# The impact of clouds on radical concentrations: Observations of OH and $HO_2$ during HCCT2010

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## 1. Rationale

• Clouds occupy ~ 15% of the troposphere.

• Modelling studies have shown that clouds can influence gas-phase chemistry either directly through efficient uptake into cloud droplets or indirectly through the separation of precursors between phases (Lelieveld & Crutzen, 1990, 1991; Tilgner et al., 2005). The reduction of gas-phase oxidants can decrease the self-cleansing capacity of the troposphere and change the tropospheric lifetimes of VOCs.

• Only very few experimental data existsto support model results (Mauldin et al, 1997; Frost et al, 1999; Commane et al, 2010).

• ~ 75% reduction in $[HO_2]$ in cloud during aircraft flights has been observed previously (Commane et al, 2010) – see figure 1.
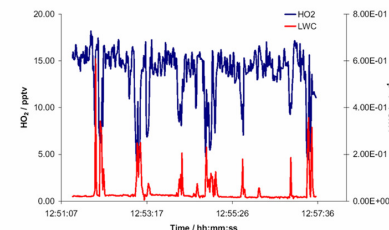


**Figure 1,** time-series of $[HO_2]$ and liquid water content during an aircraft flight over Africa, taken from Commane et al., (2010).

## 2. HCCT campaign methodology

The Hill Cap Cloud Thuringer – 2010 (HCCT-2010) campaign aimed to further investigate the connection of $HO_x$ reduction in clouds and microphysical parameters such as liquid water content.
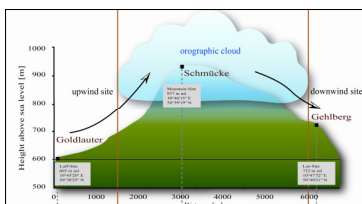


**Figure 2,** Schematic of the HCCT-2010 campaign set-up that took place in Thuringer Wald, Germany. Experiment consisted of 3 sites: Goldlauter (upwind), Schmucke (summit), and Gehlberg (downwind) and aimed to study cloud processing of gas-phase species and aerosols.

Laser induced fluorescence (LIF) at low pressures, known as the FAGE technique, was used to detect the gas-phase OH and $HO_2$ radical concentrations at the summit site both in-cloud and out of cloud. The data were compared to simple model predictions.



**Figure 3,** photo of FAGE instrument at the Schmucke site during a cloud event. Radicals were sampled from the top of the 22 m tower alongside ancillary measurements.

## 6. References

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## 7. Acknowledgements

## 3. Results
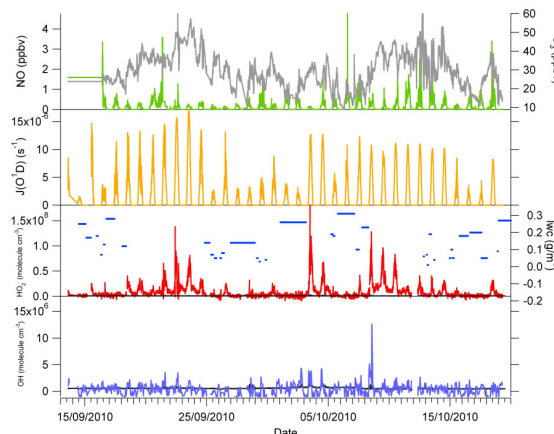


**Figure 4,** time-series of $[OH]$, $LOD_{OH}$, $[HO_2]$, lwc, $j(O^1D)$, $[NO]$ and $[O_3]$ at the Schmucke site from 14th September – 19th October 2010.

• Many cloud events occurring both during the day and night.

• ~ 65% reduction in $J(O^1D)$ on average during cloud events.

• Low concentrations of OH were observed out of cloud, but concentrations were below the limit of detection in-cloud.

• ~ 90% reduction in $[HO_2]$ during cloud events observed on average.
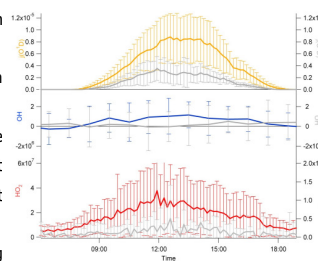


**Figure 5,** average diurnal of $j(O^1D)$, $[OH]$ and $[HO_2]$ during cloud events (grey) and out of cloud (colour).

## 4. Simple model predictions of radicals

[OH] may be estimated by balancing the rate of production with the rate of loss:

$$[OH]_{PSS} = \frac{p(OH) + k[HO_2][NO] + k[HO_2][O_3]}{k[CO] + k[CH_4]}$$

where p(OH) is the primary production of OH from the photolysis of $O_3$ and subsequent reaction of $O(^1D)$ with $H_2O$ (v).

Quadratic expression used to estimate $[HO_2]$:

$$0 = [HO_2]^2 \cdot (2.k_{HO_2+HO_2}) + [HO_2].(k_{HO_2+NO}[NO] + k_{HO_2+RO_2}[RO_2] + k_{HO_2+O_3}[O_3]) - (k_{CO+OH}[CO][OH] + 2.j(HCHO)[HCHO] + k_{RO+O_2}[RO][O_2])$$

$$0 = a[HO_2]^2 + b[HO_2] - c$$

$$[HO_2] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

• Lower concentrations of [OH] predicted out of cloud than observed suggesting missing OH sources.

• Model is able to replicate $[HO_2]$ out of cloud (red dashed line, Fig. 6) but over-estimates $[HO_2]$ in-cloud (grey dashed line, Fig. 6)

• To replicate $[HO_2]$ in-cloud observations (solid grey line, Fig. 6), a first order loss rate of $HO_2$ to clouds = 0.2 $s^{-1}$ is needed, suggesting a reactive uptake coefficient γ= 0.0125 (at cloud droplet surface area =1.5 x $10^{-3}$ $cm^2 cm^{-3}$), calculated from:

$$\gamma = \frac{4k}{\omega A}$$

Where $k$ is the first order loss rate ($s^{-1}$), $\omega$ is the mean molecular speed of $HO_2$ ($cms^{-1}$), and $A$ is the surface area ($cm^2 cm^{-3}$).
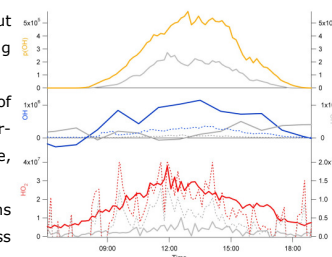


**Figure 6,** average diurnal of p(OH), [OH] and $[HO_2]$ during cloud events (grey) and out of cloud (colour). Model estimates (without heterogeneous loss to cloud droplets), in cloud (grey dash) and out of cloud (colour dash) for OH and $HO_2$ are also shown.

## 5. Conclusions and future work

• $HO_2$ concentrations were significantly depleted in cloud, with concentrations ~ 90 % lower relative to the out of cloud observations; an OH signal above the noise of the instrument was not observed during cloud events. These results suggest that heterogeneous processes in clouds do perturb the gas-phase radical chemistry.

• Further investigations studying the uptake of $HO_2$ during different cloud events.

• Does the uptake depend upon cloud microphysical properties?

• Comparison of observations with a multiphase chemistry model – Master Chemical Mechanism (MCM) coupled with Chemical Aqueous Phase Radical Mechanism (CAPRAM).