

Del Negro, L. A., D. W. Fahey, S. G. Donnelly, R.-S. Gao, E. R. Keim, G. Wamsley, E. L. Woodbridge, J. E. Dye, D. Baumgardner, B. W. Gandrud, J. C. Wilson, H. H. Jonsson, M. Loewenstein, J. R. Podolske, C. R. Webster, R. D. May, D. R. Worsnop, A. Tabazadeh, M. A. Tolbert, K. K. Kelly, and K. R. Chan, Evaluating the role of NAT, NAD, and liquid  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}/\text{HNO}_3$  solutions in Antarctic polar stratospheric cloud aerosol: Observations and implications, *J. Geophys. Res.*, 102, 13255-13282, 1997.

- **Role of aerosol variations in anthropogenic ozone depletion in polar regions**

*Aerosols and polar ozone loss.* It is now established that PSCs play a key role in the formation of the Antarctic ozone hole. One of the key questions is whether the sulfate aerosols also play a role and, if so, do volcanoes affect polar ozone depletion.

*Modeling the ozone hole.* Aeronomy Laboratory scientists, along with other colleagues, resolved the mystery of the timing and variations of Antarctic ozone hole over the past two decades. A careful examination using a numerical model revealed the key linkages between major volcanic eruptions, enhanced polar stratospheric cloud surface areas, and ozone hole chemistry. The calculations showed that the winter sedimentation of particles containing nitrogen (denitrification) of the stratosphere is not the key factor modulating the severity of the Antarctic ozone hole. Rather, the reactions occurring on stratospheric aerosols in spring were shown to likely control the ozone losses. It was also shown that the relevant chemical processes are sensitive to the aerosol abundance. Under the cold conditions that prevail in the Antarctic, changes in stratospheric surface areas due to volcanic eruptions provide the extra "trigger" to ozone depletion that is observed in some years.

*Aerosol play a major role even in polar ozone depletion.* Aeronomy Laboratory scientists and their colleagues also demonstrated that volcanic aerosols modulated the severity of the ozone hole since its inception. The rapid onset of the ozone hole observed in the 1980s was linked to enhanced polar stratospheric cloud surfaces from the eruption of the El Chichon volcano. The enhanced depletion observed following the spectacular Mt. Pinatubo eruption provided further evidence for this view. Finally, ozone losses in the generally warmer Arctic was noted to be dependent not only on volcanic aerosol surface areas, but should also display greater sensitivity to temperature, a result that has been confirmed by the Arctic depletion of recent years. This scientific information has thus led not only to a greatly improved understanding of the past behavior of one

of the key environmental issues of the 20th century (the Antarctic ozone hole), but also to increased confidence in our ability to predict the future, especially in the Arctic.

Portmann, R. W., S. Solomon, R. R. Garcia, L. W. Thomason, L. R. Poole, and M. P. McCormick, Role of aerosol variations in anthropogenic ozone depletion in polar regions, *J. Geophys. Res.*, 101, 22991-23006, 1996.

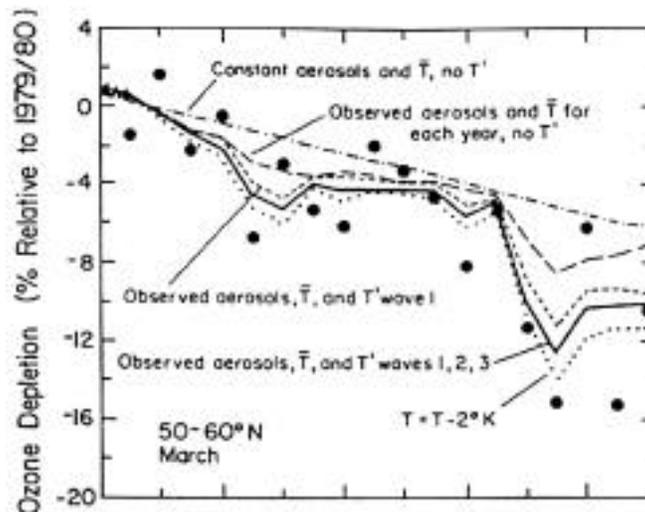
## 5. Understanding of Midlatitude Ozone Depletion

Northern mid-latitude ozone depletions of the past two decades, though small in magnitude compared to the Antarctic ozone hole, is of major societal interest. It has been a challenge to numerical modeling studies for many years to account for the changes that are not monotonic with chlorine loading or time. In addition to simulating the general trends, understanding the ups and down in those trends from one year to another is critical to establishing their cause.

### • Understanding of mid-latitude ozone depletion: Chemistry on aerosols

*Explanation of the midlatitude ozone trends.* An understanding of the detailed time evolution of the ozone depletion at midlatitudes is needed.

*Aerosols and midlatitude ozone.* In a series of two papers, Aeronomy Laboratory researchers and colleagues have shown that the variability in northern hemisphere mid-latitude ozone trends over the past two decades has been closely tied to volcanic aerosols and heterogeneous chemistry. This is a major advance in our ability to understand past ozone trends. Aerosol surface area distributions inferred from satellite-borne 1  $\mu\text{m}$  extinction measurements were used as input to a two-dimensional model to study the effects of heterogeneous chemistry upon anthropogenic ozone depletion at northern midlatitudes. It was shown that short-term (interannual) and longer-term (decadal) changes in aerosols very likely played a substantial role along with trends in anthropogenic chlorine and bromine both in triggering the ozone losses observed at northern midlatitudes in the early 1980s and in increasing the averaged long-term ozone depletions of the past decade or so. The use of observed aerosol distributions enhances the calculated ozone depletion due to halogen chemistry below about 25 km over much of the past decade, including many periods not generally thought to be affected by volcanic activity. Direct observations (especially the relationships of  $\text{NO}_x/\text{NO}_y$  and  $\text{ClO}/\text{Cl}_y$  ratios to aerosol content) confirmed the key aspects of the



Influence of Volcanoes on Midlatitude O<sub>3</sub> Depletion

## OZONE LAYER

model chemistry that is responsible for this behavior and demonstrated that aerosol changes alone are not a mechanism for ozone losses in the absence of anthropogenic halogen inputs to the stratosphere. In a second study, the authors showed that wave-driven temperature fluctuations also play a key role in establishing heterogeneous chemistry on liquid aerosols and hence in driving ozone depletion.

*Midlatitude ozone changes are intimately coupled with stratospheric aerosol changes.* The figure on the preceding page shows the quantitative comparison between the model and NOAA satellite ozone measurements achieved in this study, which involved collaboration of Aeronomy Laboratory researchers with scientists at several institutions. This work greatly strengthened scientific confidence in ozone depletion chemistry, particularly the key role of processes in sulfuric acid aerosol at mid-latitudes.

Solomon, S., R. W. Portmann, R. R. Garcia, L. W. Thomason, L. R. Poole, and M. P. McCormick, The role of aerosol variations in anthropogenic ozone depletion at northern mid-latitudes, *J. Geophys. Res.*, *101*, 6713-6728, 1996.

Solomon, S. R. W. Portmann, R. R. Garcia, W. Randel, F. Wu, R. Nagatani, J. Gleason, L. Thomason, L. R. Poole, and M. P. McCormick, Ozone depletion at mid-latitudes: coupling of volcanic aerosols and temperature variability to anthropogenic chlorine, *Geophys. Res. Lett.*, *25*, 1871-1874, 1998.

- **Cirrus clouds and ozone depletion**

*What is causing the large ozone depletions at low altitudes in the stratosphere?* Observations of the vertical profile of the ozone trends revealed a surprising amount of depletion in the lowermost stratosphere, below the altitudes where chlorine chemistry was expected to be effective. Indeed, the peak local ozone depletion has been shown to occur near the tropopause. While not critical to the total column depletion because relatively little of the ozone resides at these altitudes, understanding the reasons for the depletion profile is important to establishing the cause. Further, ozone depletion in the tropopause region plays an important role in radiative forcing of the climate system.

*Role of Cirrus particles in ozone loss.* In a series of papers in collaboration with U.S. and international researchers, Aeronomy Laboratory scientists examined the possible role that cirrus clouds could play in perturbing the chlorine partitioning of the tropopause region, much as polar stratospheric clouds do in the Antarctic. Such clouds are likely to be composed of both liquid and solid particles, and are dependent upon the water vapor content. Satellite observations of cirrus cloud optical depths and occurrence frequencies in the vicinity of the tropopause were used as input to a two-dimensional numerical model of the chemistry and dynamics of the atmosphere.

*Cirrus clouds may play a role in ozone depletion.* The model results suggest that heterogeneous reactions could enhance the local ClO mixing ratios near the tropopause by up to thirty-fold at midlatitudes. It was shown cirrus clouds probably play a significant role in depleting ozone near the tropopause at midlatitudes, especially in late spring and summer.

Borrmann, S., S. Solomon, J. E. Dye, and B. Luo, The potential of cirrus clouds for heterogeneous chlorine activation, *Geophys. Res. Lett.*, *23*, 2133-2136, 1996.

Solomon, S., S. Borrmann, R. R. Garcia, R. W. Portmann, L. W. Thomason, L. R. Poole, D. Winker, and M. P. McCormick, Heterogeneous chlorine chemistry in the tropopause region, *J. Geophys. Res.*, *102*, 21411-21429, 1997.

- **Dynamics of ozone laminae**

*Coupling between tropospheric dynamics and stratospheric ozone changes.* A comprehensive analysis of the historical record of ozone profiles since 1968 has revealed an increase in the frequency of occurrence of low ozone intrusions of subtropical air into the lower stratosphere of northern hemisphere midlatitudes. Could these intrusions contribute to lower stratospheric ozone depletion observed during the past decade?

*Analysis of data sets.* These intrusions, which from study of radar, aircraft and potential vorticity data are known to be several kilometers deep and to have areas characteristic of cyclones (millions of km<sup>2</sup>), occurring mainly in winter and spring. An additional 15 - 20% of the midlatitude stratosphere now contains at least 10% less ozone column in March than it did prior to the mid-1980s. At 14.5 km, this is equivalent to between 7 and 27% of the ozone trend reported by the sondes and SAGE II ( $7.6 \pm 4.6\%$  /decade) for this season.

*Tropospheric dynamics of ozone laminae may play a role in ozone changes.* A fraction of the lower stratospheric ozone trend in this range could thus be caused by this change in dynamical behavior.

Reid, S.J., A.F. Tuck, and G. Kiladis. On a change in the abundance of ozone minima in midlatitudes: Implications for spring-time ozone trends. *J. Geophys. Res.*, 103, submitted, 1998.

- **Role of short-lived iodocarbons and bromocarbons in ozone chemistry**

*Unusual ozone losses in unusual places.* Observations reveal significant ozone trends very close to the tropopause, where its role is small for the column ozone change but potentially significant for radiative forcing of the climate system. These changes are difficult to explain with conventional stratospheric chemistry. In addition, observations of surface ozone in polar regions reveal dramatic "polar sunrise" ozone depletion that is difficult to explain but appears to be linked to halogen abundances.

*Iodine - The forgotten halogen.* Even though all the natural sources of iodine are short-lived, their rapid transport via convection in the tropics could supply iodine to the lower stratosphere. In a similar fashion, short-lived bromocarbons such as bromoform were also suggested to contribute to the stratospheric bromine budget. We hypothesized that iodine might contribute to the observed lower stratospheric ozone trend over the past two decades. In this hypothesis, it was assumed that the reactions of IO with ClO would be very rapid, as in the case of the reactions of IO with itself or of IO with BrO. The rate coefficients for the reactions of IO were subsequently measured in the laboratory and found to be about a factor of 3 - 4 slower than assumed.

*A better understanding of ozone chemistry.* This study has prompted a great deal of laboratory kinetics investigation of iodine chemistry and several field measurements aimed at observations of iodine and its source gases. Recent measurements and model studies imply that iodine chemistry does not dominate the ozone trends observed in the tropopause region, but could contribute to them. Observations of bromoform suggest that convective transport does indeed play a significant role in the stratospheric bromine budget, as suggested.

Solomon, S., R. R. Garcia, and A. R. Ravishankara, On the role of iodine in ozone depletion, *J. Geophys. Res.*, 99, 20491-20499, 1994.

Gilles, M. K., A. A. Turnipseed, J. B. Burkholder, A. R. Ravishankara, and S. Solomon, Kinetics of the IO radical. Part 2: The reaction of IO + BrO, *J. Phys. Chem. A.*, 101, 5526-5534, 1997.

## 6. Understanding Stratospheric Processes Through Laboratory and Field Measurements

To calculate the current and past ozone abundances, their vertical distribution, and their changes due to natural and anthropogenic forcings, a thorough understanding of the processes that control ozone in the stratosphere is needed. Such an understanding is developed via laboratory determinations of fundamental chemical kinetic and photochemical parameters and field measurements of chemical constituents. Then, the abundances of chemical species calculated using the laboratory derived data can be compared with field observations to solidify our understanding of processes.

- **NO<sub>2</sub> measurement technique and interpretation of observations**

*Stratospheric nitrogen chemistry.* Nitrogen dioxide (NO<sub>2</sub>) is important reactive species in the ozone balance of the lower stratosphere because catalytic cycles involving NO<sub>2</sub> destroy ozone. Quantitative understanding of their role is needed for future predictions.

*Measuring NO<sub>2</sub> from aircraft.* A new Aeronomy Laboratory system for measuring NO<sub>2</sub> was added to the photochemical payload on the NASA ER-2 aircraft and over several years has greatly expanded the available *in situ* observations of NO<sub>2</sub>. The system utilizes a new lightweight ultraviolet lamp to photolyze NO<sub>2</sub> in a glass cell with the NO product detected by NO/O<sub>3</sub> chemiluminescence. Measurements of NO<sub>2</sub>, when combined with those of O<sub>3</sub>, NO, and laboratory rate constants, can be used to formulate a steady state expression that constrains the photolysis rate of NO<sub>2</sub>. At mid to high latitudes in the Southern Hemisphere fall/winter season, NO<sub>2</sub> and NO<sub>x</sub> (NO + NO<sub>2</sub>) are a small fraction of the reactive nitrogen reservoir because of low photolysis rates in the winter season. The estimated photolysis rates in these seasonal data sets are in good agreement with values inferred from airborne solar flux measurements and from radiation models of the atmosphere.

*NO<sub>2</sub> measurements and interpretations reveal the validity of the current understanding in the autumn,/winter/spring stratosphere.* The above results indicates that our understanding of UV radiation transmission in the lower stratosphere and the kinetics controlling the NO<sub>2</sub>/NO ratio is robust.

Gao, R. S., D. W. Fahey, R. J. Salawitch, S. A. Lloyd, D. E. Anderson, R. DeMajistre, C. T. McElroy, E. L. Woodbridge, R. C. Wamsley, S. G. Donnelly, L. A. Del Negro, M. H. Proffitt, R. M. Stimpfle, D. W. Kohn, S. R. Kawa, L. R. Lait, M. Loewenstein, J. R. Podolske, E. R. Keim, J. E. Dye, J. C. Wilson, and K. R. Chan, Partitioning of the reactive nitrogen reservoir in the lower stratosphere of the southern hemisphere: Observations and modeling, *J. Geophys. Res.*, 102, 3935-3949, 1997.

Gao, R. S., E. R. Keim, E. L. Woodbridge, S. J. Ciciora, M. H. Proffitt, T. L. Thompson, R. J. McLaughlin, and D. W. Fahey, New photolysis system for NO<sub>2</sub> measurements in the lower stratosphere, *J. Geophys. Res.*, 99, 20673-20681, 1994.

- **Observations of BrO**

*Stratospheric abundance of BrO.* The Aeronomy Laboratory's near UV/Visible remote sensing instruments provided the first ground-based measurements of BrO in Antarctica in 1987. Such information in other regions of the stratosphere are needed.

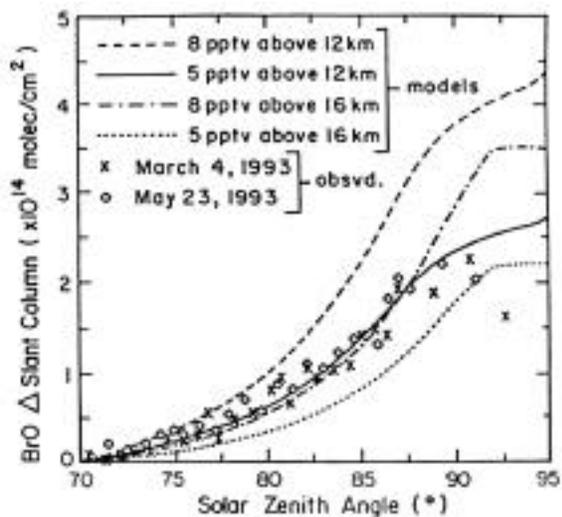
*Measurement of BrO from ground.* The methodology used in Antarctica was used to make new measurements in Colorado and in Greenland. In 1994, the first ground-based observations of this key radical at midlatitudes was presented. They showed that the slant column abundances in Colorado revealed that the mixing ratio of this gas maximizes near 15 - 20 km, where it is likely to

be about 5 - 8 pptv. In 1995, observations of BrO from Kangerlussuaq, Greenland were reported. While the primary goal of this research was to measure Arctic OCIO, an ancillary goal was to study the role of bromine in surface sunrise polar ozone depletion. A surface ozone instrument was hence also deployed, provided by the Aeronomy Laboratory's Tropospheric Chemistry Program. Extremely high BrO abundances were measured during the most severe surface ozone depletion that occurred on March 14 - 17. The bulk of the BrO was shown to resided in the boundary layer, where the mixing ratios were estimated to be at least 13 pptv at this time.

*BrO abundances in stratosphere and polar troposphere measured from by ground-based spectroscopy.* Very high BrO abundances support the view that bromine chemistry plays a critical role in the sunrise surface ozone depletion phenomenon.

Arpag, K. A., P. V. Johnston, H. L. Miller, R. W. Sanders, and S. Solomon, Observations of the stratospheric BrO column over Colorado, 40°N, *J. Geophys. Res.*, 99, 8175-8181, 1994.

Miller, H. L., A. Weaver, R. W. Sanders, K. Arpag, and S. Solomon, Measurements of Arctic sunrise surface ozone depletion events at Kangerlussuaq, Greenland (67°N, 51°W), *Tellus*, 49B, 496-509, 1997.



Stratospheric BrO Over Colorado

- **The POLARIS Mission**

*A summer in the stratosphere.* The autumn, winter, and spring times in the polar regions have been examined. However, the understand the seasonal behavior of polar stratospheric ozone as it changes from very high concentrations in spring down to lower concentrations in autumn is lacking.

*A mission in the Arctic summer.* The 1997 Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) mission was the latest in a series of airborne investigations of atmospheric ozone spanning more than a decade. The missions involve sampling from the NASA ER-2 aircraft and balloon platforms from deployment sites around the globe. The objective of POLARIS was to understand the seasonal behavior of polar stratospheric ozone as it changes from very high concentrations in spring down to lower concentrations in autumn. The POLARIS field observations were successfully completed after a total of 30 ER-2 flights and 3 balloon flights between April and September 1997 with Fairbanks, Alaska, as the principal deployment site. Members of the Aeronomy Laboratory participated as POLARIS Project Scientist and as Principal Investigators for theoretical teams and measurements of  $\text{NO}_y$ , NO,  $\text{NO}_2$ , and  $\text{O}_3$ . The analyses of the data will allow the photochemical and dynamical components of the summer changes in ozone to be evaluated and compared to observations. Interpretation and presentation of the results are underway and are expected to lead to a series of peer-reviewed publications led by Laboratory members and others within the POLARIS science team.

Details of the POLARIS mission can be found on the following web site: <http://cloud1.arc.nasa.gov/polaris/index.html>.

- **Photochemistry of stratospheric molecules**

*Photochemistry.* To understand the significance of various ozone destruction cycles, which determine the stratospheric ozone abundance and its vertical profile, the UV/visible absorption cross sections and photolysis quantum yields of trace species are needed.

*Determination of Photochemical parameters.* The absorption cross sections and photolysis quantum yields for a number of species were measured in the laboratory. It was found that the temperature dependence of the UV absorption cross sections is an important parameter in determining photolysis lifetimes. In the case of  $\text{HNO}_3$ , the photolytic lifetime in the lower stratosphere is enhanced due to decreasing cross sections at lower temperatures. The short wavelength ( $\sim 200$  nm) photolysis was also shown to be important in the mid and upper stratosphere. Also, the  $\text{NO}_3$  photolysis quantum yields for the halogen reservoir species  $\text{ClONO}_2$  and  $\text{BrONO}_2$  were found to be near unity in the wavelength regions important in the atmosphere, independent of pressure.

*Photochemistry of stratospheric molecules are better defined.* Our findings resolved an existing controversy regarding the pressure dependence of quantum yields. This extensive work enables better calculations of the ozone changes in the stratosphere and attribution of the changes to chlorine and bromine compounds.

Yokelson, R.J., J.B. Burkholder, R.W. Fox, and A.R. Ravishankara, UV Photodissociation of  $\text{ClONO}_2$ : 2. Time-Resolved Absorption Studies of product quantum yields, *J. Phys. Chem. A.*, 101 (36), 6667-6678, 1997.

Burkholder, J.B., R.K. Talukdar, A.R. Ravishankara, and S. Solomon, Temperature Dependence of the  $\text{HNO}_3$  UV Absorption Cross Sections, *J. Geophys. Res.*, 98, 22937 - 22948, 1993

- **Kinetics of the halogen monoxides important in the stratosphere**

*Chemistry of ClO.* The quantification of the ozone abundances and their changes requires accurate values of the rate coefficients for many radical-radical reactions.

*Kinetics studies of radical-radical reactions.* A new method to measure such rate constants, a pulsed photolysis system coupled to a discharge flow tube, was developed. Using this method, where the excess reagent is produced in the flow tube and its concentration measured using a diode array spectrometer, the rate coefficients for the reactions of O and OH with ClO were measured. By detecting IO via tunable diode laser absorption in a pulsed photolysis-long path absorption system, the rate coefficient for its self-reaction was measured. Similarly, using a diode array spectrometer, the rate coefficient for the self-reaction of BrO was measured. The rate coefficient for the reaction of  $\text{O}_3$  with HBr to give  $\text{HO}_2$  was measured to be very slow. From this observation, the yield of HBr in the reaction of  $\text{HO}_2$  with BrO was deduced to be negligibly small.

*Kinetics of the halogen monoxide reactions important in the stratosphere are determined.* This extensive data set helps quantify the role of halogens in the stratosphere.

Mellouki, A., R. K. Talukdar, R. K. Talukdar, and C. J. Howard, Kinetics of the reaction of HBr with  $\text{O}_3$  and  $\text{HO}_2$ : The yield of HBr from  $\text{HO}_2 + \text{BrO}$ , *J. Geophys. Res.*, 99, 22949-22954, 1994.

Harwood, M. H., J. B. Burkholder, M. Hunter, R. W. Fox and A. R. Ravishankara, Absorption cross-sections and self-reaction kinetics of the IO radical, *J. Phys. Chem. A*, 101, 853-863, 1997.

## 7. Rehabilitation of the Ozone Layer: Searching for Ozone-Friendly CFC Substitutes.

CFCs, 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, it would be important to know if they are potent greenhouse gases or cause local air pollution. Therefore, many substitutes were tested in the laboratory by measuring parameters needed to assess their atmospheric lifetimes and, in some cases, evaluate new ways in which they can affect the abundance of stratospheric ozone.

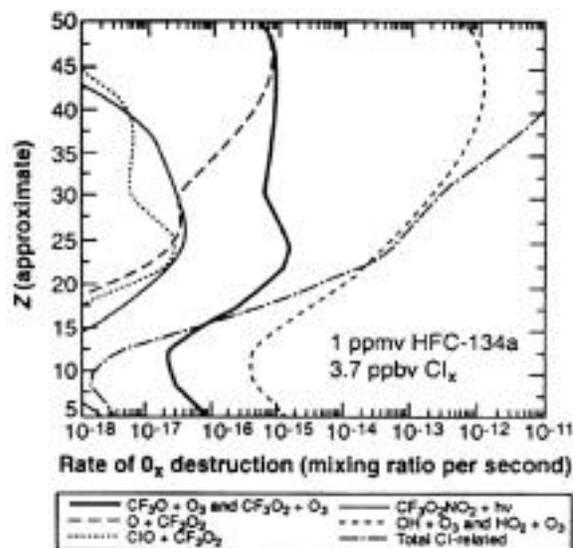
### • Do HFCs destroy ozone?

*Do CF<sub>3</sub>-containing species destroy ozone?* The successful phase out of CFCs depended on the use of numerous hydrofluorocarbons (HFCs) as replacements. The HFCs offered several advantages: they contain no ozone depleting chlorine, they contain hydrogen which provides a mechanism for tropospheric loss via reaction with OH, and in certain cases they have chemical and physical properties similar enough to the CFCs that they were “drop-in” replacements. One feature of many of the HFC compounds is that they contain a CF<sub>3</sub> functional group, which is an unusually stable fragment and a likely intermediate in the atmospheric oxidation of the HFCs. It was suggested by one research group that the radicals CF<sub>3</sub>O and CF<sub>3</sub>O<sub>2</sub>, collectively designated as CF<sub>3</sub>O<sub>x</sub>, and formed from CF<sub>3</sub> could catalytically destroy stratospheric ozone.

*Studies of CF<sub>3</sub>O<sub>x</sub> chemistry.* The kinetics of CF<sub>3</sub>O<sub>x</sub> radical reactions with various atmospheric gases including ozone were studied in our laboratory and their impact assessed using a two-dimensional model. The key findings can be summarized as follows: (1) The reaction between CF<sub>3</sub>O<sub>2</sub> and ozone is immeasurably slow. (2) The CF<sub>3</sub>O radicals react rapidly with NO to irreversibly destroy CF<sub>3</sub>O. (3) The CF<sub>3</sub>O radical reacts with other atmospheric trace constituents, e.g., methane, to sequester some of the CF<sub>3</sub>O<sub>x</sub>.

*HFCs, the most widely used CFC substitutes, are ozone friendly.* The model calculations showed that CF<sub>3</sub>O<sub>x</sub> species offer no conceivable threat to stratospheric ozone. This work provides a critically important confirmation of the environmental acceptability of the HFCs as CFC replacements.

Ravishankara, A. R., A. A. Turnipseed, N. R. Jensen, S. Barone, M. Mills, C. J. Howard, and S. Solomon, Do hydrofluorocarbons destroy stratospheric ozone? *Science*, 263, 71-75, 1994.



HFCs Do Not Destroy Ozone

- **Environmental acceptability of this evolving class of new compounds: substitutes for phased out compounds**

*CFC-substitutes.* As noted above, the phase out of CFCs require environmentally acceptable compounds, and, as proposed, they need to be tested to ensure their acceptability.

*Lifetimes of substitutes.* The studies on the atmospheric lifetimes of CFC-substitutes were a continuation, albeit with much less intensity, of the work started right after the London amendment to the Montreal protocol. The results of the findings during the past five years showed that  $\text{CF}_3\text{I}$ , if released at the Earth's surface, would be an environmentally acceptable substitute for  $\text{CH}_3\text{Br}$  because a very small fraction of the emission would reach the stratosphere. It also showed the enormous ability of iodine to destroy stratospheric ozone, if it got there. The greenhouse gas ability of a few more HFCs were also evaluated.

*A sequence of substitutes evaluated, in a timely fashion, for their acceptability.* Many of the tested substitutes were found to be environmentally friendly. This enables successful substitution of CFCs and effective decisions by industry.

Solomon, S., J. B. Burkholder, A. R. Ravishankara, and R. R. Garcia, On the ozone and global warming potentials of  $\text{CF}_3\text{I}$ , *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.

### C. **Future Plans: What's Next?**

#### *Measurements of Stratospheric Processes in the Laboratory*

Processes that affect stratospheric ozone abundances will continue to be examined. Changes in our understanding, for example, due to better definition of the heterogeneous/multiphase reactions, will guide the choice of processes studied.

Studies of photochemical processes will continue.  $\text{HO}_2\text{NO}_2$  and  $\text{IONO}_2$  will be examined in the near-term. The quantum yields in the photolysis of  $\text{Cl}_2\text{O}_2$  are still targeted. The rate coefficients for radical-radical reactions, e.g.,  $\text{OH} + \text{BrO}$  and  $\text{IO}/\text{BrO} + \text{HO}_2$ , will be investigated in the near future. When needed, other CFC and halon substitutes will be studied. Loss processes for  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  will be continued to better characterize the vertical extent of the sulfate aerosol layer.

Multiphase reactions of stratospheric species, e.g.,  $\text{HOBr}$  and  $\text{NO}_3$ , will be a focal point. Changes in the reactivity of chlorine containing species at very low temperatures due to uptake of  $\text{HNO}_3$  (i.e., the formation of the supercooled ternary solutions) will be investigated. A better formulation of the surface specific reactions on liquids will be attempted.

#### *Measurement of Stratospheric Composition and its Changes*

Measurements of chemical constituents of the stratosphere from aircraft will continue to be a major activity. The WB57F aircraft, which has a unique, proven ability to cruise at, above and below the tropopause, from equator to pole if necessary, will be used in many missions.

New instruments, for example based on chemical ionization mass spectrometry (CIMS), will be developed to measure species (e.g.,  $\text{HNO}_3$ , sulfur species, and non-methane hydrocarbons)

in the upper troposphere and lower stratosphere. Because of its important role as a sink for the reactive nitrogen species, the first priority is to measure  $\text{HNO}_3$  in the lower stratosphere and the upper troposphere using CIMS, which has proven highly successful for tropospheric measurements.

The unique observations from WB57F during April and May 1998 of single particle, real-time aerosol composition will be followed up with adequate complementary measurements, using new instruments in some cases: condensable vapors (e.g., water, nitric acid, sulfuric acid, organics), particle sizing, meteorological and tracer measurements. Extending the observations to the inner tropics and the southern hemisphere is the highest priority. The particle analysis by laser mass spectrometry (PALMS) measurements will be utilized characterizing polar stratospheric clouds and cirrus formation; no specific mission is currently scheduled, however.

Aeronomy Laboratory scientists will measure  $\text{NO}$  and  $\text{NO}_y$  on board the ER-2 aircraft in the NASA SAGE III Ozone Loss and Validation Experiment (SOLVE) Mission in early 2000 in concert with those of other reactive and long-lived species and aerosols. Flights will be made at wintertime high latitudes in the Northern Hemisphere to validate SAGE III satellite retrievals of aerosols and gases and to explore photochemical changes and aerosol formation and reactivity that lead to ozone loss in the winter polar regions.

The small scale variability in the high resolution airborne data from over 260 flights in a wide range of conditions from the equator to both polar regions, will be examined for signatures of both chemistry and dynamics. It is intended that topological and fractal methods, very high resolution three-dimensional modeling, and possibly a very high time-resolution ozone instrument, will be used.

The work connected with satellites, particularly with those measuring the same species as our airborne instruments, will continue. There will be an emphasis on water vapor trends in the stratosphere, and of fluxes of species in the upper troposphere and lower stratosphere.

#### *Interpretation of the Stratospheric Ozone and Predicting its Changes*

Stratospheric modeling efforts using two-dimensional models will continue. A major focus will be to better understand the "ups and downs" of the trends, their relationship to aerosol variability and chemistry, and coupling to the quasi-biennial oscillation (QBO). This study will be expanded to include solar activity changes, QBO, etc., with an emphasis on looking at the southern hemisphere as well as northern. Inter-annual temperature variability (some of which is QBO-induced) in the Antarctic and elsewhere will be examined. Antarctic ozone changes will continue to be examined, with an eye toward detection of the recovery of the ozone hole. Impacts of new laboratory or field data on stratospheric ozone will continue to be evaluated.

Northern Hemispheric  $\text{O}_3$ - $\text{N}_2\text{O}$  and an  $\text{O}_3$ - $\text{NO}_y$  climatologies are now being compiled that will characterize the lower stratospheric  $\text{O}_3$  abundance during the past decade. These compilations will serve as a check on photochemical models with transport and will provide baseline information for detecting changes in  $\text{O}_3$  abundance that may occur in the future.