Free Radicals and Reactive Intermediates for the SAGE III Ozone Loss and Validation Experiment (SOLVE) Mission

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This grant provided partial support for participation in the SAGE III Ozone Loss and Validation Experiment. The NASA-sponsored SOLVE mission was conducted jointly with the European Commission-sponsored Third European Stratospheric Experiment on Ozone (THESEO 2000). Researchers examined processes that control ozone amounts at mid to high latitudes during the arctic winter and acquired correlative data needed to validate the Stratospheric Aerosol and Gas Experiment (SAGE) III satellite measurements that are used to quantitatively assess high-latitude ozone loss. The campaign began in September 1999 with intercomparison flights out of NASA Dryden Flight Research Center in Edwards. CA. and continued through March 2000. with midwinter deployments out of Kiruna. Sweden. SOLVE was co-sponsored by the Upper Atmosphere Research Program (UARP). Atmospheric Effects of Aviation Project (AEAP). Atmospheric Chemistry Modeling and Analysis Program (ACMAP). and Earth Observing System (EOS) of NASA's Earth Science Enterprise (ESE) as part of the validation program for the SAGE III instrument.

The following tasks were supported under this funding:
- Harvard HO_x and $ClONO_2$ instruments for the NASA ER-2 were modified and tested to ensure their thermal stability under conditions of low temperatures.
- Two series of engineering test flights were conducted at NASA Dryden Flight Research Center. to test the thermal stability of these two instruments.
- A BrO detection system capable of measuring BrO at the 1 ppt level was designed and developed for ER-2 deployment during the SOLVE mission.
- Field support was provided to measure OH. HO_2. $ClONO_2$. ClO. BrO. $BrONO_2$. $ClONO_2$. NO_2. and Water Vapor during the SOLVE mission.
- Data reduction. analysis. and interpretation of the SOLVE data. and submittal of results to SOLVE scientific meetings and to peer-reviewed journals for publication.

The following abstracts were presented at the SOLVE Science Team Meeting that convened in Palermo. Italy. 24-29 September 2000. and at the American Geophysical Union Fall 2000 Meeting. convened in San Francisco. 15-19 December 2000. Data analysis and preparation of peer-reviewed publications continues under other NASA support.

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

T. F. Hanisco. J. B. Smith. R. M. Stimpfle. D. M. Wilmouth. K. K. Perkins. J. R. Spackman and J. G. Anderson. Harvard University: D. Baumgardner. Universidad Nacional Autonoma de Mexico: B. Gandrud. National Center for Atmospheric Research: C. R. Webster. Jet Propulsion Laboratory: S. Dhaniyala and K. A. McKinney. California Institute of Technology: T. P. Bui. NASA Ames Research Center

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
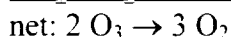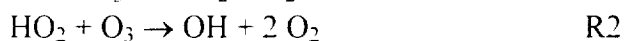
perturbations in the abundance of OH and HO$_2$ are consistent with the heterogeneous production of HOCl via ClONO$_2$ + H$_2$O → HOCl + HNO$_3$ and removal via HOCl + HCl → Cl$_2$ + H$_2$O on super-cooled ternary solution (STS) aerosols and solid nitric acid trihydrate (NAT) particles. Comparison with 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.

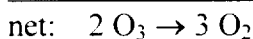**Modeling *in situ* observations of HO$_2$/OH in the arctic polar vortex aboard the NASA ER-2**
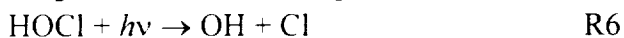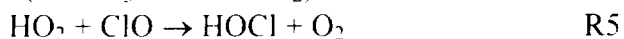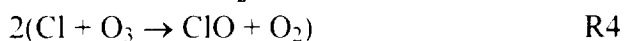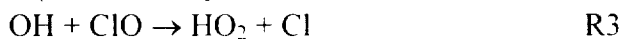
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In the processed winter polar vortex where concentration of ClO is high and NO is low, the inter-conversion of OH and HO$_2$ is controlled by reactions involving O$_3$ and ClO. The conversion of OH to HO$_2$ is dominated by the catalytic reaction sequences that destroy ozone:

Cycle 1: (30–50% of O$_3$ loss at mid latitudes)

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad R1$$
$$\underline{HO_2 + O_3 \rightarrow OH + 2\ O_2} \qquad R2$$
net: 2 O$_3$ → 3 O$_2$

Cycle 2: (5–10% of O$_3$ loss at mid latitudes and within the polar vortex)

$$OH + ClO \rightarrow HO_2 + Cl \qquad R3$$
$$2(Cl + O_3 \rightarrow ClO + O_2) \qquad R4$$
$$HO_2 + ClO \rightarrow HOCl + O_2 \qquad R5$$
$$\underline{HOCl + h\nu \rightarrow OH + Cl} \qquad R6$$
net: 2 O$_3$ → 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

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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 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 ClONO₂ and HCl following heterogeneous processing events.

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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_x 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 $\rightarrow$ H2O + Cl2 ($R1$) 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 $\rightarrow$ HOCl + O_2) and loss (HOCl + hv $\rightarrow$ OH + Cl) reactions. During the daytime the fast photochemistry of HOCl competes with heterogeneous loss via $R1$ 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 $R1$. 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 $R1$ 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. Harvard University

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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