Measurements and Modelling of Tropospheric OH and HO$_2$

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Introduction

Gas phase oxidation processes are responsible for the removal of many species emitted into the atmosphere

Oxidation processes control atmospheric lifetimes of pollutants and radiatively active gases such as CO, CH$_4$ and O$_3$ and influence air quality and climate

The hydroxyl radical (OH) dominates daytime oxidation chemistry in the troposphere

OH is primarily produced by the short wavelength (λ < 320 nm) solar photolysis of ozone, followed by reaction of O(^{1}D) with water vapour

OH interconverts rapidly with the hydroperoxy radical (HO$_2$) through reactions involving CO, O$_2$ and NO/O$_3$

Tropospheric concentrations of OH and HO$_2$ (collectively termed HO$_x$) determine the atmospheric oxidising capacity

Knowledge of OH and HO$_2$ concentrations in the atmosphere is essential to understanding atmospheric oxidation

HO$_x$ measurements are used to test chemical schemes used in atmospheric models

Validated chemical models can be used to predict air quality and climate change and influence policy decisions
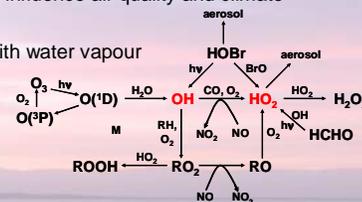
Atmospheric oxidation processes influence air quality and climate change

**Measurements of OH and HO$_2$ in the troposphere are essential to understanding atmospheric oxidation processes**

FAGE Detection of OH and HO$_2$[1,2]

OH and HO$_2$ concentrations in the troposphere are very low

Highly sensitive and selective technique required for atmospheric detection

Fluorescence Assay by Gas Expansion (FAGE) uses Laser Induced

Fluorescence (LIF) at low pressure

Ambient air drawn into low pressure detection cell (~ 1 Torr)

Laser beam passed across gas beam

On-resonance detection of OH at ~ 308 nm

HO$_2$ detection by chemical titration to OH

HO$_2$ + NO → OH + NO$_2$

Calibration of signals by H$_2$O photolysis at 184.9 nm and N$_2$O or O$_3$ actinometry
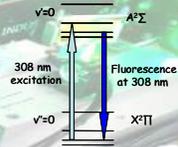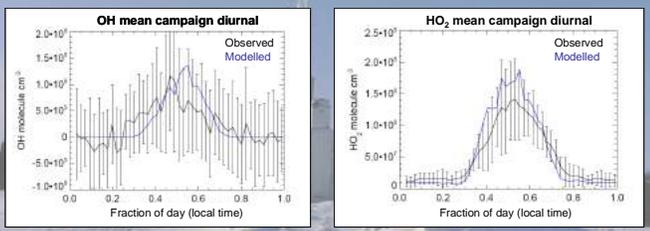
DSMACC Modelling of OH and HO$_2$[3,4]

High reactivity of OH and HO$_2$ results in limited influence of transport processes

Zero dimensional photochemical box models used for calculating OH and HO$_2$

Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC)

Flexible zero dimensional model constrained to observed O$_3$, CO, NO$_x$, VOCs

Uses the Kinetic Pre-Processor (KPP)

Photolysis rates calculated by Tropospheric Ultra-Violet (TUV) radiation model

Cloud correction factors from observed j(O^{1}D) and j(NO$_2$)

Uses the Master Chemical Mechanism (MCM) v3.1

Near explicit degradation schemes

~5600 species in over 13,500 reactions

Model run forwards to reach diurnal steady state
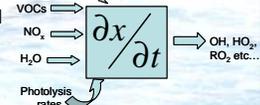
COBRA Campaign, Canada Spring 2008

Combined impact of bromine and iodine on the Arctic atmosphere

Average diurnals show OH peak concentrations of (0.8 ± 1.0) × 10^6 cm^{-3} at solar noon, with zero OH at night

Average HO$_2$ peak concentrations of (1.2 ± 1.0) × 10^8 cm^{-3} at solar noon

Night-time mean HO$_2$ (1.4 ± 1.0) × 10^8 cm^{-3}, with maximum of 5.0 × 10^8 cm^{-3}

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

Mean diurnal HO$_2$ observations (shown in black) with ± 1 standard deviation variability bars. Constrained model calculation is shown in blue.

Model calculations show HCHO photolysis is dominant HO$_x$ source (~ 50 % of total noon-time HO$_x$ production)

Observed HCHO fluxes cannot be explained by gas phase VOC oxidation alone

HCHO snow pack flux required in model to replicate observed HCHO and HO$_x$

Thermal decomposition of HO$_2$NO$_2$ identified as major HO$_x$ source at night

OP3 Campaign, Borneo 2008

Oxidant and Particle Photochemical Processes campaign[6]

Ground based measurements of OH, HO$_2$ and OH lifetime within rainforest

 - Allows determination of magnitude of OH sources and sinks

Aircraft measurements of OH and HO$_2$ over rainforest, oil palm and ocean

 - Provides information regarding vertical distribution and effects of land use

Ground based measurements show clear diurnal cycle peaking at solar noon

Up to 8.7 × 10^6 cm^{-3} OH observed (60 min average) with non zero OH at night

OH concentrations highly variable throughout the troposphere

 - Reflects the complexity of processes responsible for determining [OH]

 - Boundary layer aircraft OH similar to ground based measurements

HO$_2$ tends to decrease with increasing altitude

Large discrepancy between measured and modelled OH for ground and aircraft

 - Significant missing OH sources, additional evidence from OH lifetime data

 - Missing ground based OH in early morning attributed to HONO photolysis

 - Model failure for aircraft and ground based OH correlates with isoprene

 - Similar results obtained in other low NO$_x$ high isoprene environments[7-9]
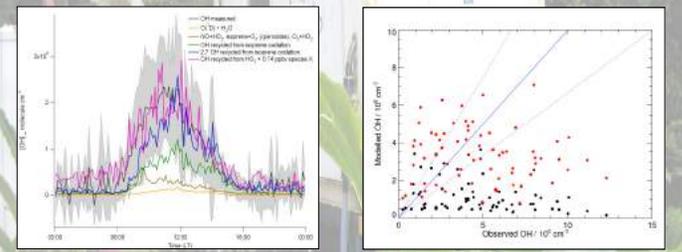

Mean diurnal ground based OH observations (shown in black) with ± 1 standard deviation variability bars (shaded) with steady state calculations incorporating OH loss from measured species and various OH production mechanisms

Modelled to observed comparison for aircraft OH data for the base MCM run (black) and a model run using the Peeters isoprene oxidation scheme (red).

Recent experimental and theoretical investigations of isoprene oxidation have questioned the mechanisms currently adopted in atmospheric models[10-12]

 - Implementation of recently proposed oxidation schemes in model

 - Peeters et al.[11] theoretical study yields greatest improvement to modelled OH

 - Further laboratory work to investigate isoprene oxidation chemistry required

Seasonal Oxidant Study, Cape Verde 2009

Long-term measurements at Cape Verde Observatory in tropical Atlantic

Relatively consistent mean diurnals between seasons

Both OH and HO$_2$ tend to zero at night

Provisional results lower than observations made in 2007,[5] but within 2σ calibration confidence

	SOS1	SOS2	SOS3
Dates	27th Feb – 8th Mar	6th – 16th June	1st – 15th Sep
Days of OH/HO$_2$	10	11	10
Mean noon-time OH / cm^{-3}	3.6 × 10^6	3 .5× 10^6	4.6 × 10^6
Mean noon-time HO$_2$ / cm^{-3}	1.8 × 10^8	2.1 × 10^8	1.8 × 10^5
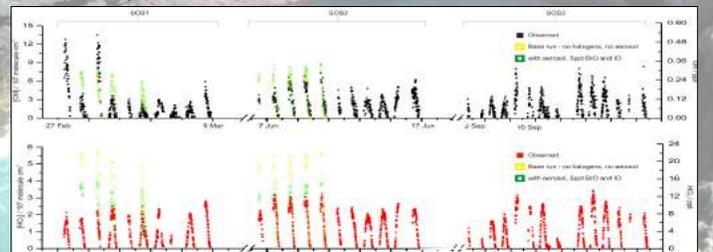
Model replicates trends in OH and HO$_2$ but currently overpredicts both species

Additional loss processes due to gas phase halogen chemistry and heterogeneous HO$_2$ uptake required in the model

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