Impact of reduced aircraft emission on HO_x Chemistry in the upper troposphere during BLUESKY Campaign 2020

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1.Introduction

Hydroxyl radicals are the most predominant daytime initiator for atmospheric oxidation processes . Due to the COVID -19 pandemic, there was a considerable reduction in emission from industry and all means of transportation during spring 2020 (April-May). The main objective of the BLUESKY campaign was to understand the effect of this lockdown on the atmospheric composition such as trace gases, aerosols and cloud properties. The HALO (High Altitude and Long Range Research) aircraft had been equiped with a set of gas phase and aerosol measuring instruments. OH and HO_2 were measured with HORUS (HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy), during eight research flights from the boundary layer up to 14 km. The findings during the BLUESKY campaign are compared with results from steady state chemical box model and also with measurements from previous campaign HOOVER 2 which was along a similar flight trajectories during June 2007.

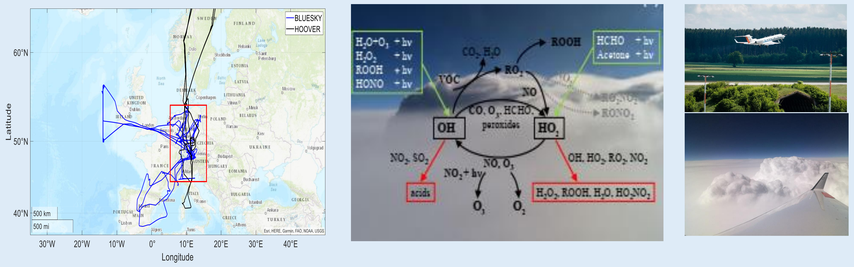


Fig 1a shows the flight track during Bluesky (Blue line) and HOOVER 2 (Black line). The red solid box shows the area used for comparing the results for this study. Fig 1b shows the HOx cycle in the atmosphere. Fig 1 c shows the take off of HALO aircraft during BLUESKY (top) and a cloud chasing event during the campaign (bottom).

2. HORUS (HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy).

The HORUS works on the principle of LIF-FAGE where ambient air is straightend and decelerated to minimize wall loss and allow in-situ calibration with the help of a shrouded inlet and the air is drawn to the first inlet section (35-70mbar less than the ambient pressure) where an OH scavenger (propane 1.7%) is added at every 2 minutes for 30 seconds to determine the chemical OH background. This is followed by a low pressure (3 -13mbar) detection cell where the OH radicals are exposed to 308 nm laser radiation which subsequently emit fluorescence light and is detected by a micro channel PMT.

Detection of HO_2 is achieved in the second detection cell where the incoming HO2 radicals are chemically converted to OH by adding a small flow of NO to achieve an internal NO concentration of 3e+13 molec/cc (average), which is sufficeint to convert HO_2 to OH. The possible inteference such as RO2+NO is quantified by adding different NO amounts.

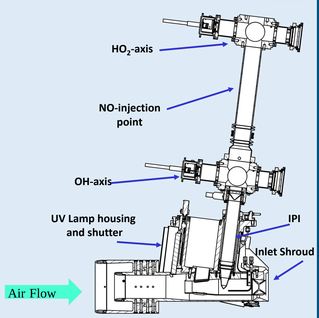


Fig 2 : Drawing of the Inlet Shroud and HORUS-Instruemnt

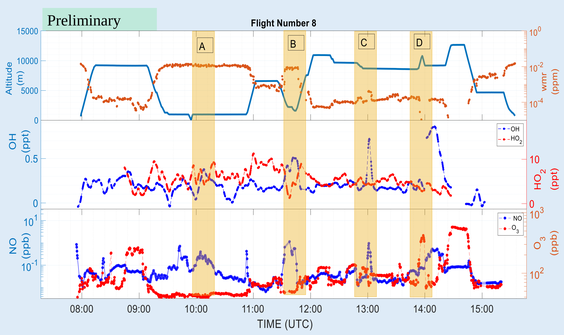


Fig 3: HOx and other relevant measurements during a typical flight during BLUESKY campaign (flight 8). Section A and B shows the low approaches towards Bordeaux and Madrid respectively. Section C represents a convective outflow measurement where increased OH concentration is measured due to the reaction of HO_2 with elevated NO, while a similar reaction is represented in Section D but the spike in NO is due to lighting. All datas are interpolated using a low pass 5 minutes gaussian interpolation method.

3. Comparison with CAABA-MECCA and EMAC model

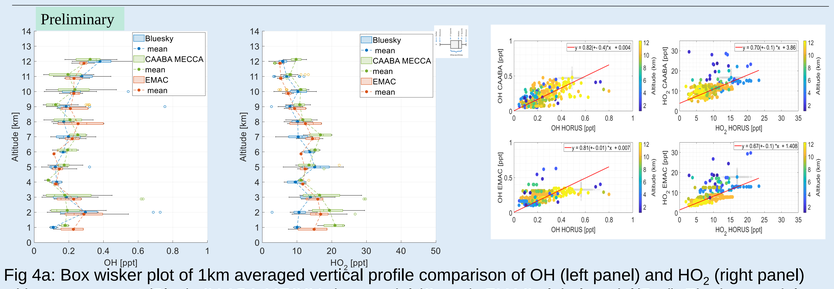


Fig 4a: Box wisker plot of 1km averaged vertical profile comparison of OH (left panel) and HO_2 (right panel) with measurement (Blue), CAABA-MECCA box model (Green) ,EMAC global model(Red). The box model was constrained using the measured meterogical and trace gas data during the campaign and the missing trace gas datas were taken from the corresponding EMAC model along the flight trajectories .The results shows on average an overall correlation of 80% for OH and 70% for HO_2. The 1σ uncertainity for the measurement is 21% and 24% for OH and HO_2 respectively. Later this data has been taken for further comparison and budget calculations. Fig 4b:The overall correlation plot between HORUS measurement and CAABA –MECCA ,EMAC models colorcoded as a function of altitude.The error bar (grey) shows 1σ uncertainity of the measurements.

4. Comparison with HOOVER-2 campaign

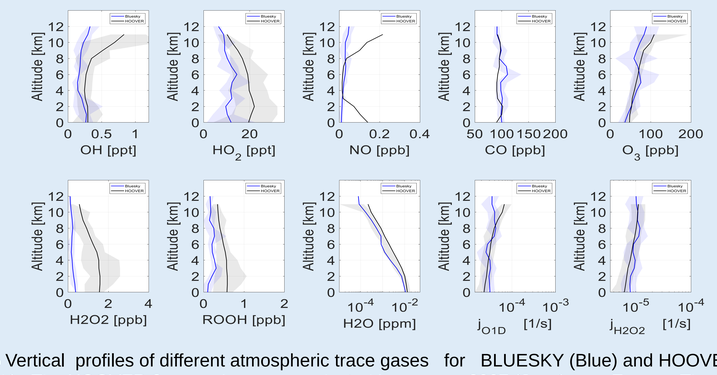


Fig 5 Vertical profiles of different atmospheric trace gases for BLUESKY (Blue) and HOOVER 2 (Black) . The HOOVER 2 campaign was conducted in summer 2007 (June) over Europe. The shaded area represents the 1σ standard deviation from averaging data on 1 km altitude bin. The comparisons shows a decrease in concentration of OH,HO_2,H_2O_2,ROOH ,H_2O and O_3 partly due to the reduced emission due to COVID -19 lockdown and possibly due to the reduced convection events during the measurement period.

5. HO_x Primary production

The photolysis of ozone and the subsequent collision with water is described as the primary production of OH $P(OH) = \varphi OH \cdot jO^1D \cdot [O3]$. Whereas the photolysis of peroxides and the reaction of HO2 with NO and O3 contributes to the secondary OH production

$S(OH) = j_{H_2O_2}[H_2O_2] + j_{MHP}[ROOH] + k^*[O_3][HO_2] + k^*[NO][HO_2]$.

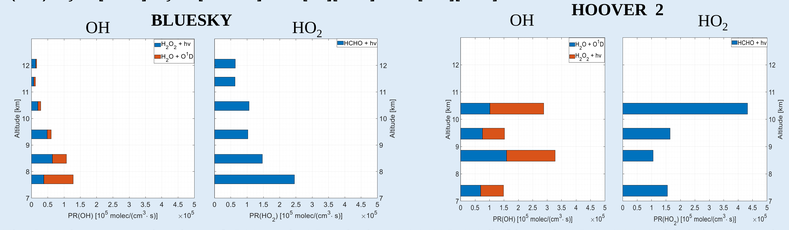


Fig 6. Primary production of OH and HO_2 during BLUESKY (left) and HOOVER 2 (right). The primary production during BLUESKY above 8km was reduced by more than a factor of 2 due to the reduced concentration of water, ozone and peroxides .The fractional contribution of peroxides that transported upward from boundary layer is also considered as a primary OH production source which reduced during Bluesky possibly due to lesser large scale convection events.

6. HOx budget calculations

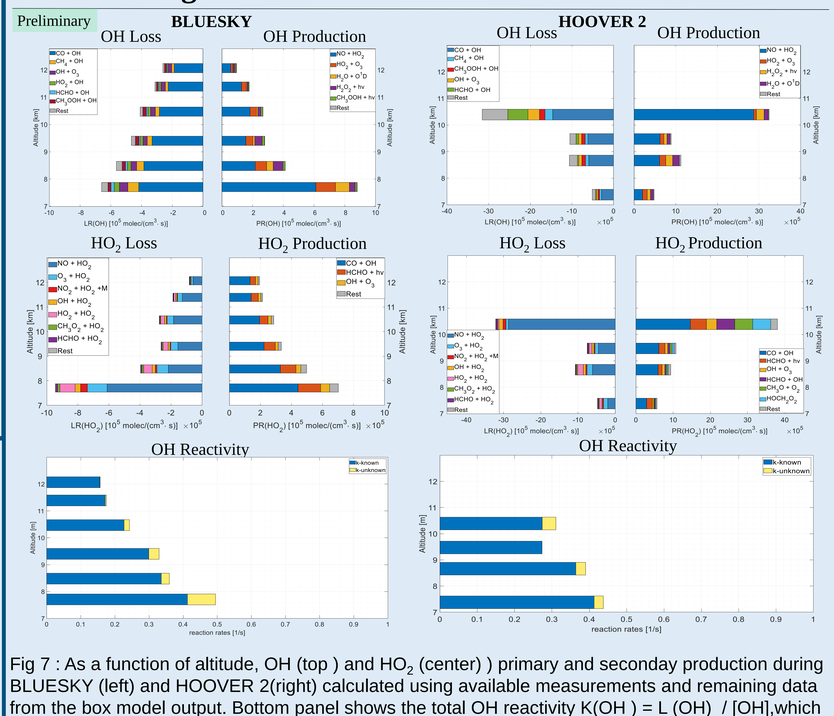
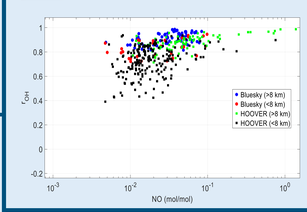


Fig 7 : As a function of altitude, OH (top) and HO_2 (center)) primary and seconday production during BLUESKY (left) and HOOVER 2(right) calculated using available measurements and remaining data from the box model output. Bottom panel shows the total OH reactivity K(OH) = L (OH) / [OH],which describes the known OH reactivity under steady state assumption. Its is found that the observations is on average able to explain 87% to 98% and 90% to 99% of OH reactivity for BLUESKY and HOOVER 2 respectively. The missing reactivity is possibly due to the limited knowledge of NMVOC's during the measurement and its contribution towards OH reactivity .

7. OH recycling probability and oxidative capacity



The primary producion of OH and the recyling reaction with in HOx cycle determines the OH concentration and there by the oxidative capacity of the atmosphere.The ability of a single OH molecule recycling back through the atmospheric chemical system indicates the stability and oxidate capacity described by (rOH = $\frac{S(OH)}{P(OH)+S(OH)}$). The budget analysis shows that in the upper troposphere the recycling of OH is mainly controlled by NO. Fig 8 shows the rOH as a function of NO mixing ratio.

8.Conclusion

(i) The HOx measurements obtained during BLUESKY campaign showed a good agreement with the atmospheric chemistry model EMAC and the steady state box model CAABA MECCA.

(ii)During the BLUESKY campaign ,the OH and HO_2 concentration in the troposphere was found comparable to previous campaigns but reduced by a factor of 2.5 and 2 respectively on average in the upper troposphere .

(iii)This reduction in the OH concentration is partly due to less NO in the upper troposphere due to reduced aircraft emission and, potentially due to low concentration of primary precursors such as H2O,O3,peroxides for the HOx production as a result of less convective outflow during the measurement period and it is currently under investigation.

Acknowledgements
I would like to say thank you to the scientists, pilots, engineers and all coordinators from the BLUESKY and DLR teams, for the operational and logistical support throughout the BLUESKY 2020 measurement campaign.

Reference

1.The Oxidation Capacity of the Summertime Asian Monsoon Anticyclone; PhD Thesis 2020, Daniel Marno, Max Planck Institute for Chemistry, Mainz.
2. Räumliche und jahreszeitliche Verteilung von OH- und HO2-Radikalen in der Troposphäre über Europa; PhD Thesis 2011 ; Eric Regelin , Max Planck Institute for Chemistry, Mainz