HO_x Budgets during HOxComp: a Case Study of HO_x Chemistry under NO_x limited Conditions

Y. F. Elshorbany[1,2,8*], J. Kleffmann[1], R. Kurtenbach[1], A. Hofzumahaus[3], H.-P. Dorn[3], E. Schlosser[3], T. Brauers[3], H. Fuchs[3], F. Rohrer[3], A. Wahner[3], Y. Kanaya[4], A. Yoshino[5], S. Nishida[5], Y. Kajii[5], M. Martinez[6], M. Rudolf[6], H. Harder[6], J. Lelieveld[6], H. Berresheim[7], T. Elste[7], C. Plass-Dülmer[7], G. Stange[7], P. Wiesen[1]

[1]Physikalische Chemie, FB C, Bergische Universität Wuppertal, Wuppertal, Germany. [2]Environmental Research Division, National Research Centre, Cairo, Egypt. [3]Forschungszentrum Jülich, ICG-2: Troposphäre, Jülich, Germany. [4]Research Institute for Global Change, Yokohama 236-0001, Japan. [5]Tokyo Metropolitan University, Tokyo, Japan. [6]Max-Plank Institute für Chemie, Atmospheric Chemistry Department, Mainz, Germany. [7]Deutscher Wetterdienst, Meteorologisches Observatorium, Hohenpeissenberg, Germany. [8]now at Max-Plank Institute für Chemie, Atmospheric Chemistry Department, Mainz, Germany. *yasin.elshorbany@mpic.de, Tel. +49 (6131) 305450, Fax. +49 (6131) 305511.

www.mpic.de

JÜLICH FORSCHUNGSZENTRUM

Introduction

- The hydroxyl radical (OH) is the primary oxidant in the atmosphere, responsible for the oxidation and removal of most natural and anthropogenic trace gases.
- Recent studies have shown that measured OH radical concentrations under NO_x limited, rural conditions are many times higher than modelled OH, from which NO independent OH regeneration pathways were proposed.
- Very recently, studies showed that uncertainties in HO_2 measurements as result of RO_2 interferences may lead to even higher than the currently estimated gap, thus persisting the need for new OH sources.

Aim of the Work

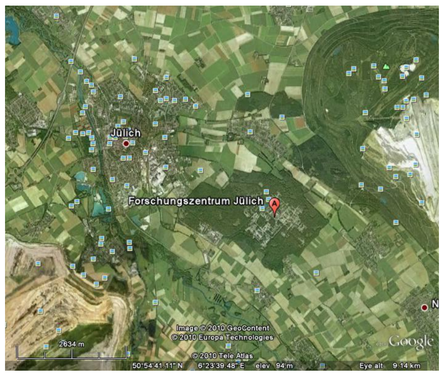
➢ Detailed analysis of the HO_x radical budgets under low NO_x, rural conditions employing a zero dimensional photochemical box model based on the Master Chemical Mechanism (MCMv3.1).

➢ The model results to be compared and contrasted with the different HO_x radical measurements performed during the international HOxComp campaign carried out in Jülich, Germany during summer, 2005.

Field Measurements

The formal part of the campaign included three days of ambient measurements from July 9–11, 2005 and six days of chamber experiments in the SAPHIR chamber from July 17–23, 2005, of which only the ambient measurements are considered herein.

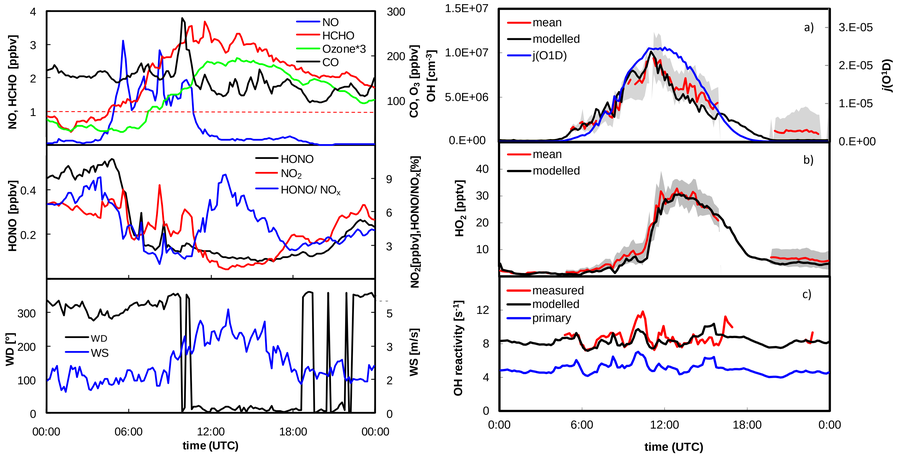
The HOxComp campaign took place on the campus of the Jülich Research Centre (50° 54´ 33´´ N, 06° 24´ 44´´ E)., ~2 km south-east of the city of Jülich but surrounded from all other directions by deciduous forest, agricultural areas, and main roads.



OH ambient measurements were performed by four different instruments: three Laser-Induced Fluorescence (LIF) instruments operated by *Max-Planck Institute Mainz* (MPI-LIF); *Forschungszentrum Jülich* (FZJ-LIF) and the *Japan Frontier Research Centre for Global Change* (FRCGC-LIF) and one Chemical-Ionization Mass-Spectroscopy (CIMS) instrument operated by *Deutscher Wetterdienst* (DWD-CIMS), each using their own calibration scheme. All LIF instruments measured additionally HO_2 through the chemical conversion to OH by addition of NO in the gas expansion, followed by LIF detection of the additionally formed OH.

Measured trace gases included HONO, HCHO, NO, NO_2, CO, O_3, volatile organic compounds (VOCs) and photolysis frequencies *j*(NO2), *j*(O^1D), *j*(HCHO), *j*(HONO) and meteorological parameters.

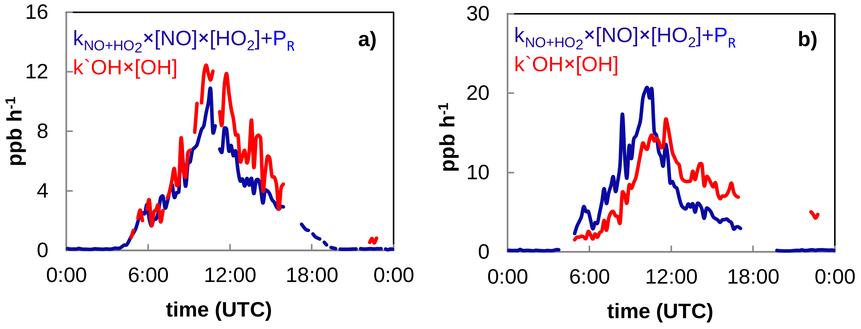
Measured and Modelled Species



Left: 10 min average diurnal profiles of the measured parameters on July 10th during HOxComp. The figure shows the high NO_x conditions from 6-10 h and the low NO_x conditions from 11-18 h.

Right: 10 min average measured and modelled OH, HO_2 and OH reactivity during the HOxComp campaign. Grey-shaded areas determine the minimum and maximum measured HO_x levels.
Simulated HO_x diurnal profiles lay within the measurement range of all instruments. OH reactivity is in excellent agreement with that measured.

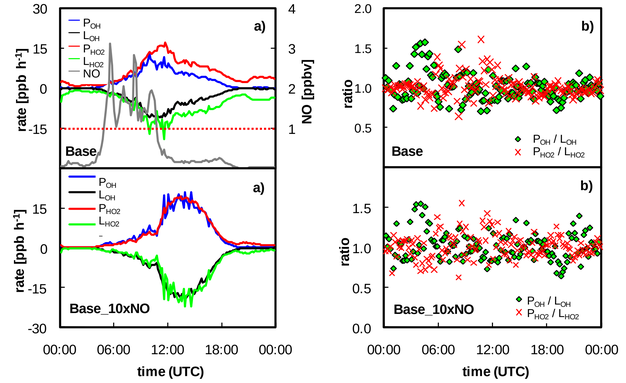
Turnover rates



Turnover rates calculated based on measured OH reactivity and a) mean measured OH and HO_2 by the FRCGC_LIF and FZJ_LIF and b) by measured OH and HO_2 by MPI_LIF. $P_R = j(HONO)[HONO] + P_{OH}(O_3) + P_{OH}(alkenes)$.
Turnover rates calculated based on the mean measured OH and HO_2 by FRCGC_LIF and FZJ_LIF (a) indicate the need for additional OH source during the low NO_x period. In addition to the afternoon gab, turnover rates calculated using measured OH and HO_2 levels by MPI_LIF (b) would reveal an excess OH production during the high NO_x period.

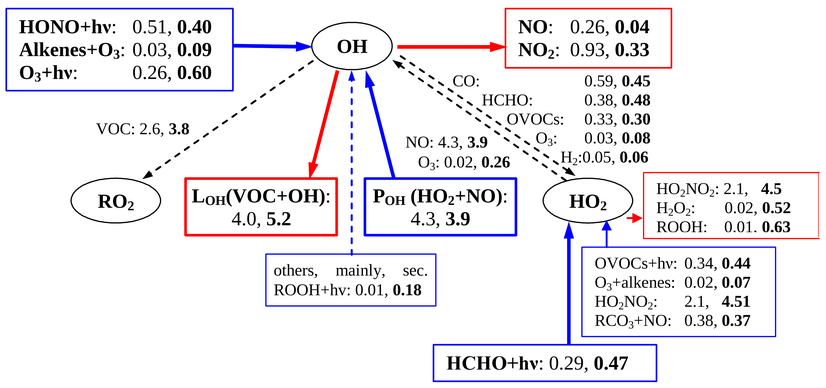
➢ Different measured HO_x levels by different instruments may lead to different conclusions!

Radical Production and Destruction



a) Total production and destruction rates of OH and HO_2 and b) ratio of production to destruction rates of OH and HO_2 during the HOxComp campaign using the base model (upper panel) in comparison to that of the Base_10xNO scenario (lower panel). The upper panel (a) shows the complete radical recycling during the high NO_x period and the less efficient recycling during the low NO_x period. The lower panel shows that increasing the NO levels (artificially by 10 times) resulted in efficient radical recycling.

Flux Diagram



Average daytime fluxes of the key radical sources and sinks during HOxComp calculated by the MCM for the low NO_x period (bold letters) in comparison to that of high NO_x period.
The secondary OH radical loss (L_{OH} (VOC+OH) = $L_{OH}(OH \rightarrow RO_2) + L_{OH}(OH \rightarrow HO_2)$) and production ($P_{OH}(HO_2+NO)$) are balanced during the high NO_x period but indicating a net radical loss during the low NO_x period. Secondary radical production of P_{OH}(ROOH+hv) and $P_{OH}(HO_2+O_3)$ during the low NO_x period is more than an order of magnitude higher than during the high NO_x period.

Conclusion

Measured HO_x diurnal profiles were well simulated. Turnover rates calculated based on measured OH and HO_2 indicate an afternoon gab, which may due to: Uncertainties in HO_2 measurements and/or the need for additional OH sources. Nevertheless, more field measurements-modelling comparisons under similar condition are urgently needed to explore the source of this gap.