# OH and $HO_2$ during the north Canadian spring

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## 1. Introduction

- OH is the dominant daytime oxidant in the troposphere.
- Thus understanding the chemistry of OH, and the closely coupled $HO_2$, radicals has implications on air quality and climate change.
- Comparison of reliable field observations of OH and $HO_2$ with numerical model predictions provides a useful method to test our understanding.
- Polar regions have been highly impacted by climate change.
- Large uncertainties remain about oxidation chemistry in these extreme cold environments.
- The Combined impact Of Bromine and iodine on the Arctic atmosphere (COBRA) campaign to the east coast of Hudson Bay during spring 2008 aimed to reduce some of these uncertainties.

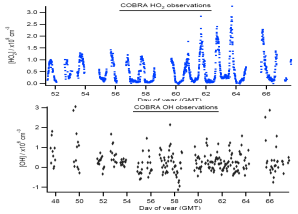

Location of the COBRA field site in northern Canada during spring 2008.

Container laboratories on the coast of Hudson Bay during COBRA.

## 2. Leeds FAGE instrument for OH and $HO_2$ detection[1,2]

- Fluorescence Assay by Gas Expansion (FAGE) involves excitation of OH from its ground $X^2\Pi$ state into the first electronically excited $A^2\Sigma$ state.
- Fluorescence occurs as OH relaxes back to its ground state.
- The fluorescence lifetime is increased through the reduction in the rate of collisional quenching, by the operation being carried out at low pressures (~0.7-4Torr).
- $HO_2$ is detected through its chemical titration with NO to produce OH, for subsequent detection by FAGE.

The Leeds FAGE instrument during the COBRA campaign.

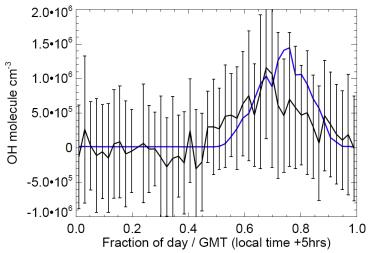



$HO_2$ and OH data time series during the COBRA campaign.

## 3. OH and $HO_2$ ($HO_x$) photochemistry during the north Canadian spring

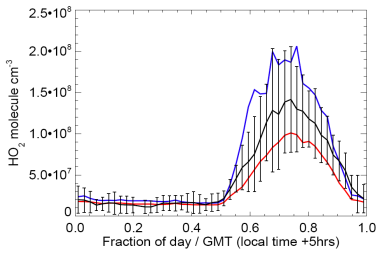
- Average diurnals show zero OH at night and peaking around (0.8 ± 1.0) × $10^6$ molecule $cm^{-3}$ at solar noon.
- $HO_2$ levels up to 0.5 × $10^8$ molecule $cm^{-3}$ were observed at night, with the average daily peak of (1.3 ± 0.6) × $10^8$ molecule $cm^{-3}$ at solar noon.
- An observationally constrained box model has been used to interpret these observations.

[OH] mean campaign diurnal



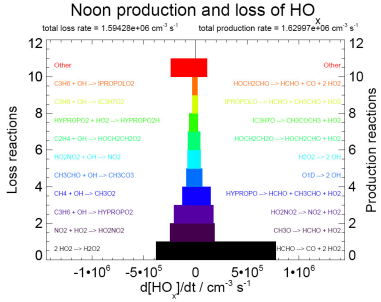

Mean diurnal OH observations, shown in black, with ±1 standard deviation variability bars. Constrained model calculation shown in blue .

$HO_2$ mean campaign diurnal




Mean diurnal $HO_2$ observations, shown in black, with ±1 standard deviation variability bars. Model calculation with constrained HCHO shown in blue and model calculation with HCHO calculated from oxidation of observed hydrocarbons in red.

Noon production and loss of $HO_x$



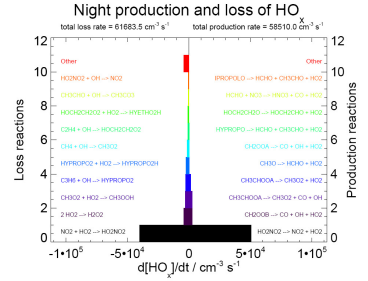

Analysis of the most important reactions for production and loss of noon time modelled $HO_x$.

- The model shows the major source of $HO_x$ radicals to be the photolysis of HCHO (~48% of the total noon time $HO_x$ production).
- Observed HCHO levels (not shown) cannot be explained through hydrocarbon oxidation alone.
- Observed fluxes of HCHO from the snow pack reported in the literature (4.9 × $10^{11}$ molecule $m^{-2}$ $s^{-1}$)[4,5] could explain the missing HCHO.
- The major loss of $HO_x$ in this environment was found to be $HO_2$ self reaction.

## 4. Night time $HO_2$

- Campaign average levels of $HO_2$ of 0.14 × $10^8$ molecule $cm^{-3}$ were observed at night time during COBRA.
- Box model simulations reproduced night time $HO_2$.
- The thermal decomposition of $HO_2NO_2$ is identified as the major source of $HO_x$ radicals at night.
- The low temperatures experienced during the campaign allow concentrations of $HO_2NO_2$ to build up during the day, and release $HO_x$ again during the night.

Night production and loss of $HO_x$




Analysis of the most important reactions for production and loss of night time modelled $HO_x$.

## 5. Conclusions

- OH and $HO_2$ observations were made on the east coast of Hudson Bay over a period of several weeks during February and March 2008.
- Box model calculations reproduce the general trend in observed OH and $HO_2$ concentrations.
- A box model study shows HCHO photolysis to be the primary source of $HO_x$ in this environment.
- HCHO generated from oxidation of observed hydrocarbons cannot reproduce the observations. Implying a secondary source of HCHO, potentially from snow pack emission.
- The thermal decomposition of $HO_2NO_2$ is identified as the major source of $HO_x$ radicals at night.

## 6. Acknowledgements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- All involved in the COBRA campaign
- NERC
- International Polar Year


Sunset at the office

## 7. References


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