A quantitative analysis of the reactions involved in stratospheric polar ozone depletion

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Introduction

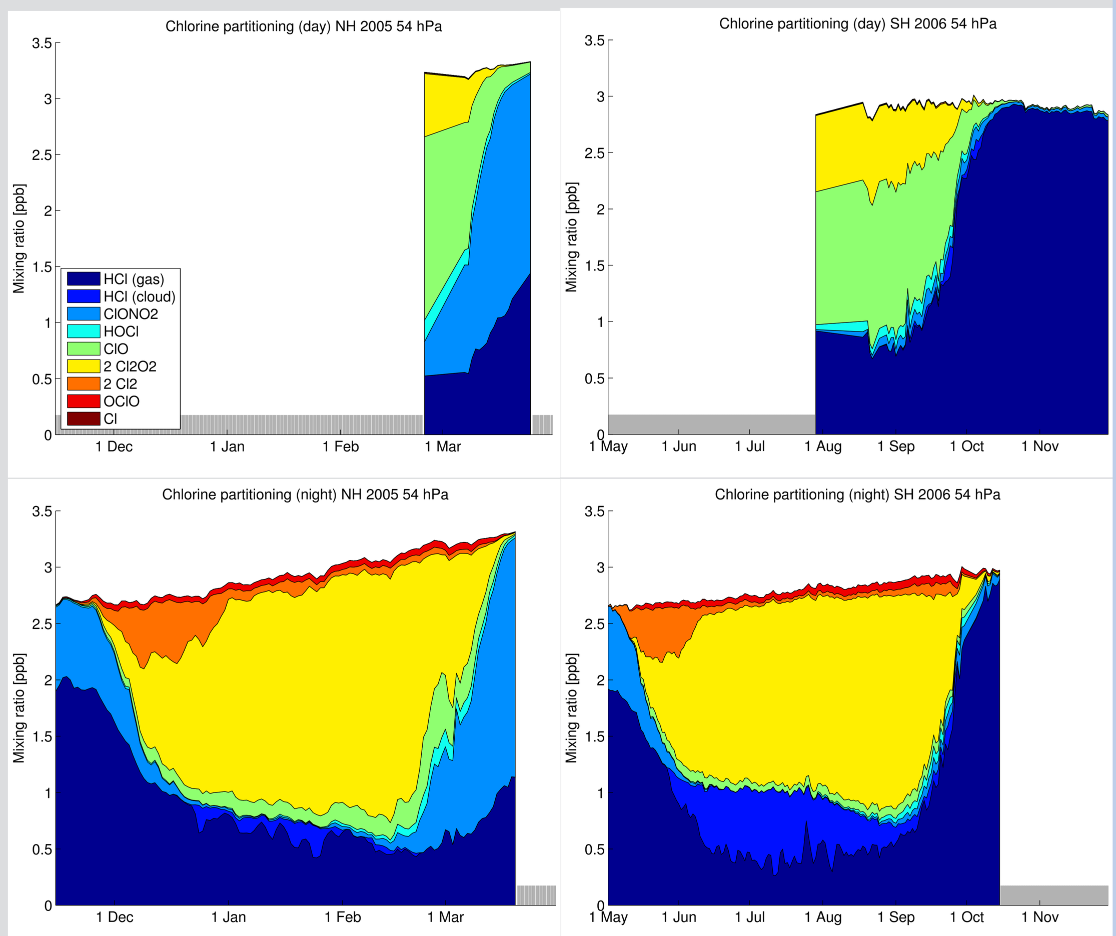
- Quantitative analysis of chemical reactions involved in stratospheric polar ozone depletion
- Quantitative estimates of importance of single reactions or reaction cycles are rare. No comprehensive and quantitative study of the reaction rates averaged over polar vortex under conditions of heterogeneous chemistry so far.
- Mixing ratios and reaction rates obtained from ATLAS Chemistry and Transport Model driven by ECMWF ERA Interim reanalysis data.
- One Arctic winter (2004/2005) and one Antarctic winter (2006) in a layer in the lower stratosphere around 54 hPa.

Method

- ATLAS is a global Lagrangian (trajectory-based) Chemistry and Transport Model including gas phase stratospheric chemistry, heterogenous chemistry on PSCs and a particle-based denitrification module. Includes 47 chemical species and more than 180 reactions.
- Vortex edge assumed at 36 PVU modified PV. Average only over air parcels with less than 30% extra-vortex air mixed in (do not mix up different chemical regimes).
- Reaction rates are changes over 24 h (one diurnal cycle)
- Daytime averages: less than 80° solar zenith angle, nighttime averages: more than 100° solar zenith angle.
- Days without sufficient data for averaging are not shown (grey bars).

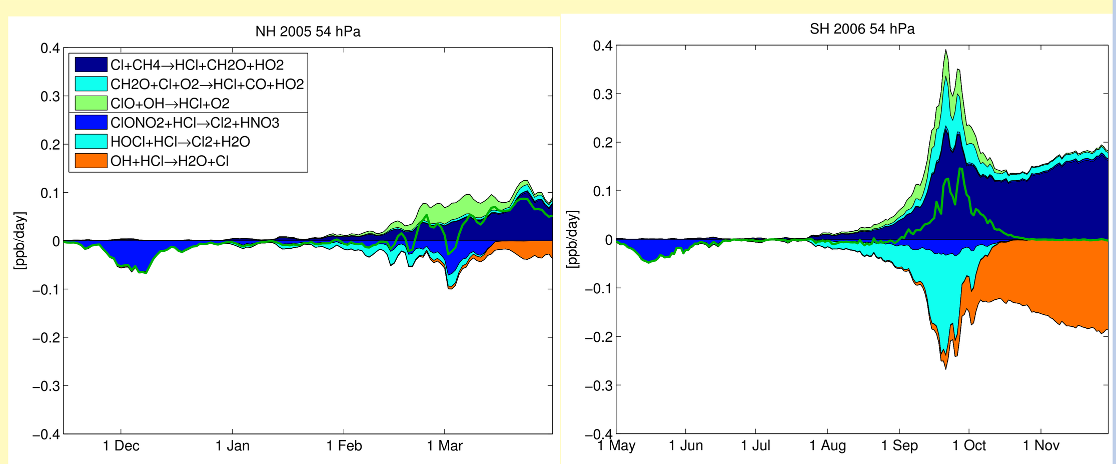
Chlorine

Partitioning Cly



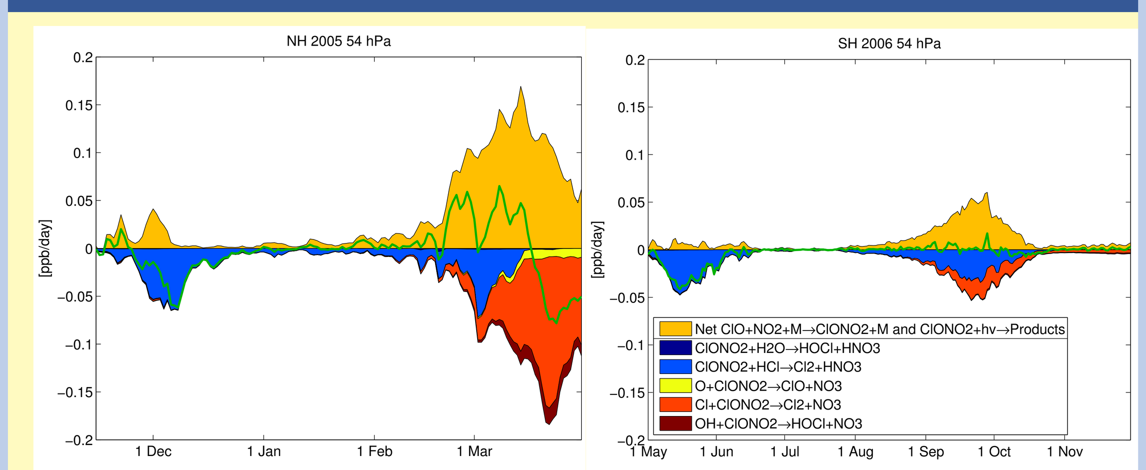
Vortex averaged partitioning of inorganic chlorine species Cl_y. Left: Arctic, Right: Antarctic, Top: Day, Bottom: Night.

HCl production and loss reactions



Vortex averaged reaction rates of reactions involving HCl. Green line: Net change of HCl. Left: Arctic, Right: Antarctic. Deactivation into HCl due to low ozone and denitrified conditions in SH and change in activation from $ClONO_2 + HCl$ in early winter to $HOCl + HCl$ later in SH visible.

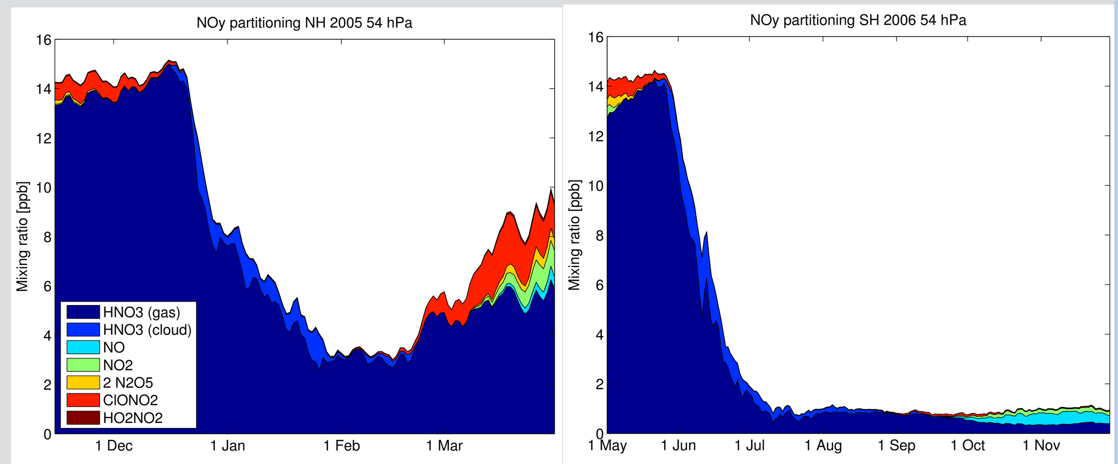
ClONO2 production and loss reactions



Vortex averaged reaction rates of reactions involving $ClONO_2$. Green line: Net change of $ClONO_2$. Left: Arctic, Right: Antarctic. Deactivation into $ClONO_2$ in NH when NO_x is produced by shift in $ClONO_2$ equilibrium in NH, later $ClONO_2$ depleted to form HCl.

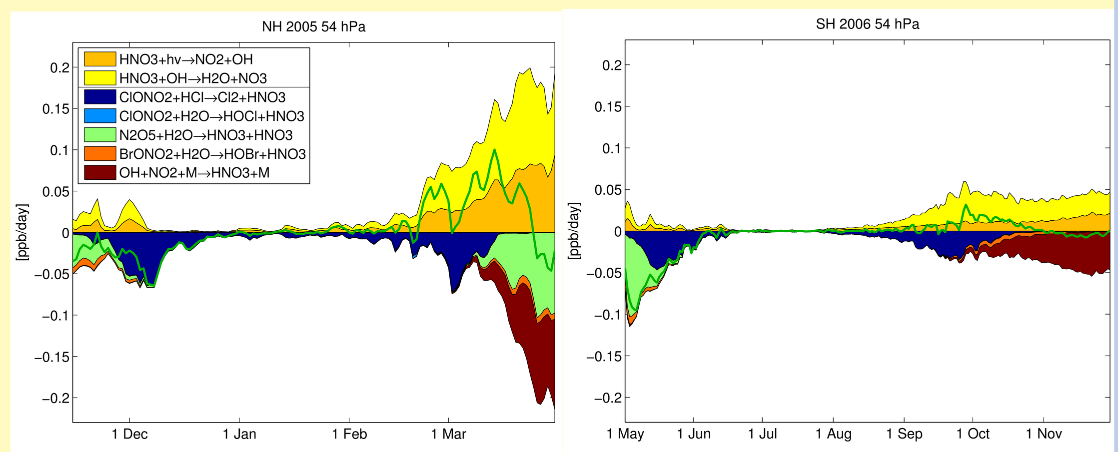
Nitrogen

Partitioning NOy



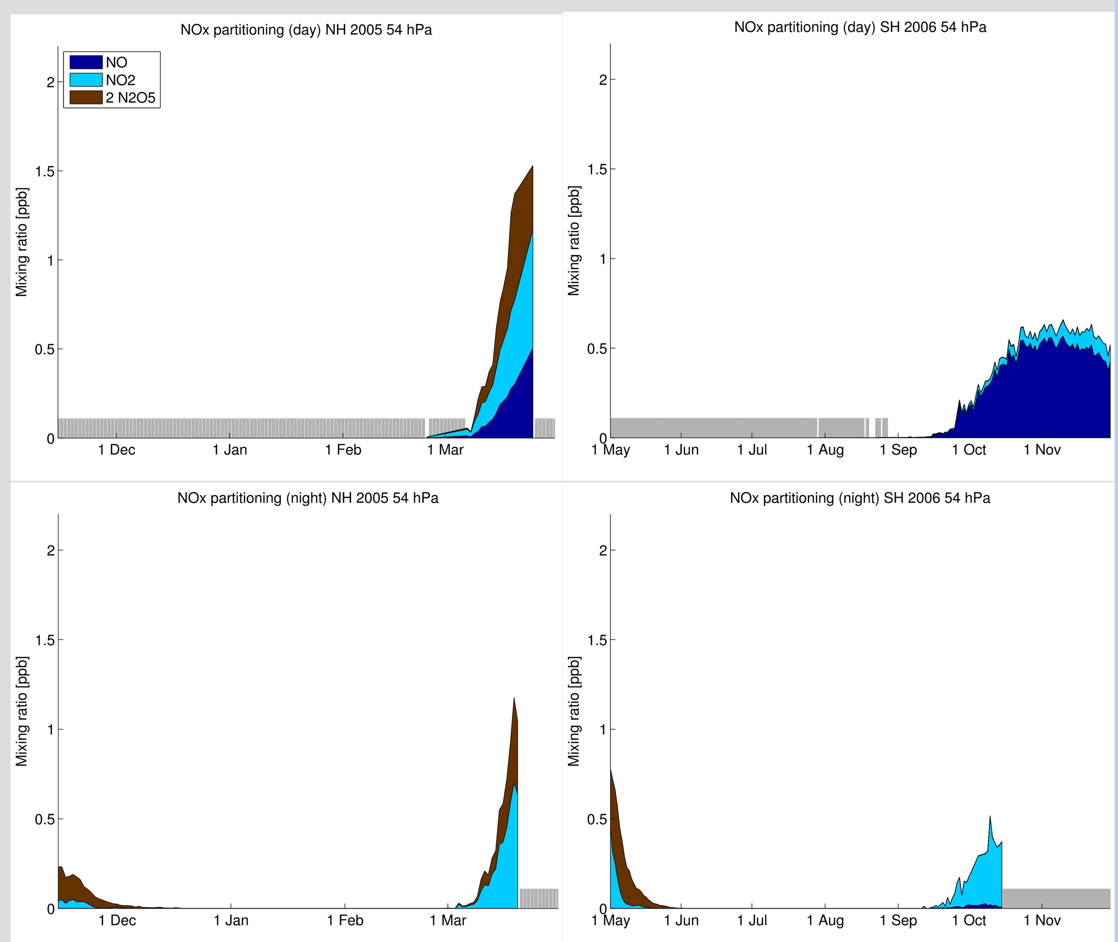
Vortex averaged partitioning of NO_y. Left: Arctic, Right: Antarctic. Change is dominated by denitrification.

NOx production and loss reactions



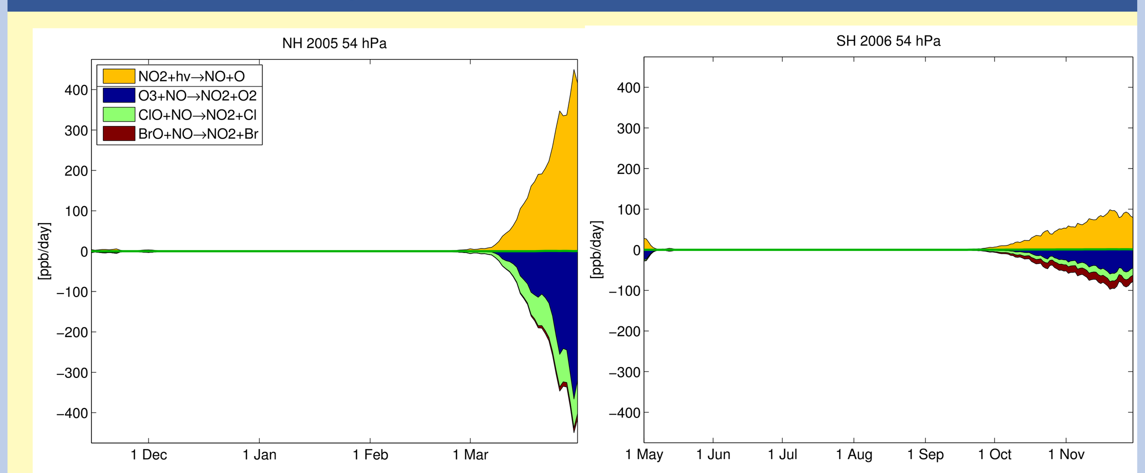
Vortex averaged reaction rates of reactions changing (an extended) NO_x ($NO + NO_2 + NO_3 + 2\,N_2O_5 + ClONO_2 + BrONO_2 + HO_2NO_2$). Green line: Net change of extended NO_x. Left: Arctic, Right: Antarctic.

Partitioning NOx



Vortex averaged partitioning of NO_x. Left: Arctic, Right: Antarctic, Top: Day, Bottom: Night.

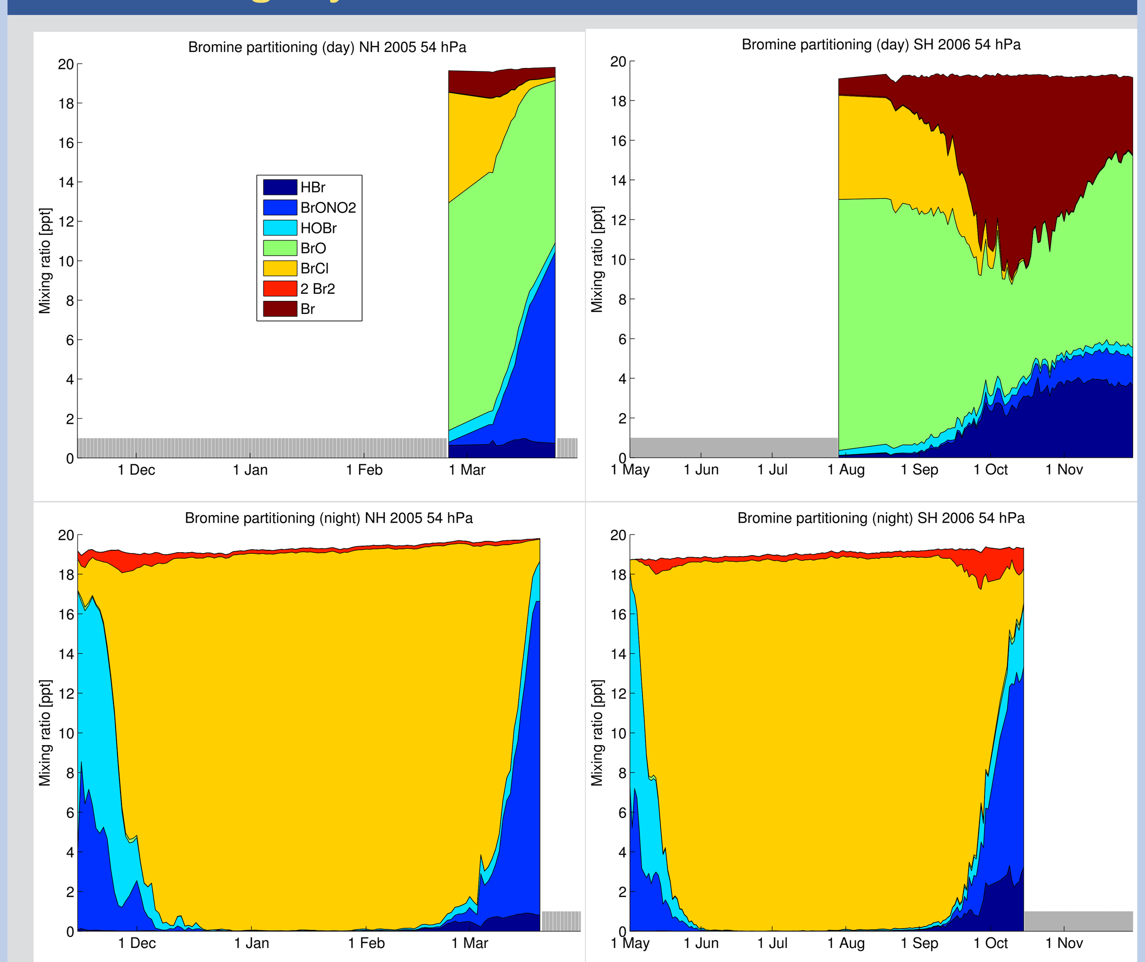
NOx partitioning reactions



Vortex averaged reaction rates of reactions changing NO to illustrate NO_x partitioning. Left: Arctic, Right: Antarctic.

Bromine

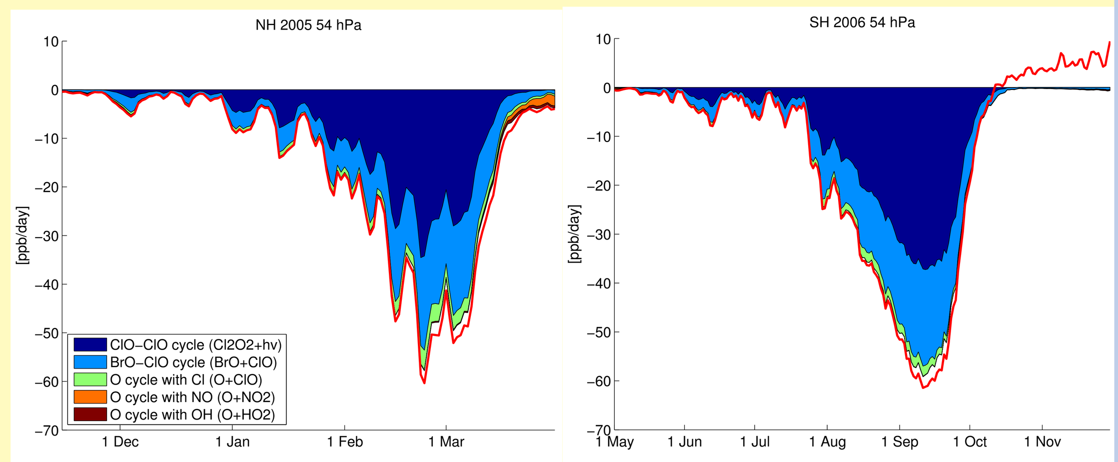
Partitioning Bry



Vortex averaged partitioning of inorganic bromine species Br_y. Left: Arctic, Right: Antarctic, Top: Day, Bottom: Night.

Ozone

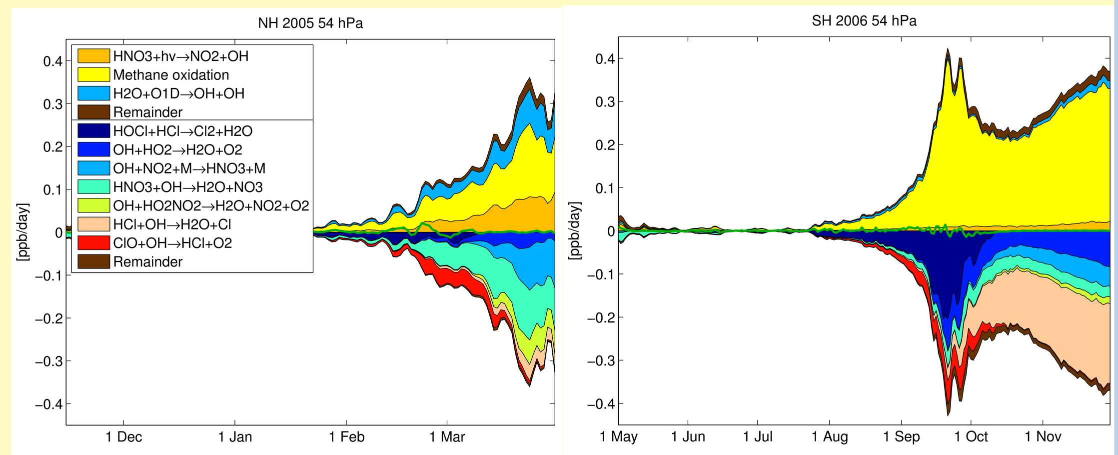
Catalytic ozone depletion cycles



Vortex averaged net loss rates of odd oxygen by different catalytic cycles. Red line: Net loss rate of ozone. Contribution of different cycles shown by reaction rates of rate limiting step. Left: Arctic, Right: Antarctic.

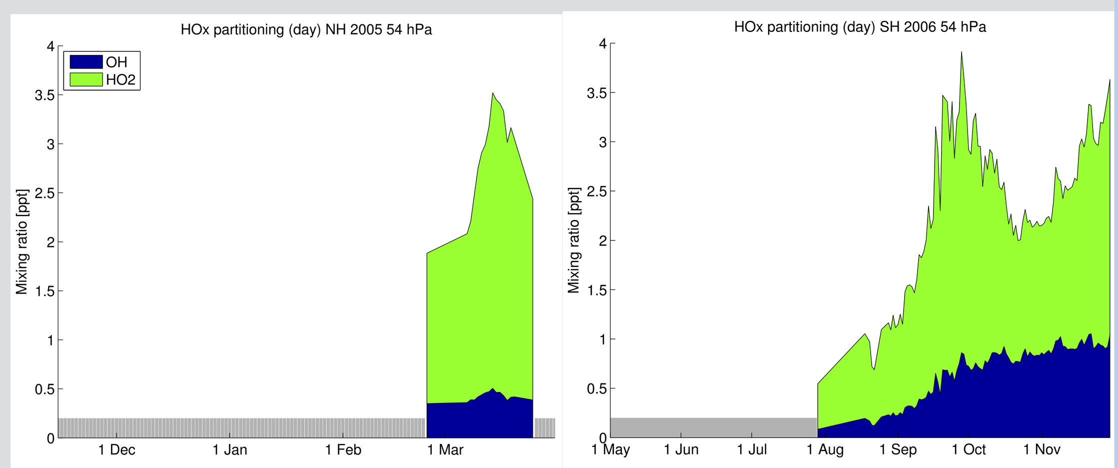
Hydrogen

HOx production and loss reactions



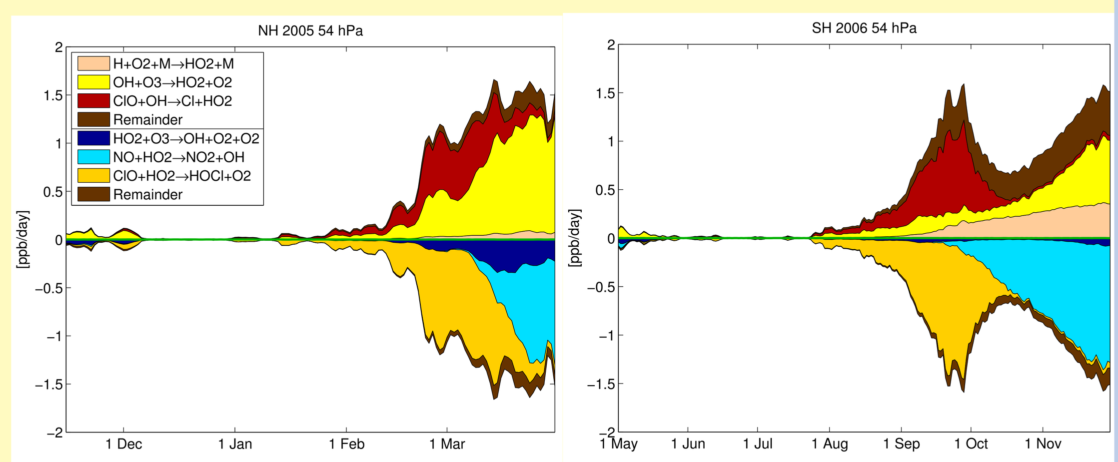
Vortex averaged reaction rates of reactions changing (an extended) HO_x ($OH + HO_2 + H + HOCl + HOBr + HO_2NO_2$). Green line: Net change of extended HO_x. Left: Arctic, Right: Antarctic.

Partitioning HOx



Vortex averaged partitioning of HO_x (only day, no HO_x at night). Left: Arctic, Right: Antarctic.

HOx partitioning reactions



Vortex averaged reaction rates of reactions changing HO_2 to illustrate HO_x partitioning. Left: Arctic, Right: Antarctic.

Some selected findings

- ClO dimer cycle contributes 50% to vortex averaged ozone loss (54 hPa) in both hemispheres. ClO–BrO cycle contributes 40%.
- In southern hemisphere, clear shift from chlorine activation by $ClONO_2 + HCl$ in early winter to $HOCl + HCl$ later in winter. $HOCl + HCl$ accounts for 70% of activation of HCl in SH, and for 30% of activation in NH.
- ClO_x peaks at 2.0–2.5 ppb. 70% of ClO_x present as ClO during daytime.
- HO_x peaks at 4 ppt. HO_x mainly produced from CH_4 oxidation in SH. In NH, production by HNO_3, CH_4 and H_2O comparable. Partitioning OH/HO_2 results in 20%–40% OH in SH and in 10%–20% OH in NH.
- NO_x smaller than 2 ppb in NH and smaller than 0.75 ppb in SH due to denitrified conditions there. Partitioning NO/NO_2 during daytime 80%–90% NO in SH and 20%–40% NO in the NH. Higher NO caused by much lower ozone in SH.
- 60%–80% of NO_x production in spring caused by the $HNO_3 + OH$, remainder caused by $HNO_3 + h\nu$. Deactivation of ClO_x by formation of $ClONO_2$ in NH by shift in equilibrium between ClO, NO_2 and $ClONO_2$, which in turn is caused by the production of NO_x.

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