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In Situ Detection of OH, HO_2, ClO, BrO, NO_2, $ClONO_2$, $BrONO_2$, ClOOCl, H_2O, and O_3 from the ER-2

Summary of Research
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NASA Grant NAG-1-2007, "*In Situ* Detection of OH, HO_2, ClO, BrO, NO_2, $ClONO_2$, $BrONO_2$, ClOOCl, H_2O, and O_3 from the ER-2"

We review here the scientific progress that has emerged during the period January 1, 1998 through March 31, 2001, supported by NASA Grant NAG-1-2007. Results from the SOLVE[1] and POLARIS[2] missions, and continuing work on prior missions, taken in order, include:

- Radical control of ozone in the northern hemisphere stratosphere
- Evolution of NO_2 over the arctic winter and its effects on reactive chlorine
- The first measurements of ClOOCl in the stratosphere: *In situ* observations from the 1999–2000 arctic polar vortex
- Quantifying reprocessing of chlorine via $HOCl + HCl \rightarrow H_2O + Cl_2$ in the arctic polar vortex with *in situ* observations
- Quantifying the rate of heterogeneous processing in the arctic polar vortex with *in situ* observations of OH and HO_2
- Chlorine partitioning in the arctic vortex: Cl_x/Cl_y determined from *in situ* measurements in the stratosphere
- Bromine in the arctic vortex: *In situ* observations of BrO in the stratosphere
- Examining transport into the vortex middleworld using H_2O, CH_4, CO_2, and N_2O measured during the arctic winter, 1999–2000
- Hydrogen radicals, nitrogen radicals, and the production of O_3 in the upper troposphere
- Mechanisms for midlatitude ozone loss: Heterogeneous chemistry in the lowermost stratosphere
- The inorganic chlorine budget
- Inorganic chlorine partitioning in the summer lower stratosphere: Modeled and measured $[ClONO_2]/[HCl]$ during POLARIS
- The NO_x-HNO_3 system in the lower stratosphere: Insights from *in situ* measurements and implications of the J_{HNO3}-OH relationship
- Comparing atmospheric $[HO_2]/[OH]$ to modeled $[HO_2]/[OH]$: Identifying discrepancies in reaction rate constants
- Dehydration and denitrification in the arctic polar vortex during the 1995–1996 winter
- The role of HO_x in super- and subsonic aircraft exhaust plumes
- Sources, sinks, and the distribution of OH in the lower stratosphere
- Twilight observations suggest unknown sources of HO_x
- Troposphere-to-stratosphere transport in the lowermost stratosphere from measurements of H_2O, CO_2, N_2O, and O_3
- Accuracy of *in situ* water vapor measurements in the troposphere and lower stratosphere with the Harvard Lyman-α hygrometer

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[1] SAGE III Ozone Loss and Validation Experiment (**SOLVE**), October 1999-March 2000, NASA Dryden, CA, Westover AFB, MA, and Kiruna, Sweden

[2] Photochemistry of Ozone Loss in the Arctic Region In Summer (**POLARIS**), March–September 1997, NASA Ames Research Center, Moffett Field, CA; Fort Wainwright U. S. Army Base, Fairbanks, AK; and Barbers Point Naval Air Station, HI

- Evaluation of the seasonal cycle of water vapor in the stratosphere derived from tropical tropopause temperatures using a CO photochemical clock
- Establishing the dependence of $[HO_2]/[OH]$ on temperature, halogen loading, O_3, and NO_x based on *in situ* measurements from the NASA ER-2
- Monitoring potential photochemical interference in laser-induced fluorescence measurements of atmospheric OH

These results are reported in the following publications.

1. Hintsa, E. J., P. A. Newman, H. H. Jonsson, C. R. Webster, R. D. May, R. L. Herman, L. R. Lait, M. R. Schoeberl, J. W. Elkins, P. R. Wamsley, G. S. Dutton, T. P. Bui, D. W. Kohn, and J. G. Anderson, "Dehydration and denitrification in the arctic polar vortex during the 1995–96 winter," *Geophys. Res. Lett.* **25**(4), 501–4, February 15, 1998.
2. Hintsa, E. J., K. A. Boering, E. M. Weinstock, J. G. Anderson, B. L. Gary, L. Pfister, B. C. Daube, S. C. Wofsy, M. Loewenstein, J. R. Podolske, J. J. Margitan and T. P. Bui, "Troposphere-to-stratosphere transport in the lowermost stratosphere from measurements of H_2O, CO_2, N_2O and O_3," *Geophys. Res. Lett.* **25**(14), 2655–8, July 15, 1998.
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Abstracts of publications in press or in preparation for submittal in 2001 are provided below.

Constraints on the seasonal cycle of stratospheric water vapor using *in situ* measurements from the ER-2 and a CO photochemical clock

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We use *in situ* measurements of CO obtained in the tropics from 1995 to 1997 on the NASA ER-2 aircraft and a simple photochemical model to calculate the elapsed time between the entry of air into the stratosphere and the observation, which we define as the

photochemical "age" of the air. Assuming this age represents the transit time of the air mass from a boundary at 390 K to its measured altitude, we calculate boundary condition values of CO_2 derived from *in situ* measurements of this species from 400 to 480 K. We validate the approach by comparing these CO_2 boundary values with an independent representation of the boundary condition from observations of CO_2 in air that had recently entered the stratosphere (as indicated by simultaneous measurements of N_2O, CO, and potential temperature). For 5 of the 6 flights, differences between CO_2 boundary condition values determined using the photochemical age of the air and those derived from independent measurements can be accounted for with isentropic mixing of midlatitude stratospheric air into the tropics. Having validated the photochemical ages of the sampled stratospheric air, we use the same analysis of *in situ* water data to provide water vapor boundary condition values that constrain the seasonal cycle of water vapor entering the stratosphere. Based on these constraints we evaluate the seasonal cycle of entry-level water vapor derived from tropical tropopause temperatures from the radiosonde network between 10°S and 10°N. We conclude that while average saturation mixing ratios provide a suitable boundary condition for water vapor entering the stratosphere, the uncertainties in saturation mixing ratios derived from radiosonde temperatures and the lack of coverage prevents distinguishing between ascent preferentially occurring over the western equatorial Pacific or throughout the tropics. With the assumption that vertical diffusion and midlatitude mixing have a negligible effect on the calculated age, ascent velocities can be inferred from the photochemical ages. These ascent velocities show a seasonal cycle that is inconsistent with our current understanding of the dynamics driving the stratospheric circulation and with independent estimates of tropical vertical ascent rates.

Quantifying the rate of heterogeneous processing in the arctic polar vortex with *in situ* observations of OH

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We present simultaneous *in situ* observations of OH, HO_2, $ClONO_2$, HCl, and particle surface area inside a polar stratospheric cloud undergoing rapid heterogeneous processing. A steady state analysis constrained by *in situ* observations is used to show that calculations of HO_x during a processing event are extremely sensitive to the assumptions regarding aerosol composition and reactivity. This analysis shows that large perturbations in the abundance of OH and HO_2 are consistent with the heterogeneous production of HOCl via $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$ and removal via $HOCl + HCl \rightarrow Cl_2 + H_2O$ on super-cooled ternary solution (STS) aerosols and solid nitric acid trihydrate (NAT) particles. Comparison with observations of OH show that modifications to surface reactivity to account for high HNO_3 content in STS aerosols and low HCl coverage on NAT particles are appropriate. These results indicate that with the low HCl levels in this encounter and in a processed polar vortex in general, reactions on STS aerosols dominate the total heterogeneous processing rate. As a consequence, the formation of NAT does not lead to significantly faster reprocessing rates when HCl concentrations are low and STS aerosols are present. Model calculations that include these modifications to uptake coefficients for STS and NAT will lead to significantly slower reprocessing and faster recovery rates of chlorine in the springtime arctic polar vortex.

Modeling *in situ* observations of HO_2/OH in the arctic polar vortex aboard the NASA ER-2

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In the processed winter polar vortex where concentration of ClO is high and NO is low, the inter-conversion of OH and HO_2 is controlled by reactions involving O_3 and ClO. The conversion of OH to HO_2 is dominated by the catalytic reaction sequences that destroy ozone:

Cycle 1: (30–50% of O_3 loss at mid latitudes)

$OH + O_3 \rightarrow HO_2 + O_2$ R1
$\underline{HO_2 + O_3 \rightarrow OH + 2\,O_2}$ R2
net: $2\,O_3 \rightarrow 3\,O_2$

Cycle 2: (5–10% of O_3 loss at mid latitudes and within the polar vortex)

$OH + ClO \rightarrow HO_2 + Cl$ R3
$2(Cl + O_3 \rightarrow ClO + O_2)$ R4
$HO_2 + ClO \rightarrow HOCl + O_2$ R5
$\underline{HOCl + h\nu \rightarrow OH + Cl}$ R6
net: $2\,O_3 \rightarrow 3\,O_2$

The production rate of HO_x from the primary sources is slow compared to the inter-conversion rates R1-R5 so that the relative concentration of OH and HO_2 can be expressed as the ratio

$$\frac{HO_2}{OH} = \frac{k_{OH+O_3}[O_3]+k_{OH+ClO}[ClO]}{k_{HO_2+O_3}[O_3]+k_{HO_2+ClO}[ClO]} \qquad \text{Eq. 1}$$

The direct comparison of Eq. 1 with observations of HO_2/OH provides an unprecedented constraint on the rates of OH + ClO and HO_2 + ClO. These comparisons show that calculations of HO_2/OH using recent laboratory measurements of the rates of R1, R2, R3, and R5 agree with observations during SOLVE to within 15%.

The first measurements of ClOOCl in the stratosphere: The coupling of ClOOCl and ClO in the arctic polar vortex

R. M. Stimpfle, D. M. Wilmouth, R. J. Salawitch, J. G. Anderson and T. P. Bui

The existence of the weakly bound dimer of chlorine monoxide, ClOOCl, is fundamental to the most destructive chlorine-catalyzed ozone loss mechanism in the stratosphere. Yet ClOOCl has never been observed in the stratosphere by *in situ* or remote means. Here we report the first *in situ* measurements of ClOOCl, acquired from a NASA ER-2 aircraft, deployed from Kiruna, Sweden to the east over Russia during the joint US-European mission of the winter of 1999/2000. ClOOCl is detected by thermal dissociation into two ClO fragments that are subsequently detected using a resonance fluorescence technique. Using the photochemical steady state approximation we use the direct observations of the ratio of $[ClOOCl]/[ClO]^2$ to show that, during the daytime, the ratio of k^{Prod}/J, determined from JPL 2000 recommendations, is ~12% less that the direct observations. This is substantial agreement give the estimated error of ±30%. Thus we have quantified the existence of ClOOCl and confirmed its central role in the extraordinary losses of ozone observed in arctic and antarctic regions during late winter.

Examining transport in the vortex region using *in situ* water vapor and tracer measurements during SOLVE

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Water vapor plays a critical role in the chemistry of the arctic winter stratosphere through heterogeneous processes that contribute to rapid ozone loss. Since the large-scale stratospheric overturning circulation feeds the arctic vortex, a spatial and temporal understanding of the pathways by which air enters and leaves the vortex is crucial to predicting future ozone loss, especially given the potential lowering of temperatures in the arctic stratosphere due to climate forcings. *In situ* measurements of H_2O and long-lived tracer species, CH_4, CO_2, and N_2O, from the NASA ER-2 in the northern hemisphere winter enable, for the first time, an examination of the processes by which mid- and high- latitude overworld ($\theta > 380$ K) air enters the middle world ($320 \text{ K} < \theta < 380$ K) in the presence of the vortex. H_2O-CO_2 and H_2O-N_2O correlations reveal a similar relationship between young air masses ($N_2O > 240$ ppbv) in the extra-vortex overworld and those in the vortex middle world. Since vortex overworld air parcels are distinctly older ($N_2O < 240$ ppbv), this analysis can discriminate between downwelling motion wholly within the vortex and the alternate pathway across the vortex edge along isentropic surfaces in the middle world. Specifically, it allows an investigation of the permeability of the vortex wall from the overworld down into the middle world. Outside the vortex overworld, relatively high water vapor concentrations indicative of the summer phase of the seasonal cycle in water vapor were observed at middle and high latitudes. Transport of these air parcels across the vortex edge into the vortex middle world may have a significant impact on ozone in the vortex region. Lastly, this analysis can enhance the current knowledge of the processes responsible for changes in midlatitude ozone.

Constrained models of inorganic chlorine partitioning during the SOLVE campaign: Understanding the recovery of $ClONO_2$ and HCl following heterogeneous processing events.

P. B. Voss, R. M. Stimpfle, D. M. Wilmouth, K. K. Perkins, T. F. Hanisco, E. J. Lanzendorf, J. R. Spackman, J. B. Smith, and J. G. Anderson.

We develop constrained numerical integration (CNI) models that are tightly linked to observations and are therefore intermediate between simple steady-state approximations and comprehensive models incorporating complete photochemistry. For the POLARIS campaign, which examined the gas-phase lower stratosphere, CNI models constrained by OH observations provided the most precise and accurate implementation of inorganic chlorine photochemistry. These flexible models also allow greater control over inputs and assumptions, providing a rigorous comparison of independent and dependent variables. Using data from the SOLVE campaign, we employ CNI models to analyze heterogeneous processing and the recovery of reactive chlorine into its reservoir forms. Specifically, we examine the time constants of the recovery process and as well as the accuracy and precision of the model relative to observations of $ClONO_2$, ClOOCl, and ClO, and HCl. The quasi-independence of the time constant and model-measurement discrepancy provides the necessary leverage to evaluate the rate coefficients, calculated photolysis rates, observations, and model assumptions.

A highly constrained model of inorganic chlorine partitioning during the SOLVE campaign: the activation and deactivation of reactive chlorine in the early spring.

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In situ observations of $CLONO_2$, ClOOCl, ClO, HCl made during the SOLVE campaign provide an unprecedented opportunity to examine heterogeneous chlorine chemistry in the arctic winter stratosphere. At temperatures below ~195 K, these reactions rapidly convert $ClONO_2$ and HCl into photolabile Cl_2 and HOCl, leading to substantial loss of ozone in the high latitude spring. We develop constrained models that are tightly linked to observations (via parameterized OH and heterogeneous reaction rates). These flexible models allow precise control over inputs and assumptions, providing a rigorous comparison of independent and dependent variables. Using back trajectories and observations of fine-scale structure in the tracer fields, we attempt to link air parcels across multiple flights and thereby provide initial conditions for a few selected model runs. Along one of these constrained trajectories, we find O_3 is lost at an observed rate of

46 ppb/day in late February and early March. Calculations show that approximately 20–30% of this loss can be attributed to ClO (via dimer formation) while 15–30% is due to the ClO + BrO catalytic cycle. We also find that the heterogeneous reaction rates for $CLONO_2$ + HCl and HOCl + HCl on sulfate aerosol and NAT are approximately an order of magnitude too fast to reproduce observed Cl_y partitioning.

In situ observations of the effects of HOCl removal via heterogeneous processes in the arctic polar vortex

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The heterogeneous loss of HOCl and HCl via HOCl + HCl + aerosol → H2O + Cl2 (*R*1) plays an important role in the activation of chlorine during the polar winter. HO_x is strongly coupled to HOCl via fast gas phase production (HO_2 + ClO → HOCl + O_2) and loss (HOCl + $h\nu$ → OH + Cl) reactions. During the daytime the fast photochemistry of HOCl competes with heterogeneous loss via *R*1 and interferes with a quantitative evaluation of this reaction. On the January 23rd flight of the SOLVE mission, however, the NASA ER-2 flew through a chemically homogeneous airmass during sunrise, when HOx is most sensitive to perturbations in HOCl. The concentrations of HO_x observed during this flight are the lowest encountered in the lower stratosphere at these solar zenith angles, and are only a small fraction of the levels expected from gas phase production and loss processes. Simultaneous *in situ* observations of OH, HO_2, ClO, $ClONO_2$, HCl, H_2O, NO, NO_2, HNO_3, O_3, temperature and particle surface area are used along with photolysis rates calculated along the flight path to model the evolution of HO_x during sunrise and demonstrate its sensitivity to *R*1. The analysis shows that the observations are consistent with the near complete heterogeneous removal of HOCl the night prior to flight intercept, making this data the most compelling observational evidence to date for the occurrence of *R*1 in the polar lower stratosphere.

Bromine in the arctic vortex: *In Situ* observations of BrO in the stratosphere

D. M. Wilmouth, R. M. Stimpfle, and J. G. Anderson

Bromine monoxide was detected *in situ* in the stratosphere with an instrument onboard the NASA ER-2 aircraft, January-March 2000, as part of the SOLVE (SAGE III Ozone Loss and Validation Experiment) mission. Observations were made during twelve flights, most of which occurred above the arctic circle and within the arctic vortex. Due to the recent redesign and enhancement of our BrO instrument, the data acquired here represent a significant improvement in sensitivity, spatial resolution, and precision over previous *in situ* ER-2 measurements. With these improved data, BrO levels are available throughout the course of each flight, the fraction of BrO can be determined from concurrent total inorganic bromine measurements, and the impact of BrO on ozone loss can be more accurately evaluated. Also, of particular interest are observations of BrO during the day and at night and relative measurements from inside and outside the vortex.

Partitioning and budget of inorganic chlorine in the arctic vortex determined from *in situ* stratospheric measurements

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The first *in situ* observations of ClOOCl in the arctic stratosphere were made onboard the NASA ER-2 aircraft, January-March 2000, as part of the SOLVE (SAGE III Ozone Loss and Validation Experiment) mission. These measurements in combination with concurrent observations of ClO provide an unprecedented opportunity to measure the abundance of active chlorine ($Cl_x \approx ClO + 2\times ClOOCl$) in the vortex at any time, day or night. Along with total inorganic chlorine (Cl_y, inferred from *in situ* measurements of organic chlorine source gases), the partitioning of inorganic chlorine into its active form, Cl_x/Cl_y, can be calculated. The Cl_x/Cl_y ratio provides a critical measure necessary to assess the ozone-destruction capability of chlorine. Highly elevated Cl_x/Cl_y levels are characteristic of the polar vortex, while decreasing intravortex Cl_x/Cl_y provides evidence of chlorine recovery. In addition to the active chlorine species, ClO and ClOOCl, the reservoir species, $ClONO_2$ and HCl, were also measured *in situ* on board the ER-2 during SOLVE. The simultaneous observation of these four species provides the first opportunity to test whether they quantitatively account for total inorganic chlorine in the arctic vortex. An analysis of the stratospheric chlorine budget from POLARIS in 1997 (Bonne *et al.*, 2000) found good agreement between the measured chlorine species and inferred Cl_y, i.e., $(ClO + ClONO_2 + HCl)/Cl_y = 0.92 \pm 0.10$. Current SOLVE analyses indicate that there is a discrepancy in the inorganic chlorine budget of approximately 20%.

Constraints on the mechanism of chlorine deactivation: Implications for ozone loss following denitrification

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Measurements of ClO, ClOOCl, $ClONO_2$, and HCl obtained during SOLVE reveal almost complete conversion of inorganic chlorine to reactive chlorine within the 1999–2000 arctic vortex. To maintain these elevated levels of reactive chlorine requires the near absence of nitrogen radicals, specifically of NO_2. The conversion of reactive chlorine to the reservoir species, HCl and $ClONO_2$ proceeds through the reactions:

$ClOOCl + h\nu \rightarrow Cl + Cl + O_2$

$Cl + CH_4 \rightarrow HCl + CH_3$

and

$HNO_3 + h\nu \rightarrow NO_2 + OH$

$NO_2 + ClO \rightarrow ClONO_2$.

In situ observations of OH, HO_2, ClO, $ClONO_2$, HCl, ClOOCl, NO_2, NO, NO_y, HNO_3, temperature, pressure, and particulate surface area are used to examine the rate of HCl and $ClONO_2$ formation from ClO_x (ClO + 2 × ClOOCl) in the late February and early March arctic vortex. These data allow comparison of the calculated formation rates with the observed changes in ClO_x, $ClONO_2$, and HCl.

Ozone loss rates in the arctic vortex determined from *in situ* observations of ClO and BrO obtained during the SOLVE mission

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Calculations of the rate of ozone loss in the 2000 winter vortex based on *in situ* observations of ClO and BrO obtained from the NASA ER-2 are presented using simple rate-limiting step arguments. These results are discussed (1) using a calculational approach that provides for selection of (observable) independent variables, and (2) results obtained from coupled chemical/dynamical models.

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