HOxCOMP

Within the frame of the integration task on "Quality Assurance/Quality Control (QA/QC)" a workshop was held at Forschungszentrum Jülich on 27-28 September 2004 to prepare a comprehensive instrument intercomparison campaign of OH/HO_2 instruments (not RO_2/HO_2 instruments) at the atmosphere simulation chamber SAPHIR. The workshop objectives were:

- Bring together the world-wide OH/HO_2 radical measurement community.
- Discuss the experiments to be performed during a comprehensive instrument intercomparison campaign in Jülich next year.
- Learn about the SAPHIR chamber as a new tool to perform instrument intercomparisons under controlled atmospheric conditions. The intercomparison campaign HOxCOMP 2005 is sheduled for June to July 2005.

Local Organiser:
✉ **Hans-Peter Dorn**
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HOxCOMP Workshop

27.-28. Sep. 2004, Forschungszentrum Jülich, ICG-II: Troposphäre

Workshop objectives

- To bring together the word wide OH/HO_2 radical measurement community.
- To get familiar with the SAPHIR chamber as a new tool to perform HOx instrument intercomparison measurements under controlled atmospheric conditions.
- To find a technical solution to get the instruments attached to SAPHIR.
- To define the time frame and measurement strategy of HOxCOMP 2005.

HOxCOMP Workshop

Agenda

DAY 1 (Sept 27, Monday)	
12:00	Arrival, snacks and refreshments
12:30	Welcome by ICG-II director Andreas Wahner and Short introduction to the tasks of the ACCENT subproject "Quality Assurance of atmospheric measurements".
12:40	Theo Brauers: The atmosphere simulation chamber SAPHIR - features and photo-chemical properties.
13:10	First visit to SAPHIR.
14:00	**Presentations of participating groups (15 min + 5 min for discussion)** **Eric Schlosser**, FZJ: Laser-absorption spectroscopy (DOAS) and results of an informal comparison with LIF **Frank Holland**, FZJ: Laser induced fluorescence (LIF) and results of informal comparison of HO_2 measurements by LIF and ESR
14:40	Coffee break
15:00	**Yoshizumi Kajii**, Tokyo Metropolitan University: Measurement of OH reactivity in urban atmosphere. **Yugo Kanaya**, Frontier Research Center for Global Change, Yokohama: LIF **Dwayne Heard**, University of Leeds: LIF **Monika Martinez**, Max-Planck-Institute for Chemistry, Mainz: LIF **Hardwig Harder**, Max-Planck-Institute for Chemistry, Mainz: The Penn State LIF **Harald Berresheim**, German Weather Service: Chemical Ionization Mass Spectrometry
17:00	Discussion (formal/informal intercomparison, instrument calibration, ...)
17:45	Housekeeping notes / Transfer to the hotel
18:55	Pick up at the hotel
19:00	Dinner at a Greek Restaurant in Jülich Open end

DAY 2 (Sept 28, Tuesday)	
08:30	Pick up at the hotel
08:45	Extensive inspection of SAPHIR. Discussion of technical questions.
10:30	Coffee break
10:45	Fixing of the time schedule in 2005.
11:00	Planning of HOxCOMP 2005 (measurements in ambient air and at SAPHIR).
11:45	Final discussion, definition of action items.
12:30	Lunch at FZJ
13:30	End of workshop

ACCENT
ATMOSPHERIC COMPOSITION CHANGE
THE EUROPEAN NETWORK OF EXCELLENCE

HOxCOMP workshop

September 27 – 28, 2004

Forschungszentrum Jülich,

ICG-II: Troposphäre

Theo, Franz, James, Harald, Hartwig, Monika, Andreas, Yugo, Frank, Yoshi, Thomas, Hans-Peter, Hendrik, Georg, Franz-Josef, Dwayne, Rolf

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HOxCOMP Workshop

Outcomes

Summary of workshop
During our ACCENT HOx workshop in Jülich we decided to have the HOx intercomparison campaign from 3 weeks preferably from June 27 to July 16 2005. However, the Mainz group asked to shift the campaign by one week because they are obliged to participate in the yearly Max-Planck-meeting the week before. The new time frame would also meet our requirements perfectly. Therefore we propose a new time frame:

**** Monday July 4 to Sunday July 24 2005 **.**

At the end of this document you find the schedule based on the NEW times. We also adjusted the measurement time at SAPHIR to 4 days (5 days were proposed during the meeting) in order to limit the campaign duration to 3 weeks.

During the workshop we decided to perform a formal blind intercomparison with an independent referee. The referee will be Prof. Ulrich Schurath, Forschungszentrum Karlsruhe.
The referee supervises the execution of the intercomparison. Quick-look data should be submitted to the referee at the day of measurement or within a pre-defined time interval. The referee compares the data and does a first evaluation of the results (on a day-to-day basis). He has the possibility to discuss his finding individually with the groups in the case of obvious problems. He will receive the final data from the participants 2 months after the campaign, compare it, and report the results first to the participants. These data will be the basis of conference presentations and publications.

The measurement program (see appendix "*HOxCOMP.MeasurementProgram.2004-12-08.doc*") is still preliminary. However we did some model calculations based on our experience of chamber experiments. Please see appendix "*HOx Szenarios for Intercomparison – Model description and results*" with a selection of slides from a presentation Theo prepared for a seminar.

During the meeting we did not discuss a file format for data exchange. Since the chamber data - which will be available to you at the end of every measurement day - will be in the ENZ format we propose to use the same format for data exchange. Please see appendix "*ENZ-Format*".
File names should be given in: 'YYYY-MM-DD.name_of_your_instrument.data_set.enz' in order to have the same naming convention as the chamber data. We will send a more detailed description early next year to give you the opportunity to add comments to the file format and naming.

What do we need from you until **January 28, 2005 !**

- decision on participation in HOxCOMP 2005.
- acceptance of the time schedule (start date).
- your requirements: power, water, gases (questionnaire, please specify exactly which gases apart from synth. air you do need).
- size, weight, ... of the instruments.
- sketch / drawing of your instrument at SAPHIR.
- your needs for chamber access (for calibration etc.). How often?
- your needs for support (machine shop, container space, scaffold, crane, ...).
- information on personal (number of persons involved, duration of their stay, hotel rooms, etc..).
- approximate costs (transport costs of instruments, travel expenses of personnel).

Further information will be posted on a HOxCOMP web site. Web address and password necessary for access to internal information will be provided shortly. All presentations given during the workshop can be downloaded from there.

In case of questions please don't hesitate to call or email:

Theo Brauers: ☎+49 2461 616646 ✉ th.brauers@fz-juelich.de
Hans-Peter Dorn: ☎+49 2461 616768 ✉ h.p.dorn@fz-juelich.de

Progress Report 2007

Data of the HOxCOMP intercomparison campaign is still discussed between the participating groups and the referee. Therefore a public report is not available at the present time.

A draft manuscript of the intercomparison of OH measurements has been prepared and sent to the participants. At present the manuscript is in discussion among the participating groups and it is expected to submit the papers in the course of this year.

For any further information please get in touch with ✉ Hans-Peter Dorn.

HOxCOMP: Measurement programme

1. Ambient air measurements:

a: **Location**: outside SAPHIR (see plan)

b: **Available** online measurements:

- NO, NO2, O3, CO
- photolysis frequencies (by spectro-photometry),
- hydrocarbons C2...C6 (GC/FID); VOC C2... C10 (GC-MS)
- meteorology: T, P, wind, rel. humidity
- *availability open: HCHO (Hantzsch), HONO (LOPAP)*
- *not available: OH-DOAS*

c: **Experiments (2 days)**:

continuous measurements during daylight hours

(Sat and Sun in order to avoid local car traffic)

2. Chamber measurements in SAPHIR

a: **Location**: Instruments attached to SAPHIR

b: **Available** online measurements:

- NO, NO2, O3, CO
- photolysis frequencies (by spectro-photometry),
- hydrocarbons C2...C6 (GC/FID); VOC C2... C10 (GC-MS)
- meteorology: T, P, wind, rel. humidity
- HCHO (Hantzsch), HONO (LOPAP)
- OH-DOAS

c: **Proposed experiments (4 days)**:

- Clean air, minimum humidity (dew point: -40°C), modulation of light
- Clean air, atmospheric humidity level, stepwise addition of CO
- Clean air, atmospheric humidity level, stepwise addition of ozone
- Alkene ozonolysis using increasing alkene mixing ratios and different alkenes (louvre system closed → chamber dark, HO2 formation

HOx Szenarios for Intercomparison

Model description and results

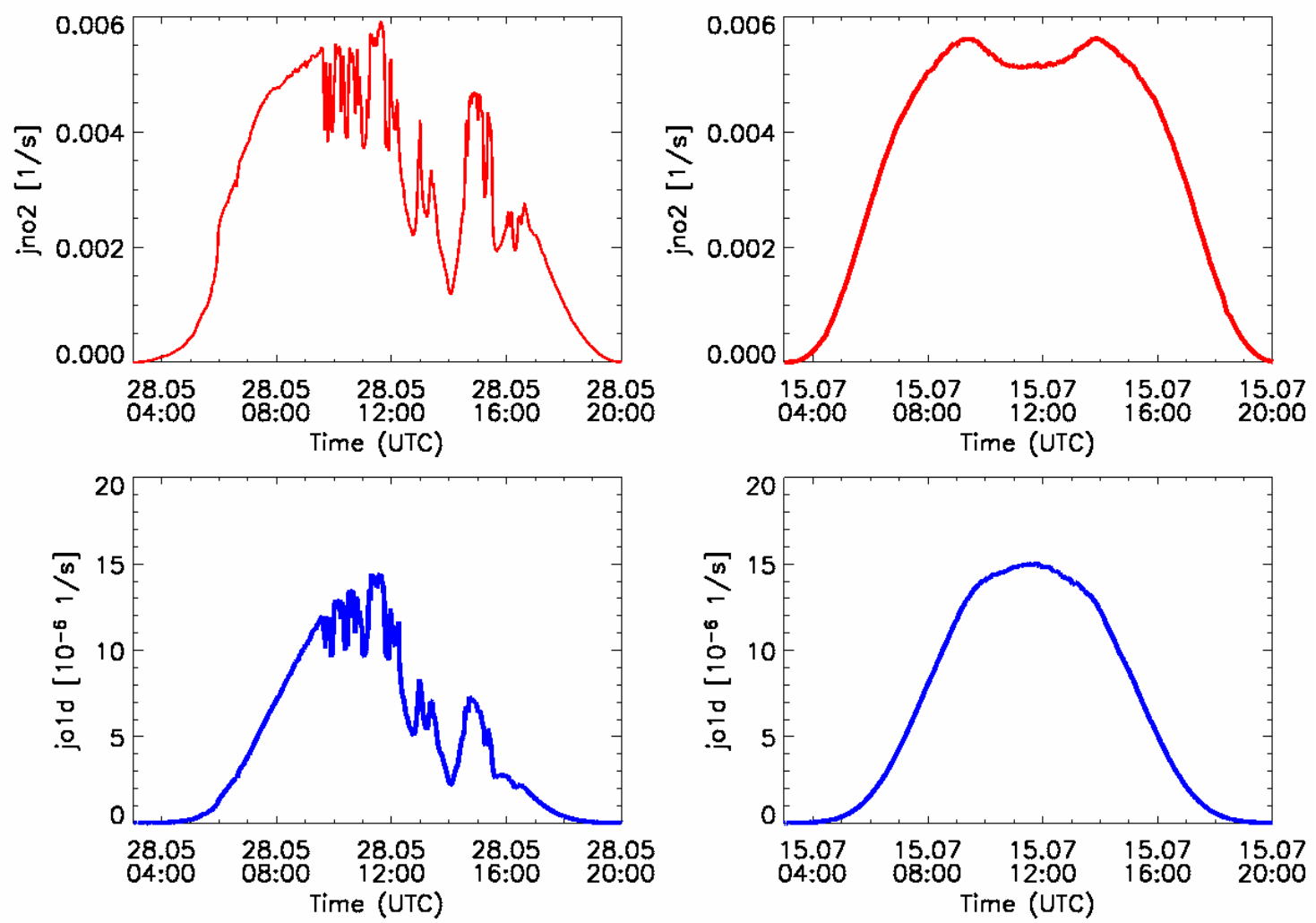
Theo Brauers

ICG-II

Forschungszentrum Jülich

Photolysis in SAPHIR

- two days 2003 selected :
  clouded (strong modulation) **– clear sky** (shadow)



Model calculation (1): Mechanism

- **simple CO / NOx / HOx / HCHO / HONO mechanism**
  (rate constants from Lit. , JPL ...)
  - **2*HO2 --> H2O2**
  - **CO+OH --> CO2+HO2**
  - **H2+OH --> HO2**
  - **H2O2+OH --> H2O+HO2**
  - **HCHO+OH --> CO+HO2**
  - **HO2+NO --> NO2+OH**
  - **HO2+O3 --> OH**
  - **HO2+OH --> H2O**
  - **NO+O3 --> NO2**
  - **NO+OH --> HNO2**
  - **HNO2+OH --> H2O+NO2**
  - **NO2+OH --> HNO3**
  - **O3+OH --> HO2**

Model calculation (2): Mechanism

- **Dillution**
  for CO / HONO / HCHO / NO2 / NO / O3 / H2O / CO2
  (CO2 as Tracer for dilution)
  - **XY + DIL --> k[XY+DIL] = CONST(ExpFlux/(270.*3600.))**
- **Photolysis**
  (Bohn and Zilkens, Atmos. Chem. Phys. Discuss., **4**, 6967-7010, 2004)
  - **H2O2+hv --> 2*OH**
  - **HCHO+hv --> CO+2*HO2**
  - **HCHO+hv --> CO+H2**
  - **HNO2+hv --> NO+OH**
  - **NO2+hv --> NO+O3**
  - **O3+hv --> 2*OH**
- **wall loss for HNO3 / HONO / HO2 / H2O2 / O3**
  - **XY + WALL --> k[XY+WALL] = CONST(3.9E-6)**
  - $3.9 \times 10^{-6} s^{-1}$ corresponds to 70h lifetime

Model calculation (3): Mechanism

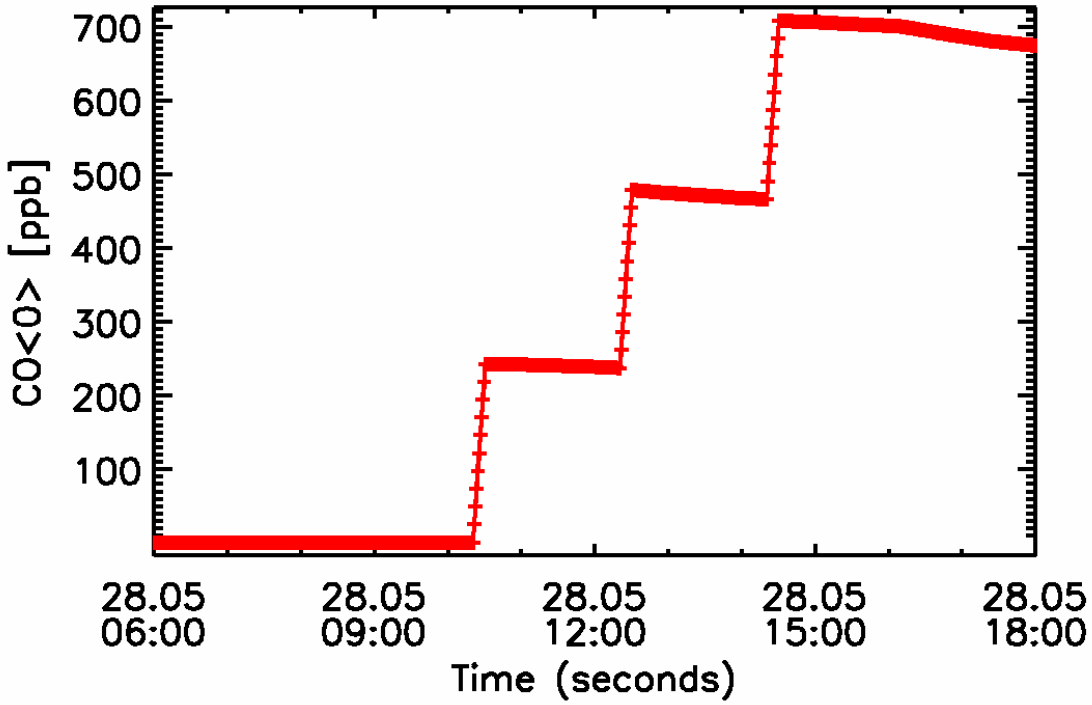
- **SAPHIR – reactivity**
  (based on recent experiments)
  k = k(OH+CO)= $2.4 \times 10^{-13} cm^3 s^{-1}$
  [Y] = 200ppb (corresponds to τ(OH) = 0.9 s)
  - **OH+Y --> HO2**
- **SAPHIR (wall) - sources for HONO / HCHO**
  - **hv --> HCHO**
    Light dependent source:
    k[hv --> HCHO]=CONST(2.8e6)
    $2.8 \times 10^6 cm^{-3} s^{-1}$ corresponds to 400ppt/h
  - **hv --> HNO2**

    k[hv --> HNO2] =CONST(8.5e13 * (1. + (RH/11.6)@2) * exp(-3950./T) * jno2)
    jno2 [1/s], T[K], RH [%]

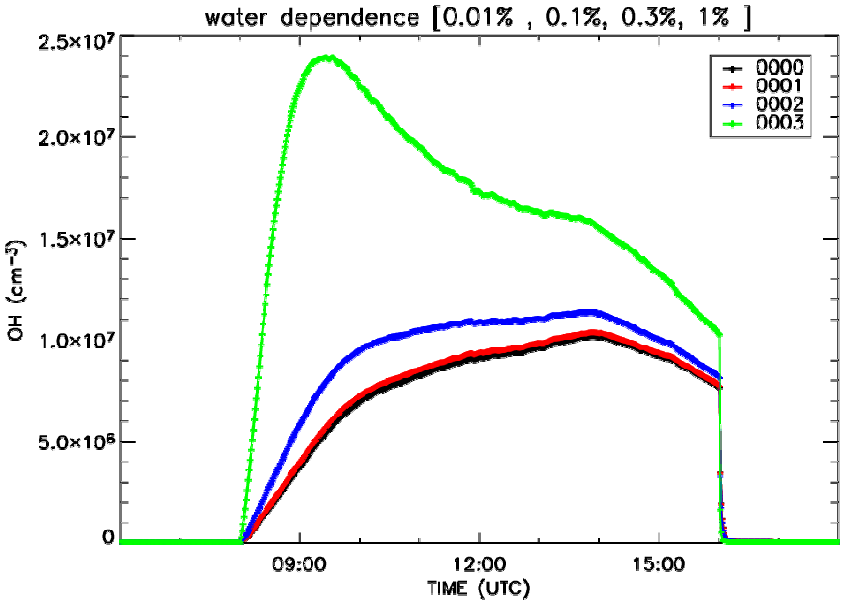
    (Rohrer et al., Atmos. Chem. Phys. Discuss., **4**, 7881-7915, 2004)

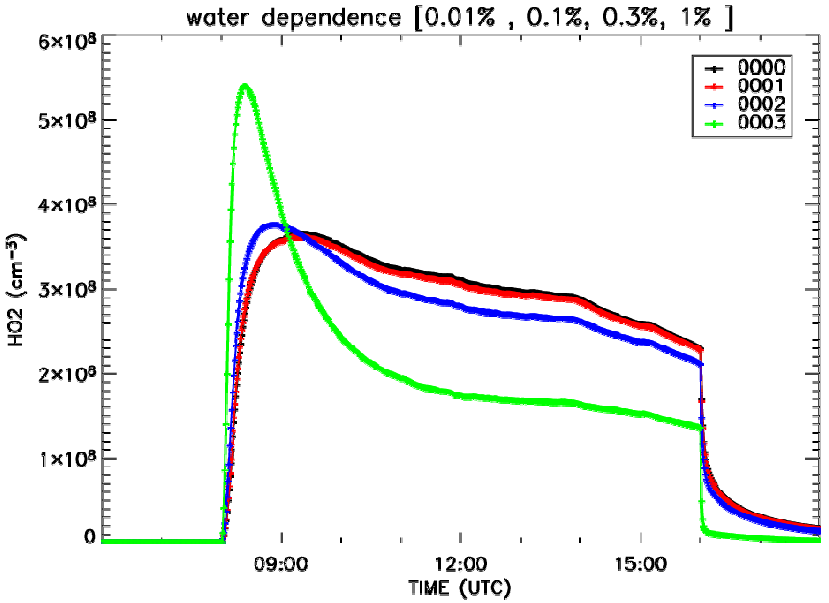
Model calculation (4): time

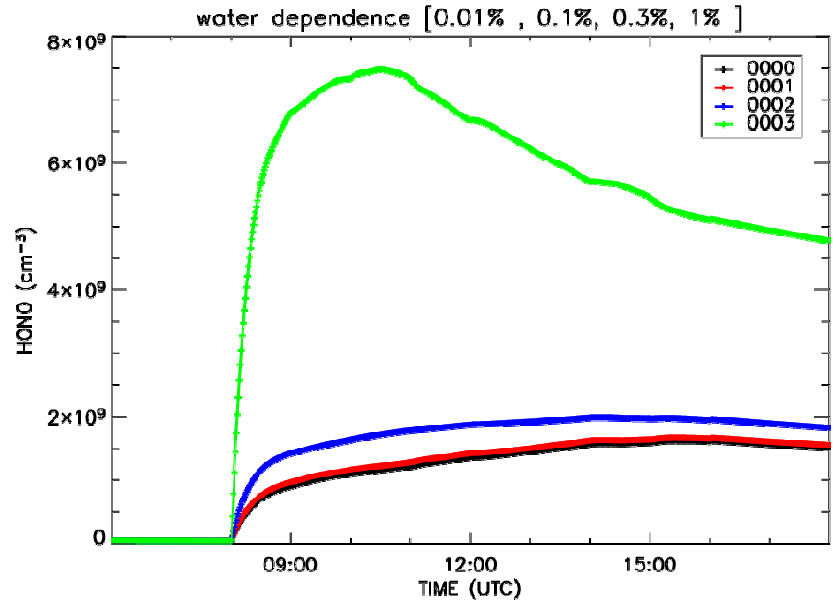
- **SAPHIR – Light modulation**
  1. **Light on** **8:00 -- 16:00**
  2. **Light on** **9:00, 11:00, 13:00, 15:00**
     Light off **10:00, 12:00, 14:00, 16:00**
- **SAPHIR CO – addition**
  1. **no CO**
  2. **CO + 240 ppb (10 min)** **10:20, 12:20, 14:20**

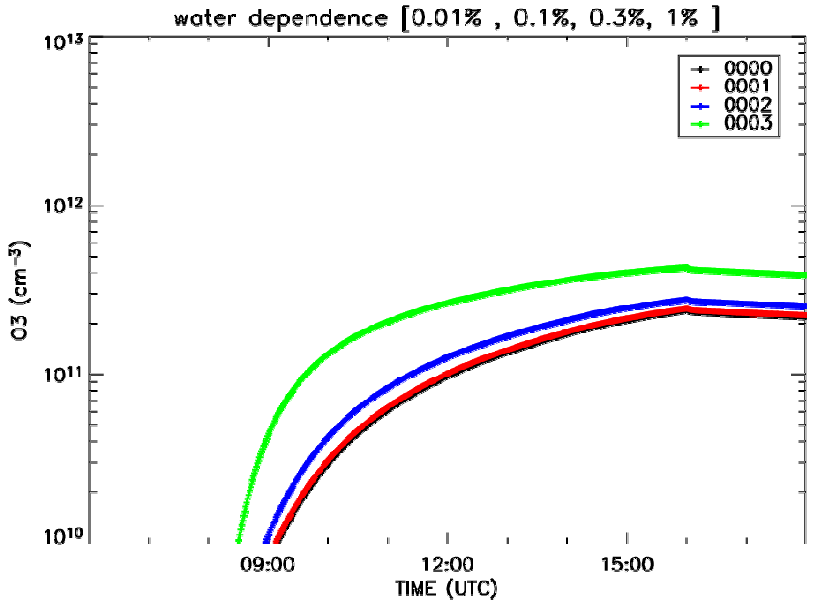


Base-Run, Light on, [O3]=0, [NO2]=0, f(H2O)

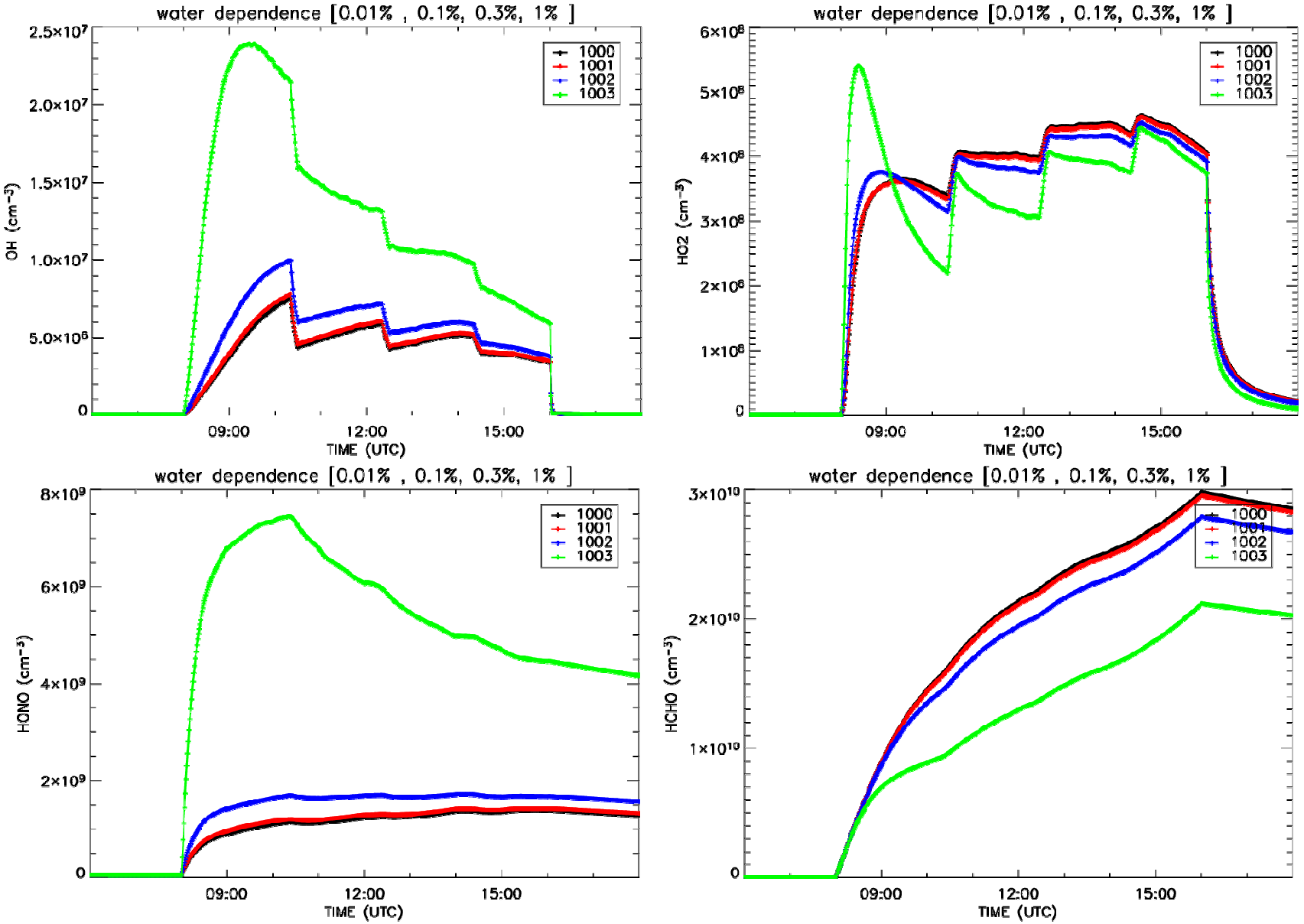




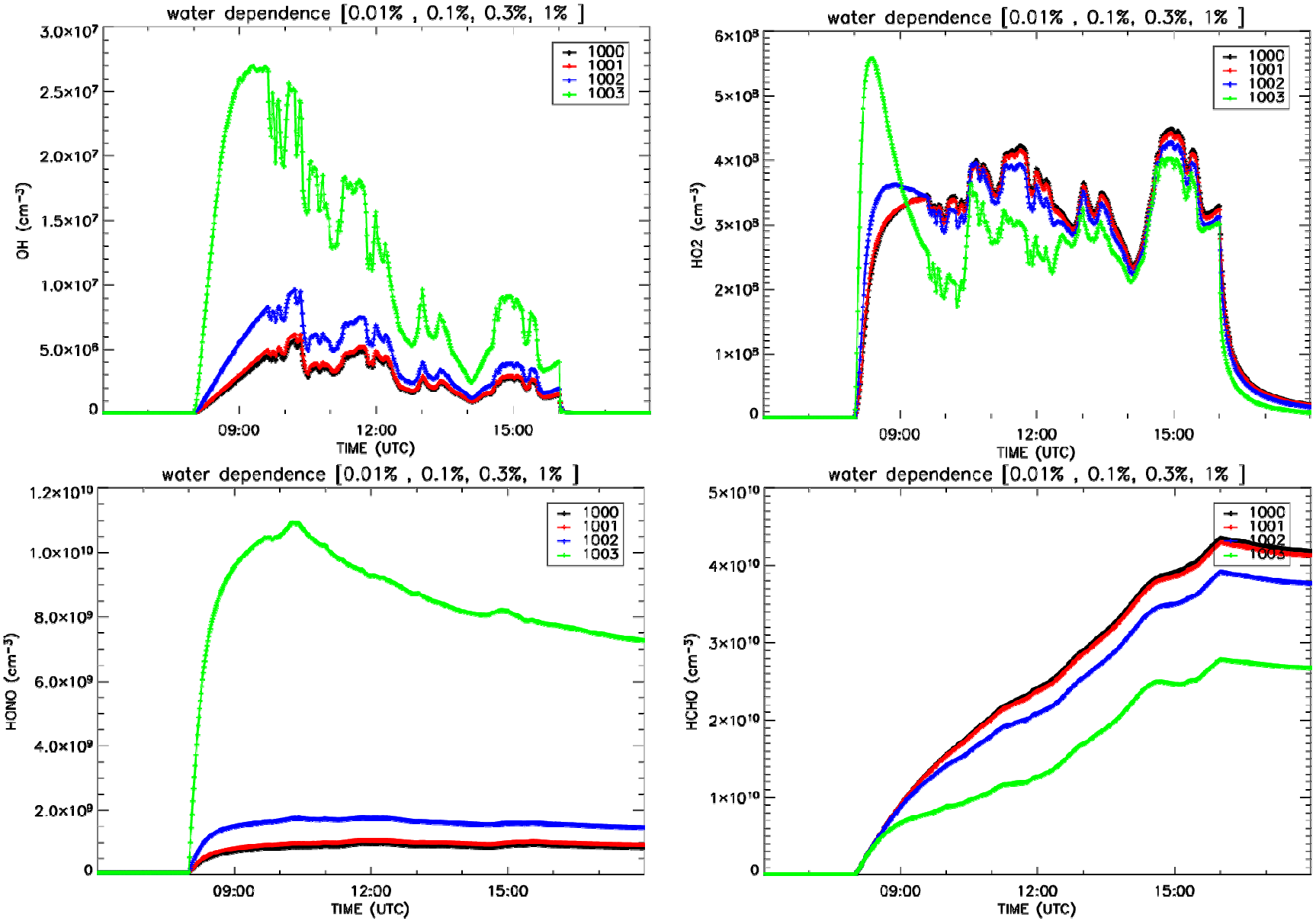




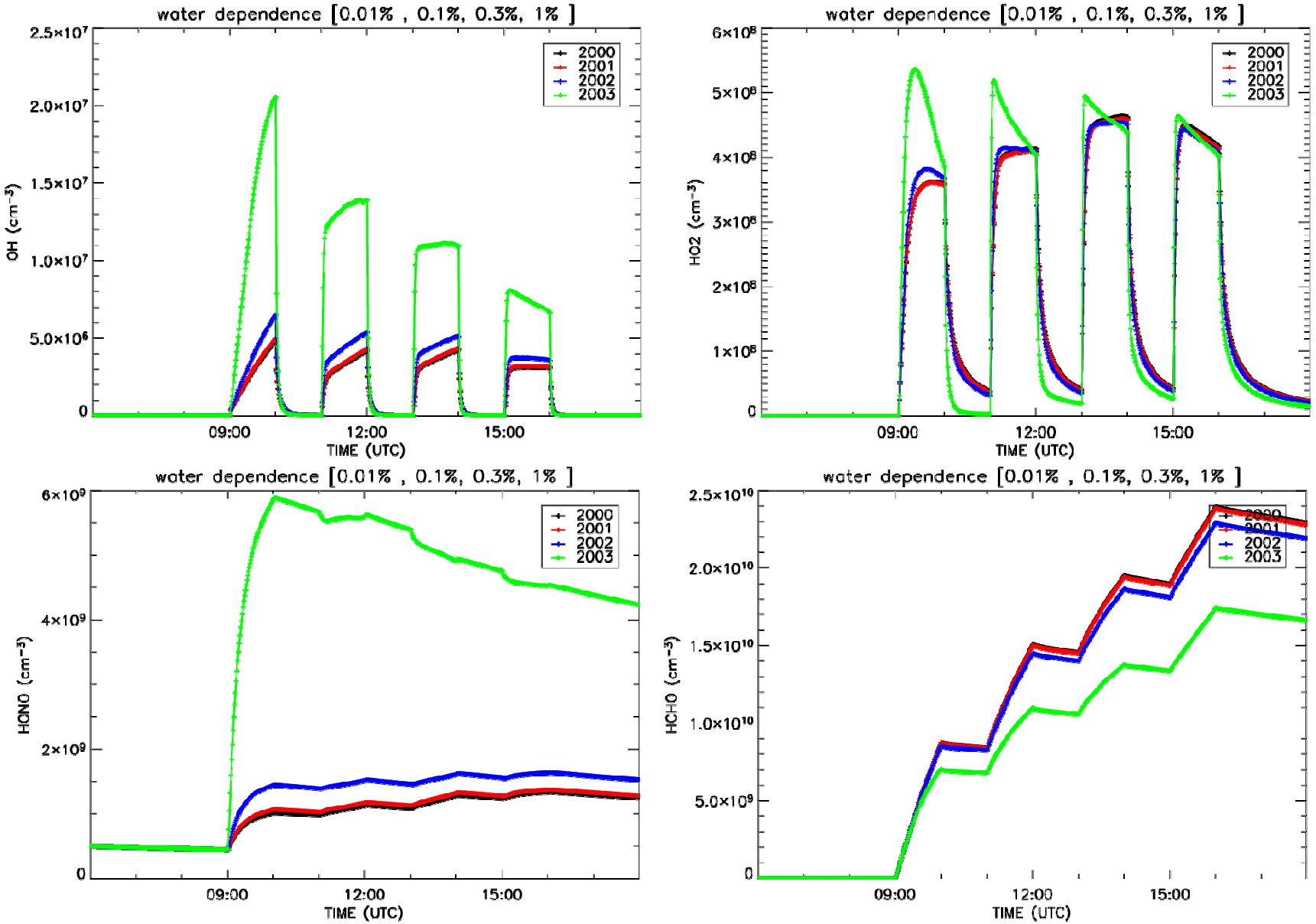
Light on, [O3]=0, [NO2]=0, f(H2O) + CO



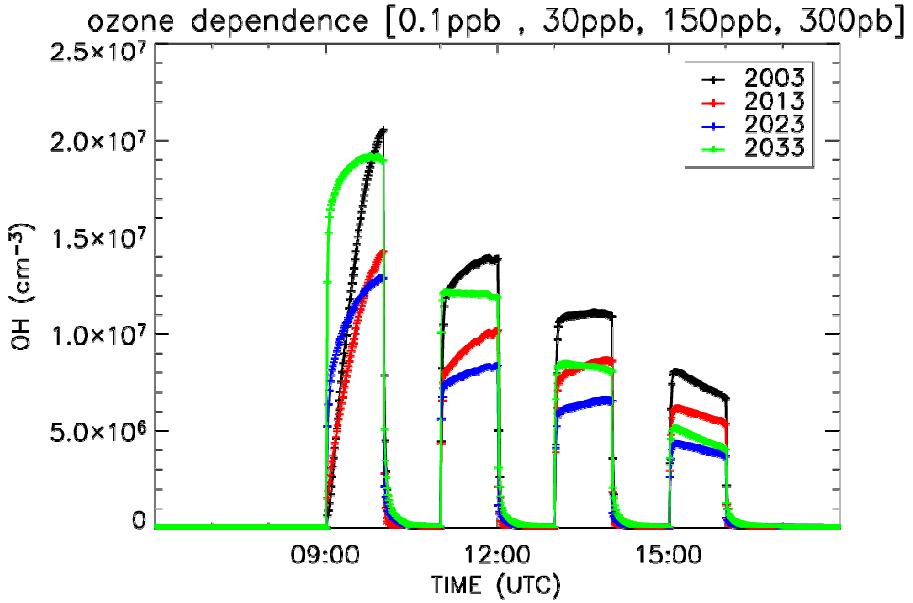
cloudy, Light on, [O3]=0, [NO2]=0, f(H2O)+CO

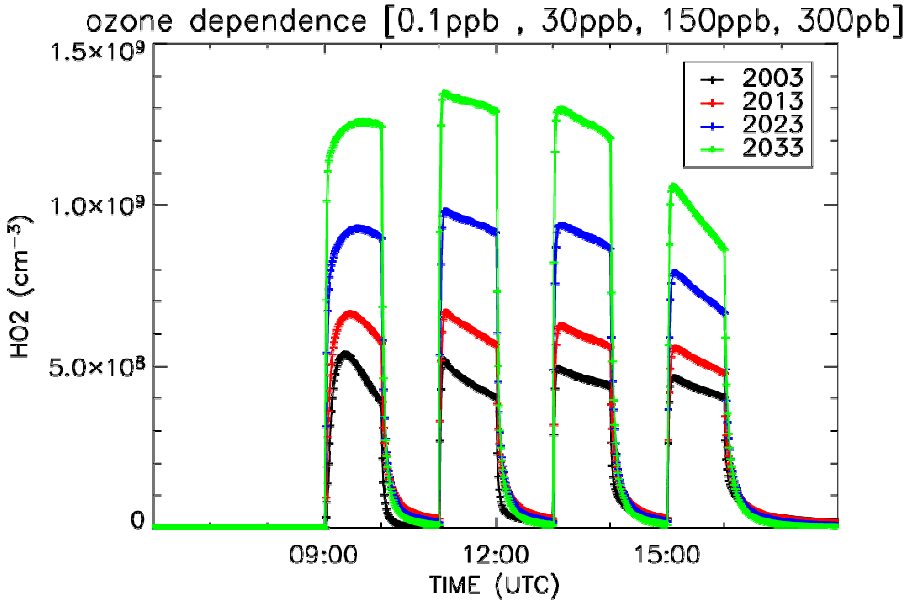


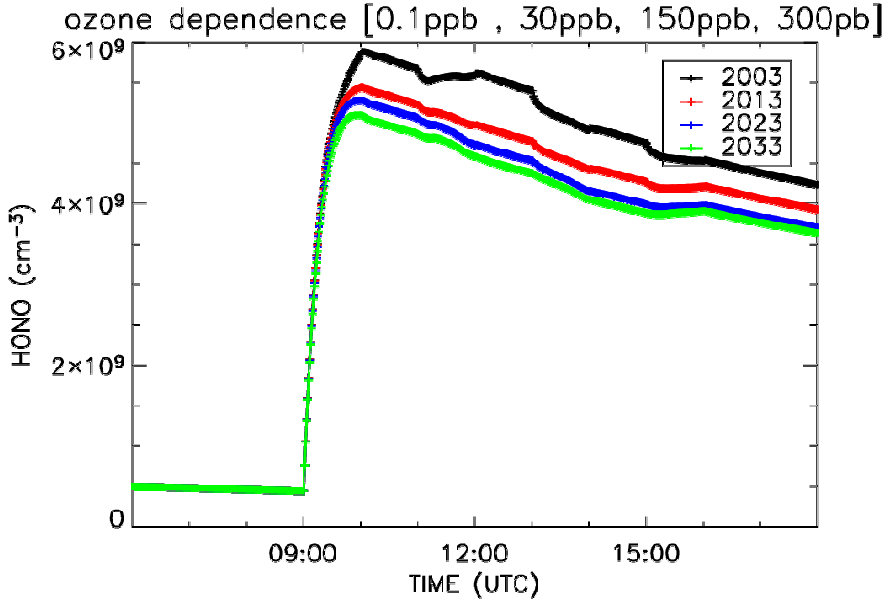
Light on/off, [O3]=0, [NO2]=0, f(H2O) + CO

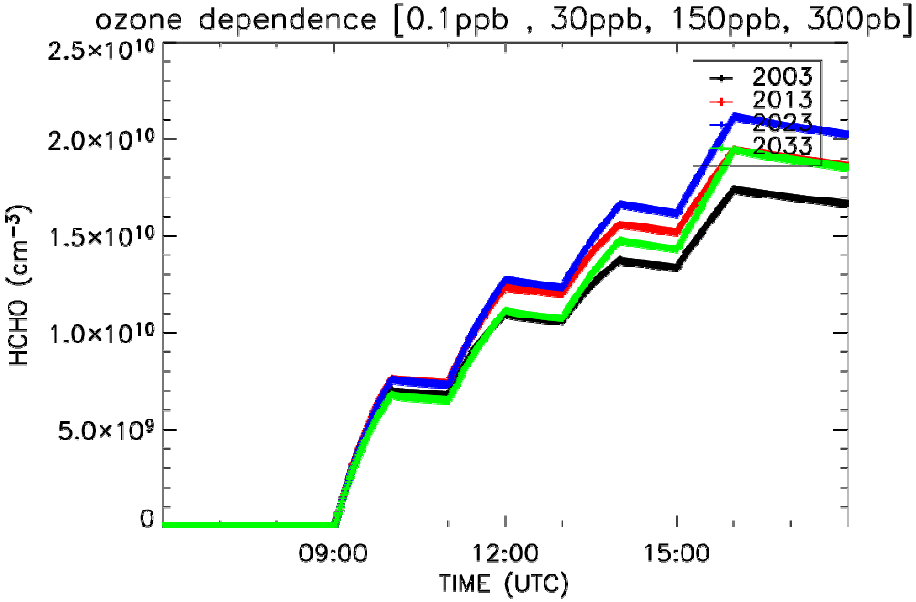


Light on/off, [NO2]=0, [H2O]=1%, f(O3)+CO









ENZ-Format

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9.9699E+009 107431625.0 234.00 1.2245E+007 1.1910E+006 7.7692E+011 9.3698E+009
107431906.0 234.00 1.1307E+007 1.2317E+006 7.5768E+011 1.0631E+010 107432218.0
134.00 1.1886E+007 1.2500E+006 7.0861E+011 1.2477E+010 107432396.0 134.00
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