Current Research in European Environmental Chambers: Measurements and Models

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contribution to International Conference
Atmospheric Chemistry Mechanisms
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Acknowledgements

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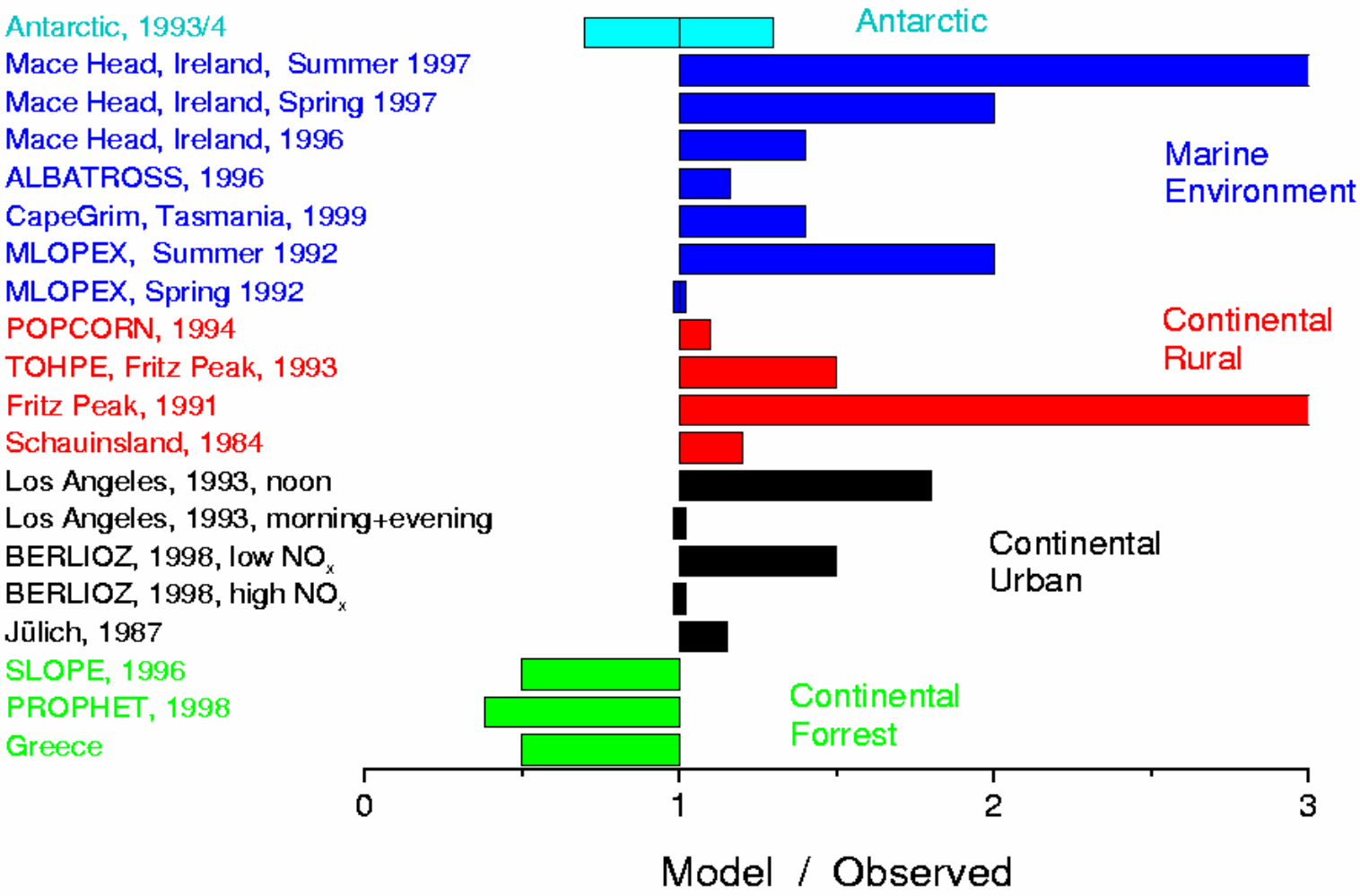
  - Rolf Häseler, Franz-Josef Johnen, Franz Rohrer, Hans-Peter Dorn, Jens Bossmeyer, Matthias Karl, Cornelia Richter, Birger Bohn, Andreas Wahner, ...
- **EUPHORE**, Valencia: Elena Gomez Alvarez, ...
- **MCM**, Leeds: Mike Pilling, Andrew Rickard, ...
- **EUROCHAMP:** Peter Wiesen and all other participants
- **Financial support**:
  - **BMBF: IDEC** (chamber results →chem. weather)
  - **EU: EUROCHAMP** (chamber related project)
  - **EU: ACCENT** (network of excellence: atmospheric composition and its change)
- **Organizers of this Conference**

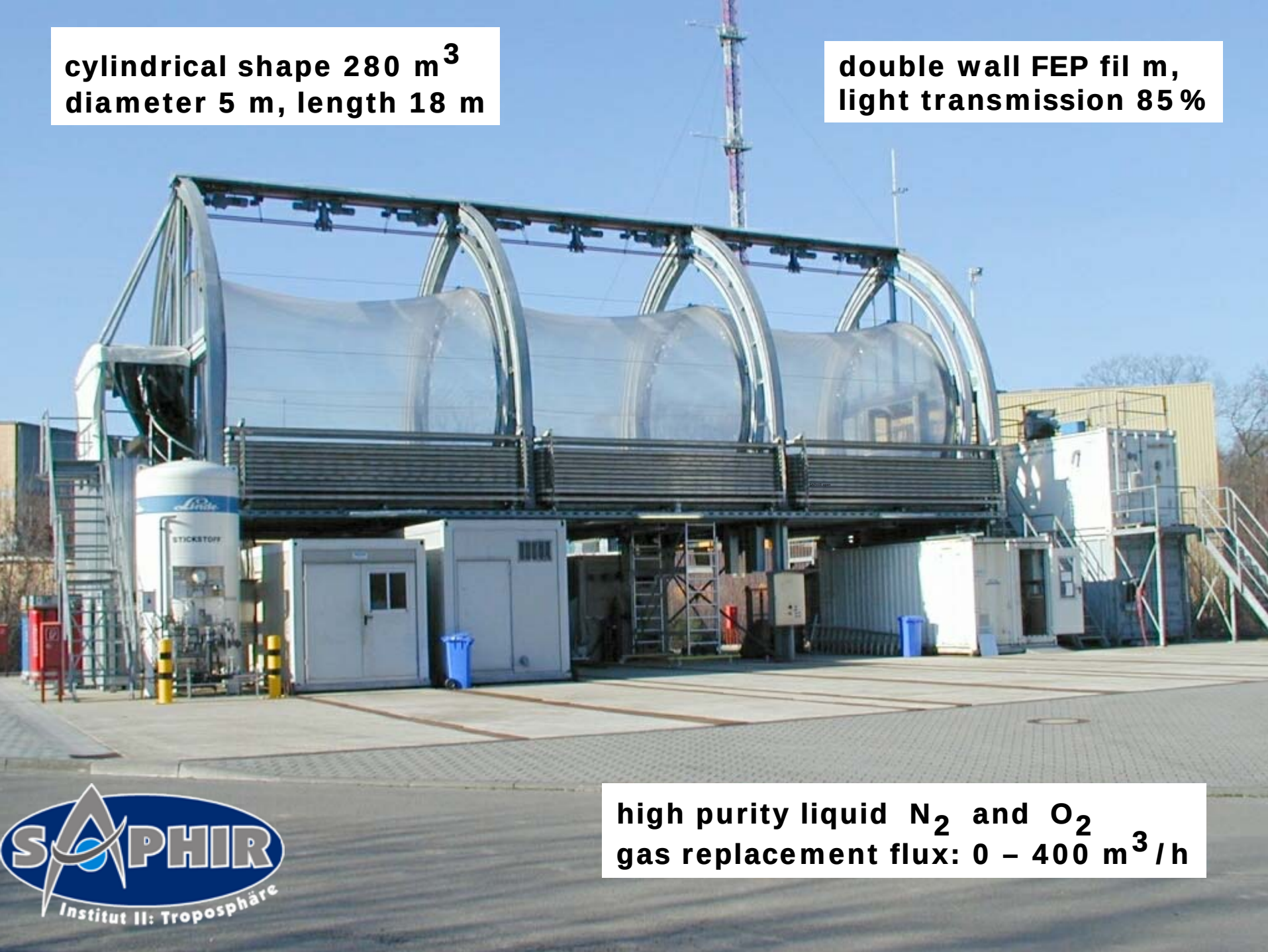
How good are tropospheric photochemistry models ?



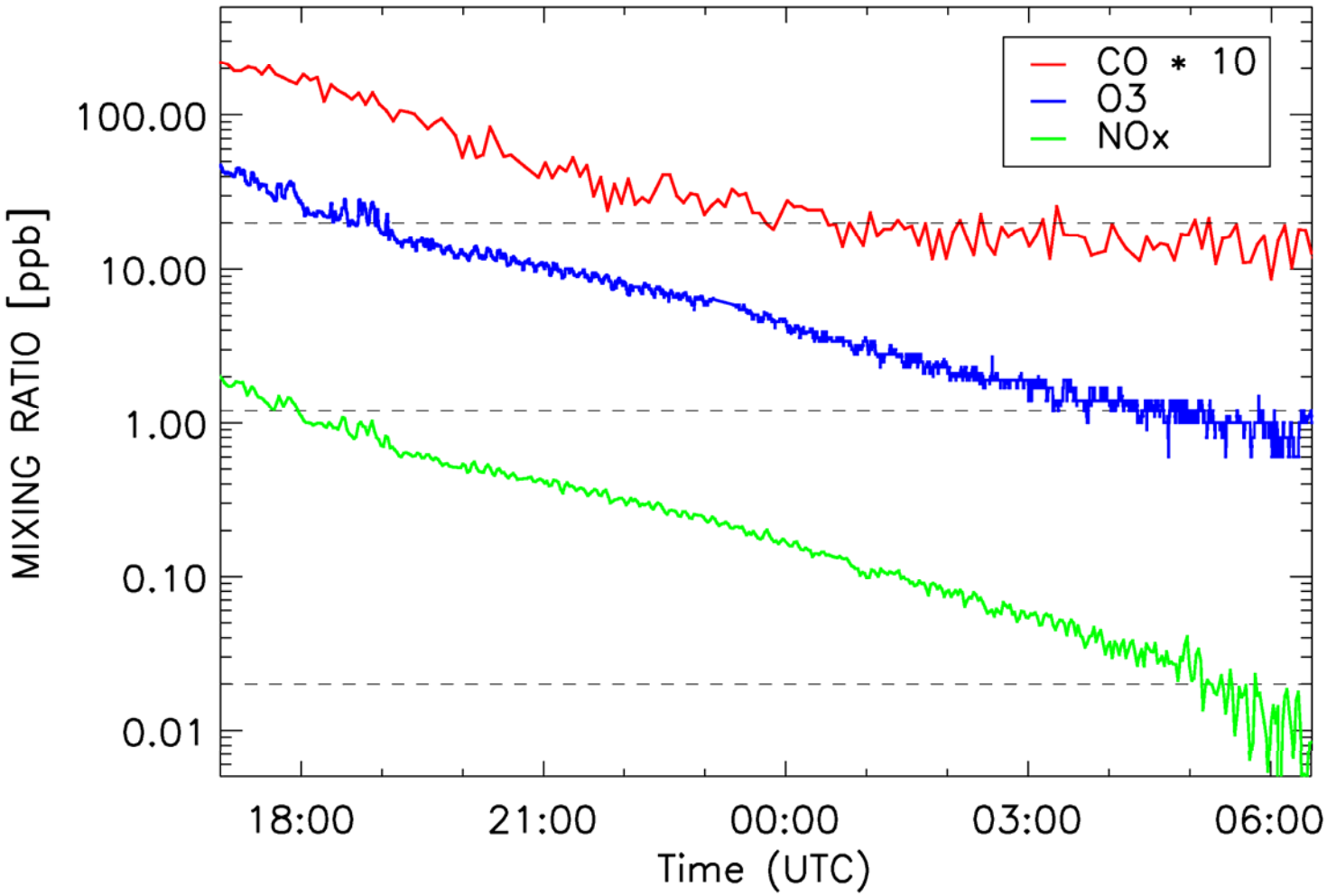
Outline

- Examples of gas phase experiments at SAPHIR and EUPHORE
  - ***comparison*** of mesurement and model
- Eurochamp, what is it good for ?
  - Quality of (chamber) measurements
  - Data base of experiments
- Summary

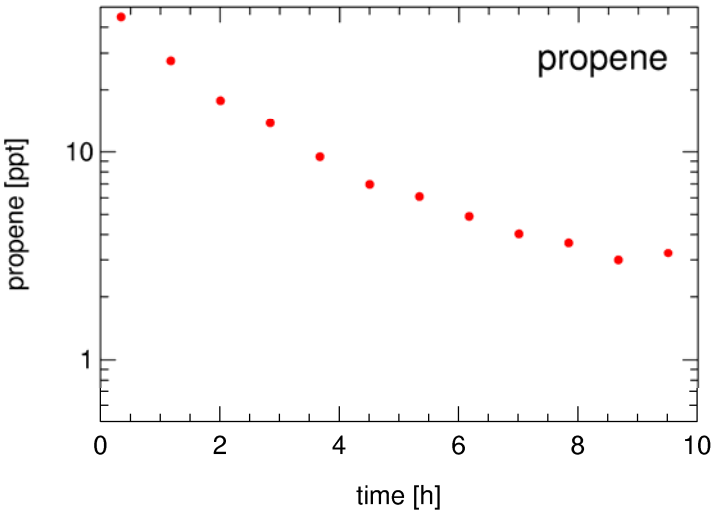

SAPHIR closed

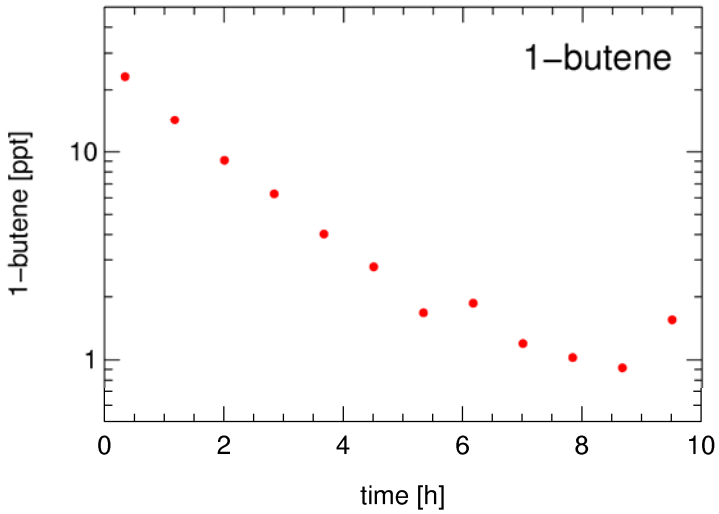

cylindrical shape 280 m3
diameter 5 m, length 18 m
double wall FEP fil m,
light transmission 85%
high purity liquid N2 and O2
gas replacement flux: 0 – 400 m3/h
SAPHIR
Institut II: Troposphäre

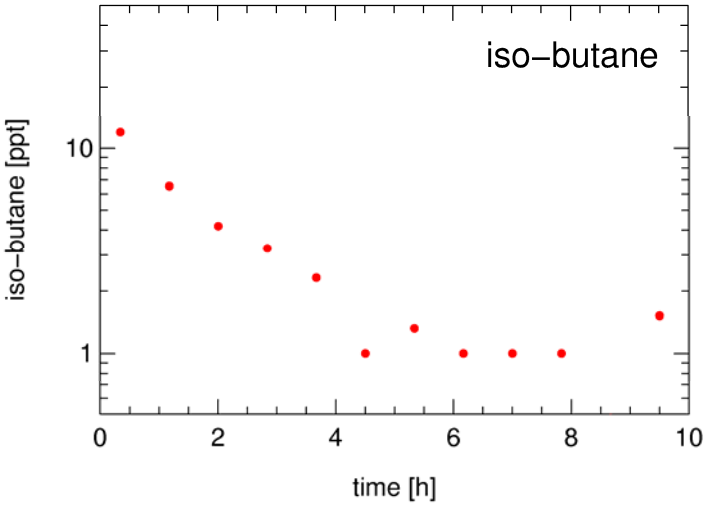
Trace gas mixing ratios during purging the SAPHIR chamber (1)



Trace gas mixing ratios during purging the SAPHIR chamber (2)



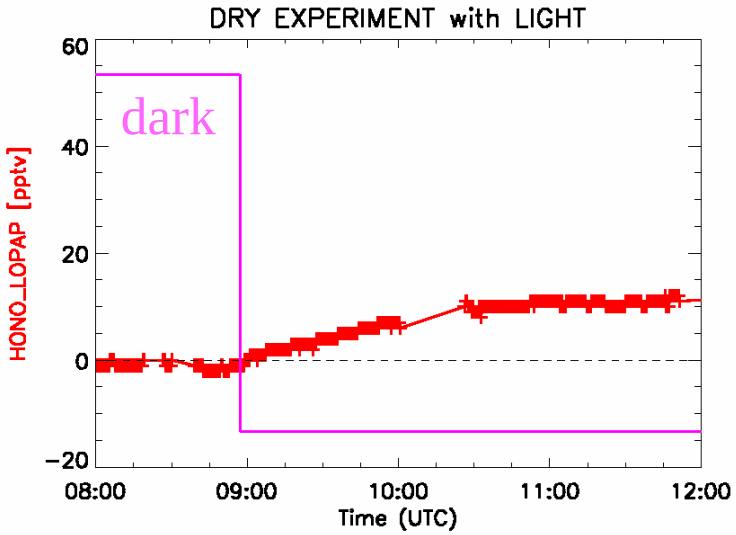


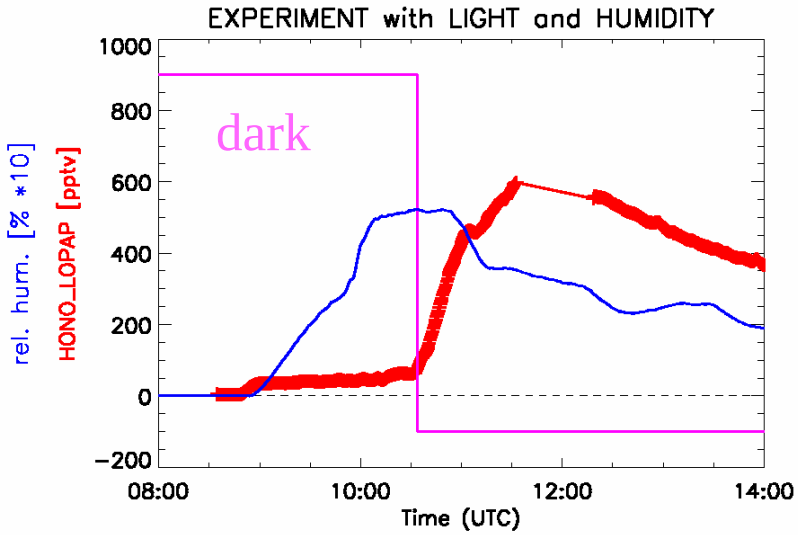


excellent gas purity
all HC < 10 ppt
(det. limit 5...10 ppt)

reproducable levels of trace gases after purge

HONO formation in clean air





- dependence only on $J(NO_2)$, temperature, and relative humidity
- $P(HONO) = a \times J(NO_2) \times (1+(rh/rh_0)^2) \times \exp(T/T_0)$
- parameters constant (± 10 %) since 1 year (chamber specific)
- published Rohrer et al., Atmos. Chem. Phys., 2005

Isoprene reaction with OH and ozone: kinetics and mechanism

Isoprene important trace gas, major biogenic source of HC

Isoprene concentrations inside SAPHIR depend on 3 processes

1. ISO + O3 → products
2. ISO + OH → products
3. ISO dilution by clean air supply

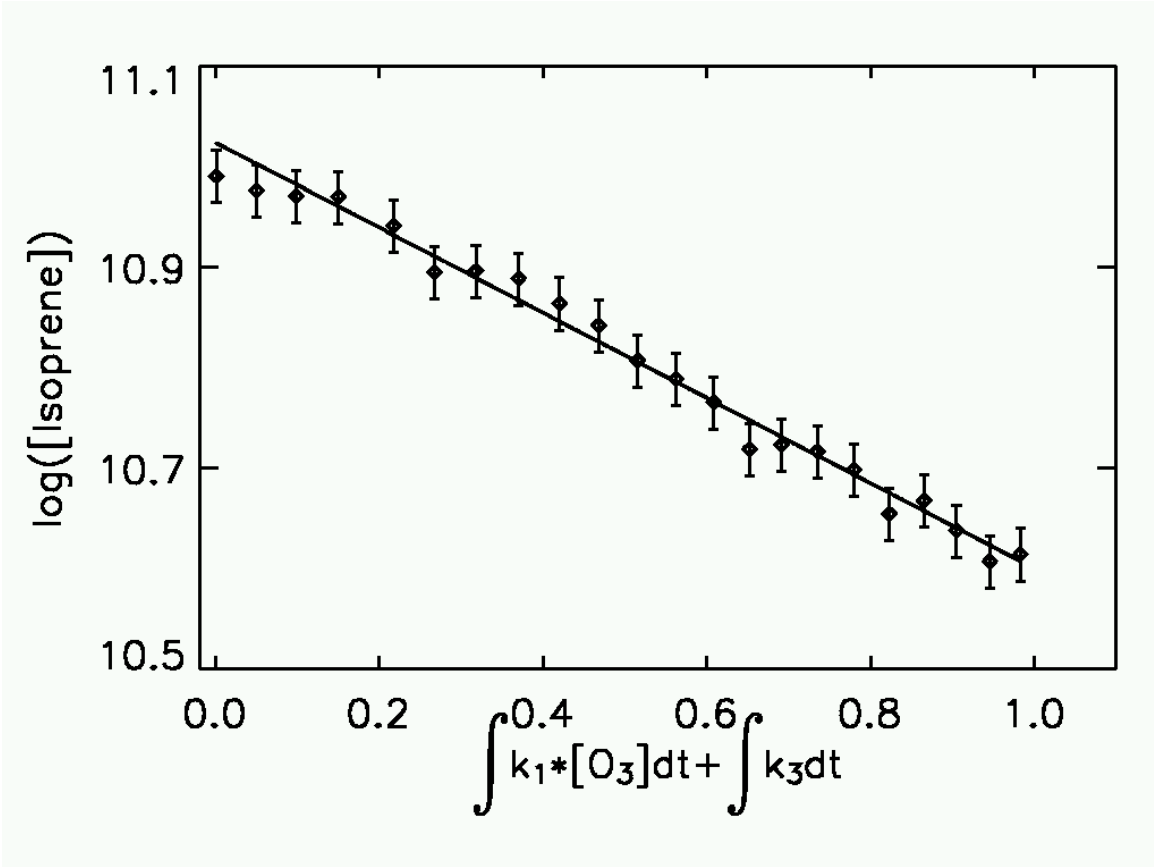
Experiment design:

simultaneous measurements of isoprene, MVK, MACR, ozone, OH, dilution air supply flow, and physical parameters

Karl et al., 2004, **Geophys. Res Lett.** (kinetics)

Karl et al., 2006, **J. Atmos. Chem.** (mechanism)

Isoprene reaction with OH and ozone determination of k(ISO+O3)



500 ppm CO added

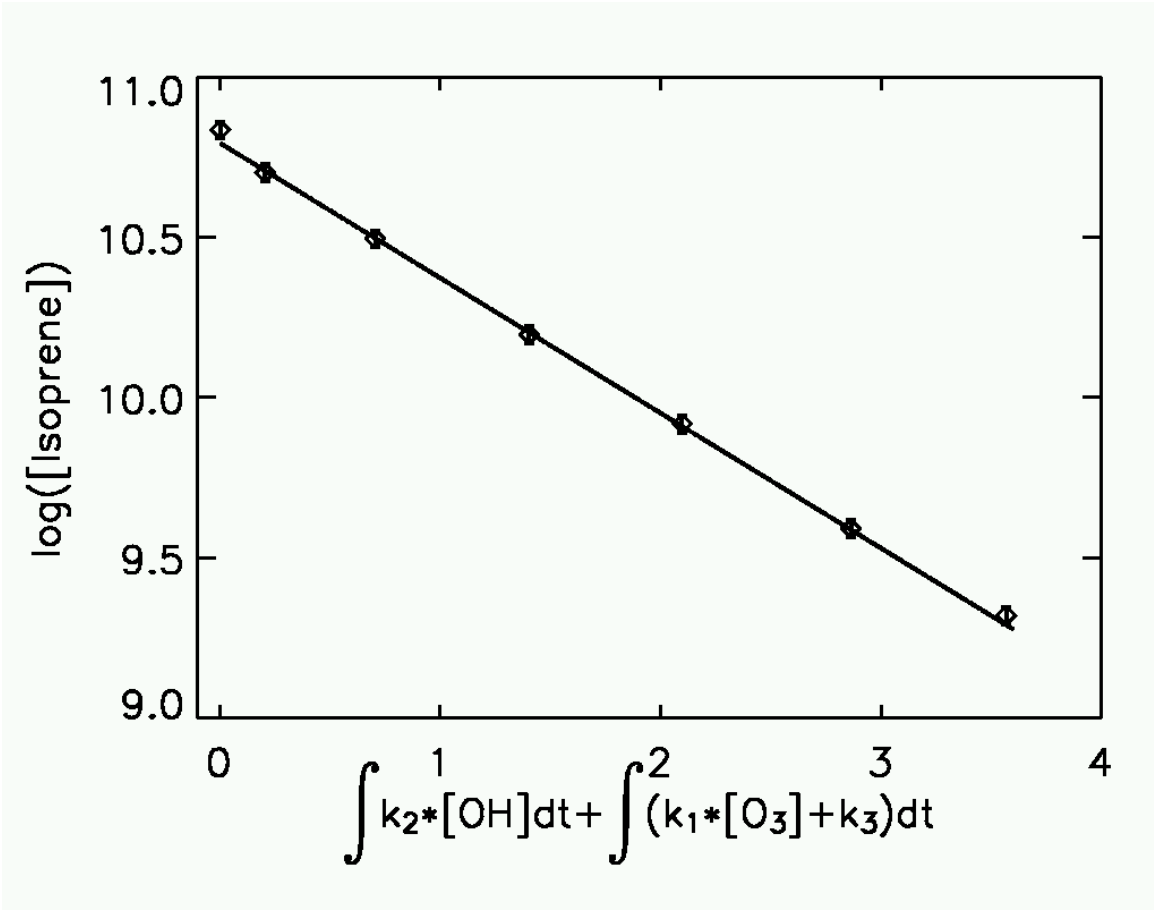
→no OH present

Result:

$k=(9.6\pm0.7)\times10^{-18}$ cm^3s^{-1}

(-2% compared to recommendation Atkinson [1994])

Isoprene reaction with OH and ozone determination of k(ISO+OH)



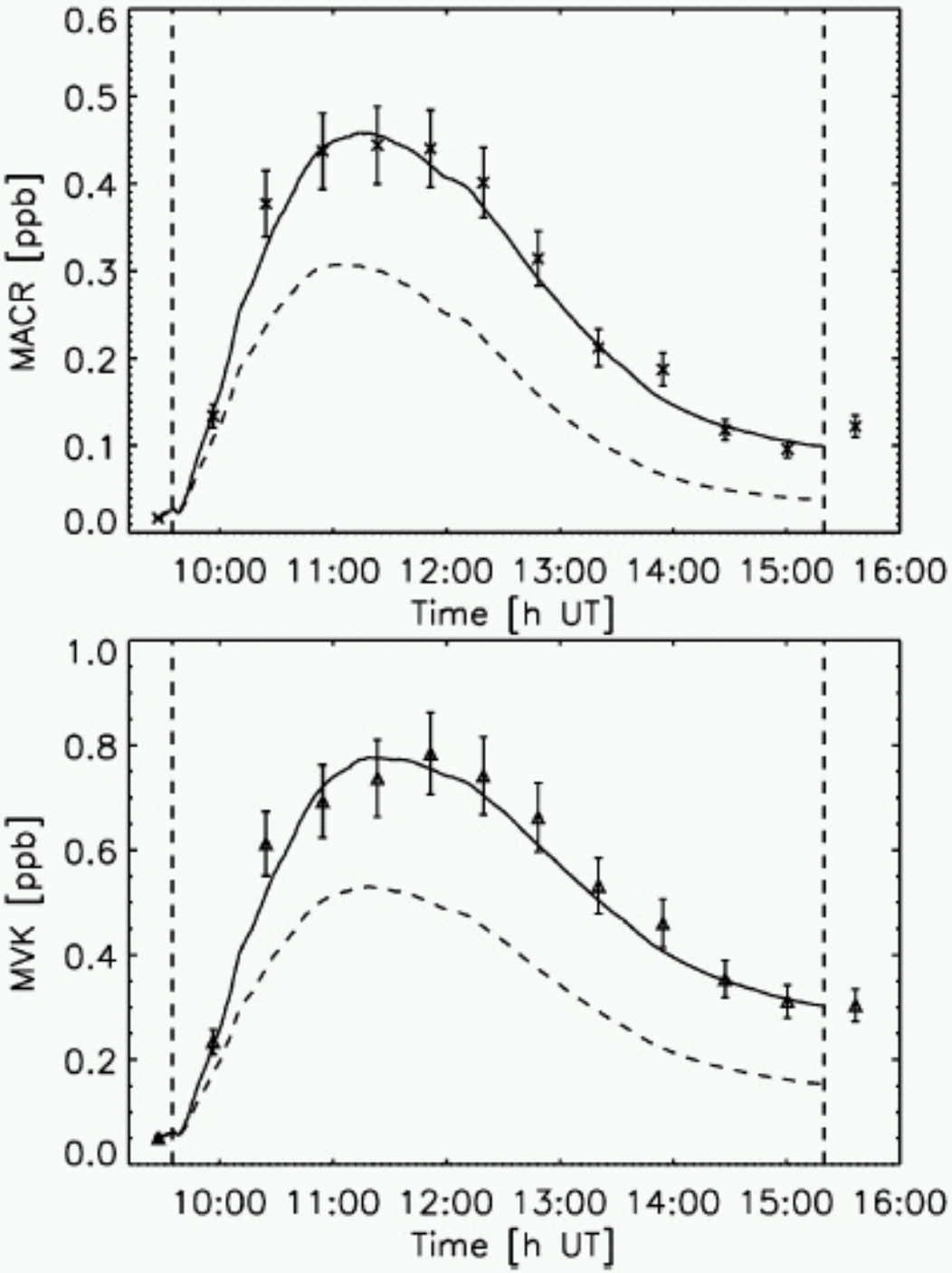
OH and ozone present

Result:

$k=(10.0\pm1.2)\times10^{-11}$ cm^3s^{-1}

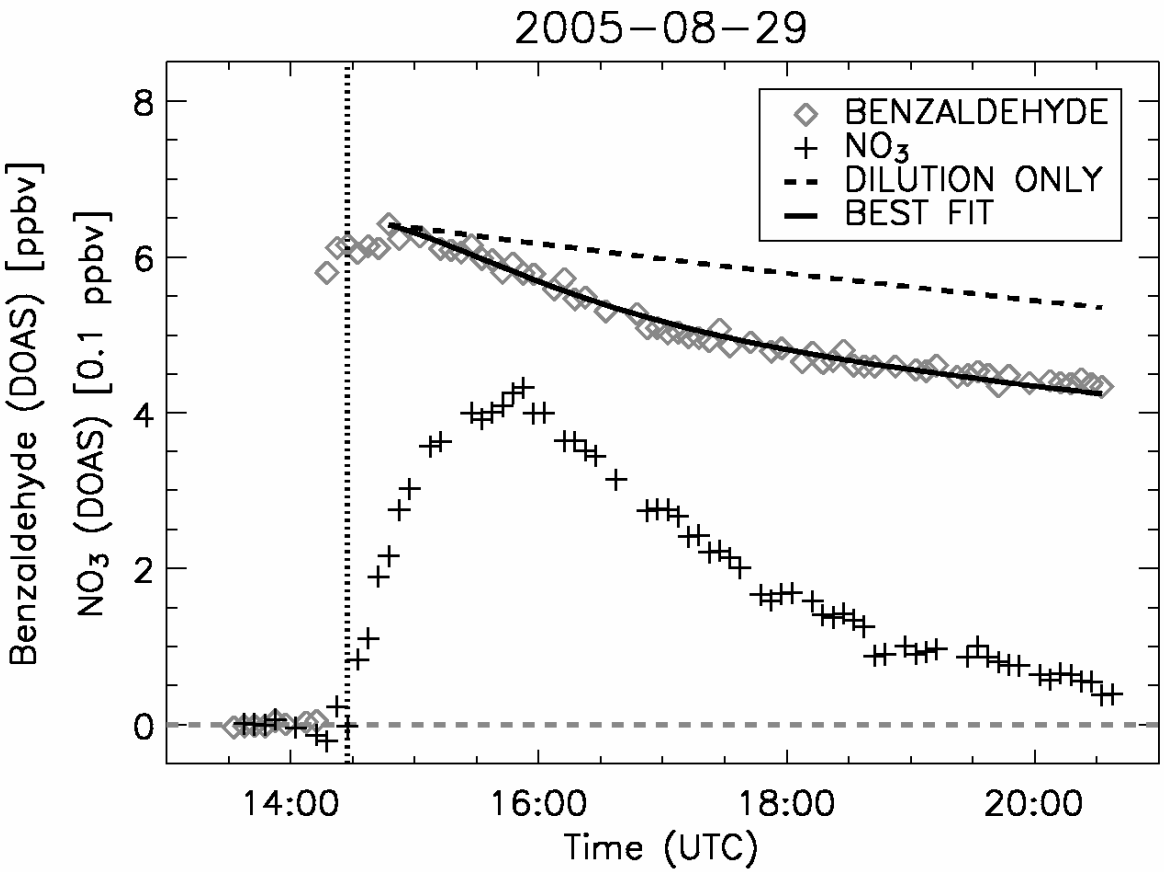
(in agreement with recommendation Atkinson [1994])

Fig. 2 Comparison of measured and modelled carbonyl product mixing ratios. A model run using values of product yield and rate coefficient for the oxidation of the respective carbonyl with OH taken from MCM (dashed line) is not able to describe the observations. Comparing the measurements with the model run using best-fit values for the parameters from χ^2-minimization, the agreement becomes very satisfactory (solid line). Upper panel shows MACR mixing ratios and lower panel shows MVK mixing ratios for experiment C (see Table 3). Measurements are displayed as crosses (MACR) and triangles (MVK), error bars denote 1–σ standard deviation of the measurements. Vertical bars indicate times when the chamber was opened and closed.



from Karl et al, 2006

absolute rate constant of NO3 + benzaldehyde



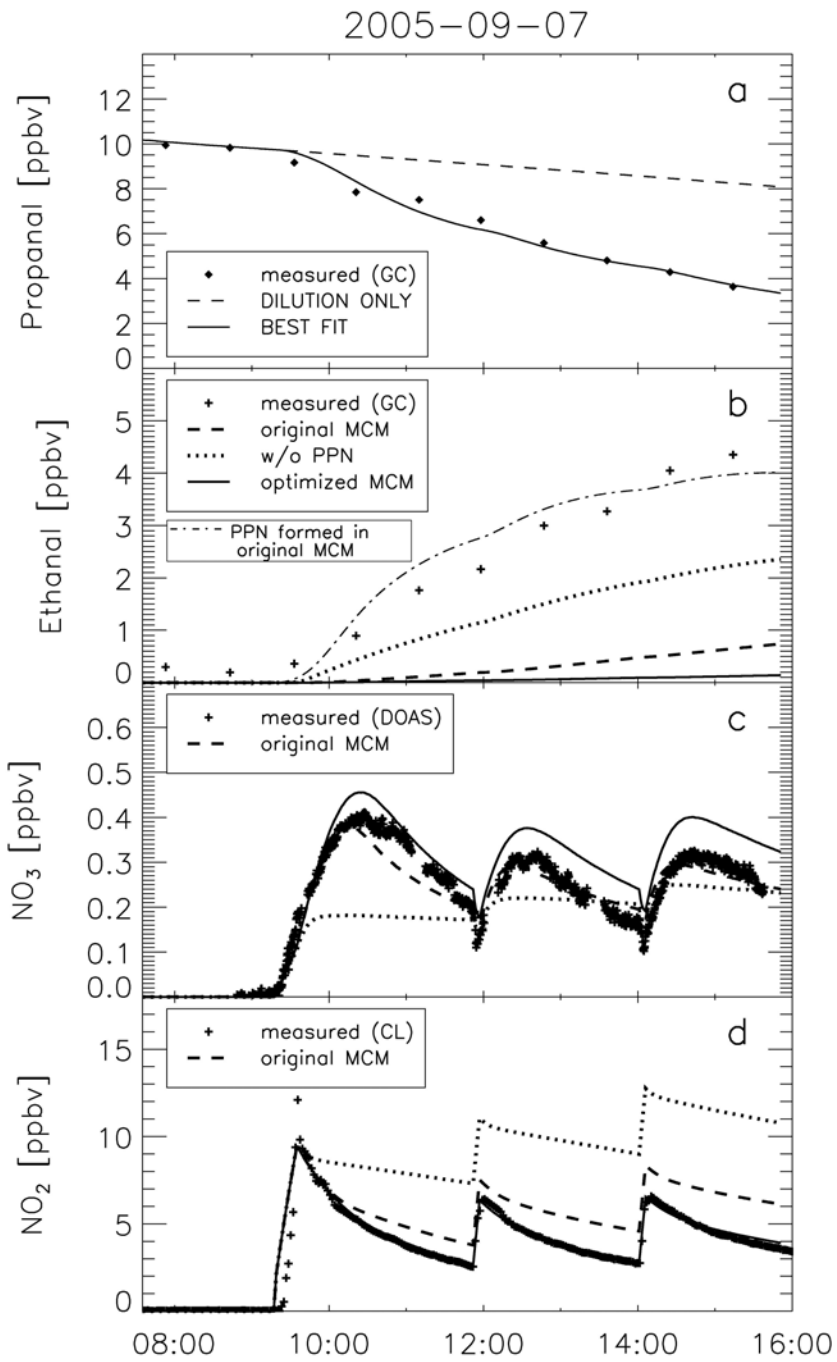
Bossmeyer et al., 2006
Geophys. Res. Lett.
2.2±0.6

Atkinson et al., 1991
J. Phys. Chem. Ref. Data
2.6±0.1

Clifford et al., 2005
J. Photochem. Photobio.A
4.3±0.3

(all in $10^{-15}cm^3s^{-1}$)

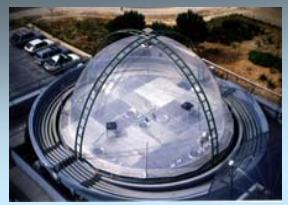
NO3 + propanal



a: fit to measured propanal for determination of absolute rate

b, c, d: measured NO3, NO2, and ethanal (3rd step product of NO3 + propanal reaction)

different models applied to explain the measured concentrations, see discussion in Bossmeyer et al., GRL, 2006



EUPHORE
(EUropean PHOto REactor)

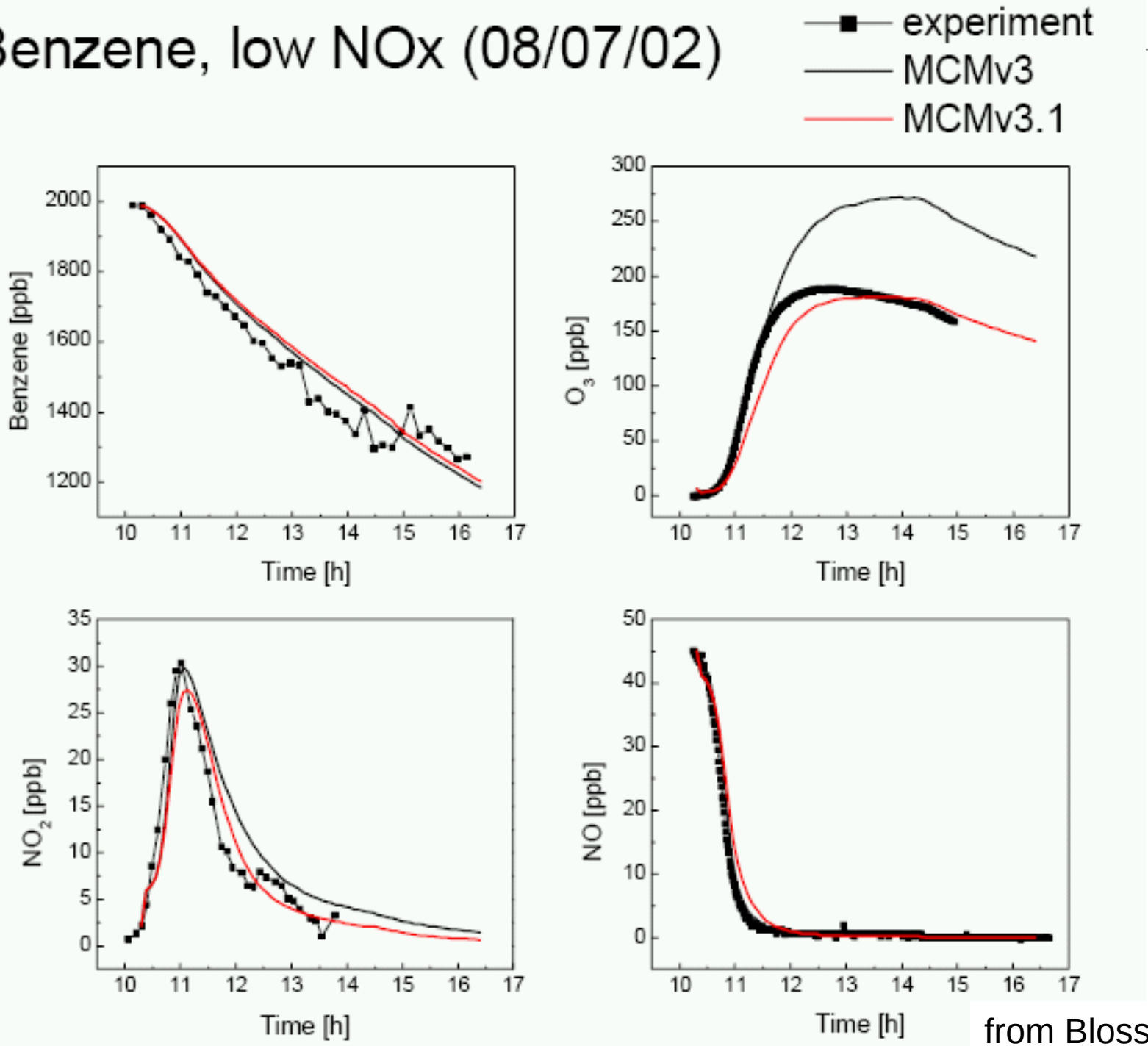
CEAM
FUNDACIÓN CENTRO DE ESTUDIOS AMBIENTALES DEL MEDITERRÁNEO

Half-spherical FEP covers each 200 m³ volume
Cooled floor
Air purification
Fan for homogenisation
Natural sunlight (>290nm)

Testing MCM vs. Euphore chamber

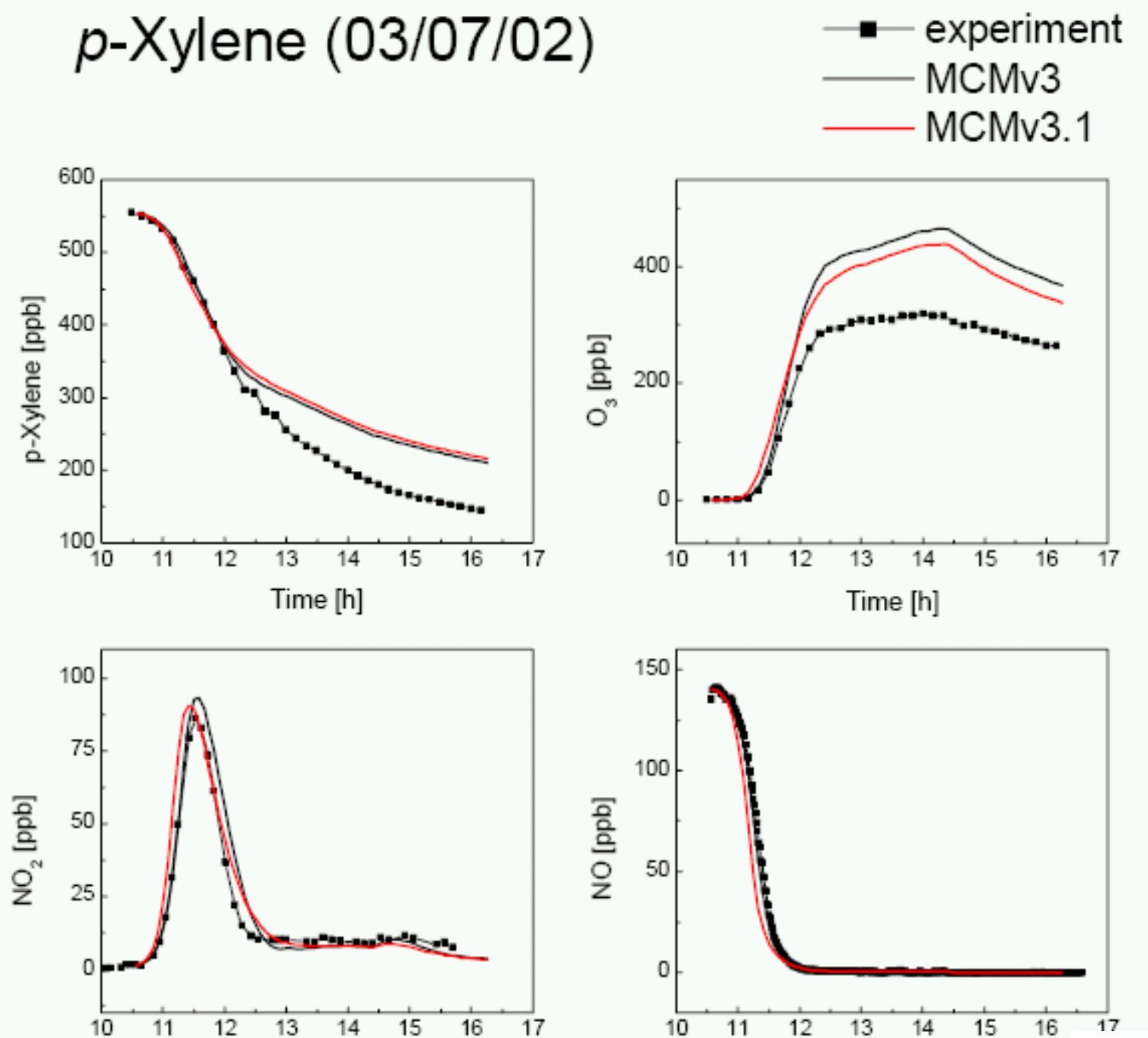
- **EUPHORE** has a key influence in the improvement of the Master Chemical Mechanism
- **Saunder et al.:** Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161-180, 2003
- **Bloss et al.:** Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data. Atmos. Chem. Phys., 5, 623–639, 2005

Benzene, low NOx (08/07/02)



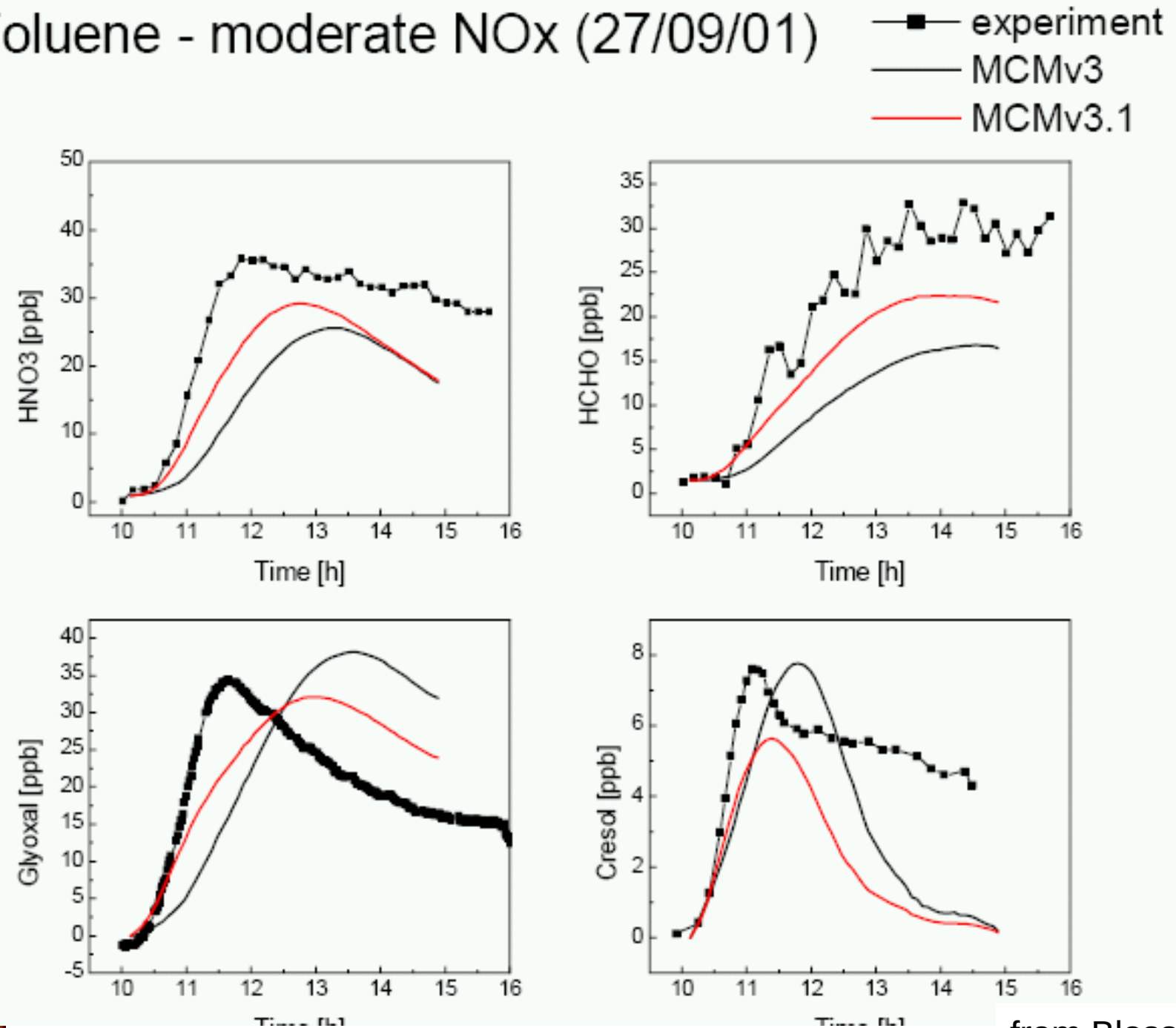
from Bloss et al, 2005

p-Xylene (03/07/02)



from Bloss et al, 2005

Toluene - moderate NOx (27/09/01)



from Bloss et al, 2005

AIDA chamber

Aerosol chamber at PSI, Villigen

SAPHIR

EUPHORE

Eurochamp overview

- **12 European laboratories with different environmental chambers**
  - CEAM, Valencia: 2 large (200 m³) outdoor (EUPHORE)
  - FZJ, Jülich: 2 large (270 m³), dark and outdoor (SAPHIR)
  - FZK, Karlsruhe: 80 m³, temperature controlled (AIDA)
  - PSI, Villigen: mid-size 30m³, aerosol
  - BUW, Wuppertal: several dedicated (1 m³)
  - CNRS, Paris: new, aerosol (4 m³)
  - CNRS, Orleans: photo reactor (7 m³)
  - SP, Boras: small size (1 m³), indoor pollution
  - JRC, Ispra: several (2-3 m³), aerosol
  - UCC, Cork: photo chemistry (4 + 6 m³)
  - Univ. Bayreuth: aerosol, kinetics (3 + 4 m³)
  - Univ. Leeds: **modeling** of chamber experiments
- **Overview with detailed data on all chambers:**
  - **http://saphir.fz-juelich.de/eurochamp/ ... table**

Eurochamp Networking Activities

- **Raw Data Analysis, Data intercomparison, and Quality Assurance**
  - **Well documented datasets:**
    - traceable (from measured quantity to *public* raw data)
    - accuracy (calibration)
    - precision (random noise, short term fluctuations..)
  - **Instrument intercomparison**
    !!! helps chamber and field research !!!
  - **Chamber intercomparison**
    - **what is the appropriate chamber for the problem ?**
- **Database of chamber experiments**

Means of quality assurance in chamber research

- **Standard experiments (quality of chamber)**
  - **Definition:**
    repeated experiment under well defined conditions
  - long series in SAPHIR, EUPHORE, PSI, AIDA
- **Instrument intercomparison (quality of instruments)**
  - **Definition:**
    typical chamber experiment with different instruments measuring the same quantity
  - performed / planned in SAPHIR, EUPHORE, PSI, AIDA
  - on: HONO, OVOC, OH, HCHO, aerosol
- **Chamber characterization (transfer of experiments)**
  - **Definition:**
    parameterization of chamber properties based on observations
  - SAPHIR: HONO source parameterization, applied to EUPHORE, PSI

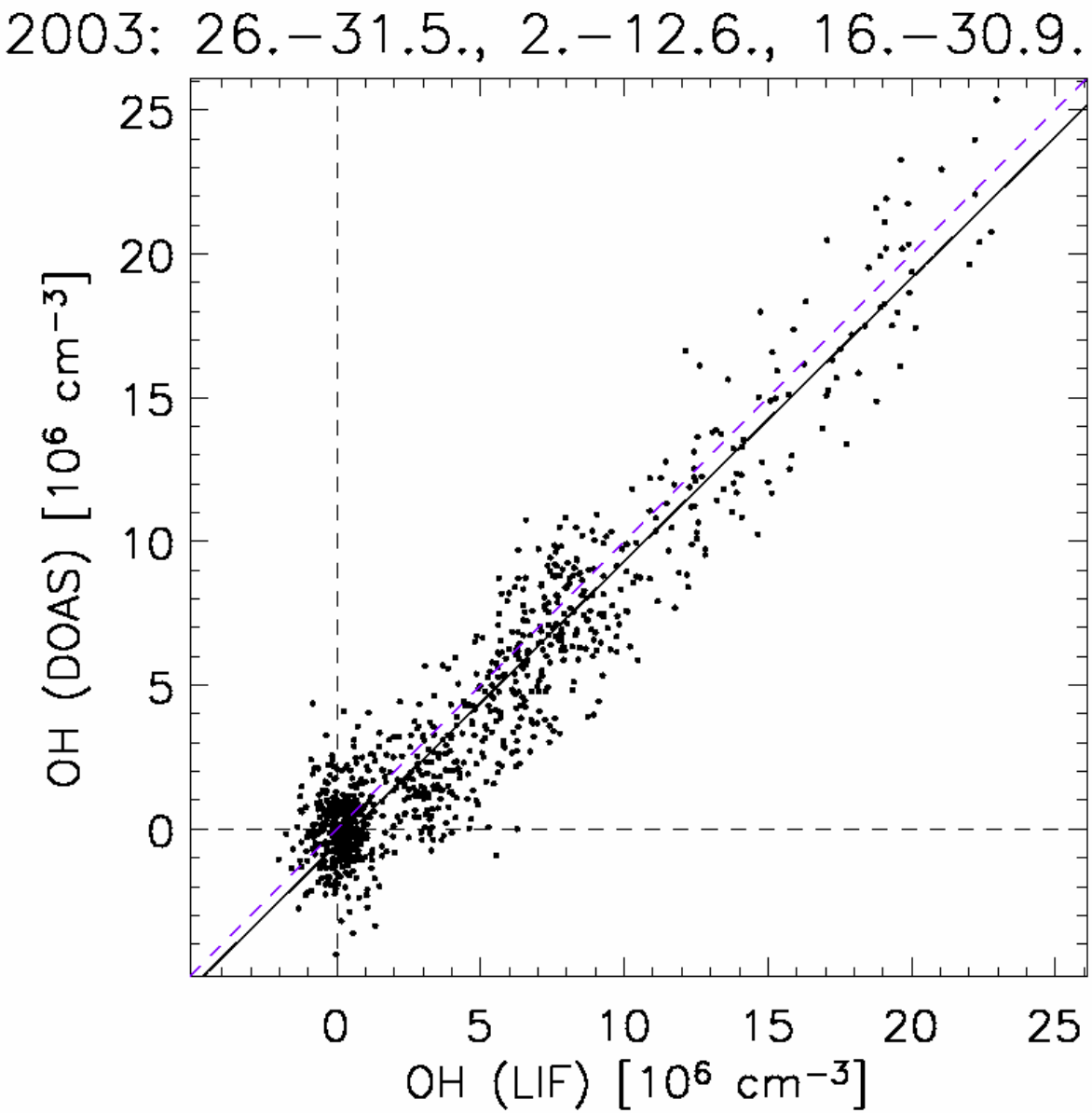
Intercomparison of instruments

- Guidelines for meaningful instrument intercomparisons in chamber experiments
- Documentation of the conditions of the chamber, the instruments , and the supporting parameters
- Definition of the measurement errors:
  separate precision (i.e. noise) and accuracy (calibration) in order to enable meaningful statistical tests
- Example OH intercomparison
  - slope depends on error of both instruments
  - linear or not depends on chi^2
  - This data set was rejected since other parameters of the instruments (laser power) were not clearly documented..
- Instrument intercomparison activity (field and chamber) will take place within ACCENT. Co-ordination of EUROCHAMP activities with ACCENT activities.

Instrument intercomparisons at SAPHIR in Jülich

- **2003**: OH: LIF vs. DOAS
- **2005**: OH and HO2
  formal multi instrument comparison
  - LIF, DOAS, CIMS, ESR
  - MPI, DWD, TMU, ULeeds, FRCGC, FZJ
- **2005**: OVOCs
  formal multi instrument comparison
  - GC, PTR-MS, DOAS
  - UInns, ULeic, UBrist, UYork, CEAM, FAL, FZK, EMPA, NILU, IfT, FZJ
- **2007**: NO3 and N2O5
  - LIF, DOAS, CIMS, CRDS, CE-DOAS, ….
  - UCB, NOAA, TMU, ULeicester, GTech, UCC, UHD, FZJ, …

Informal OH intercomparison at SAPHIR



FITEXY: y = a + bx

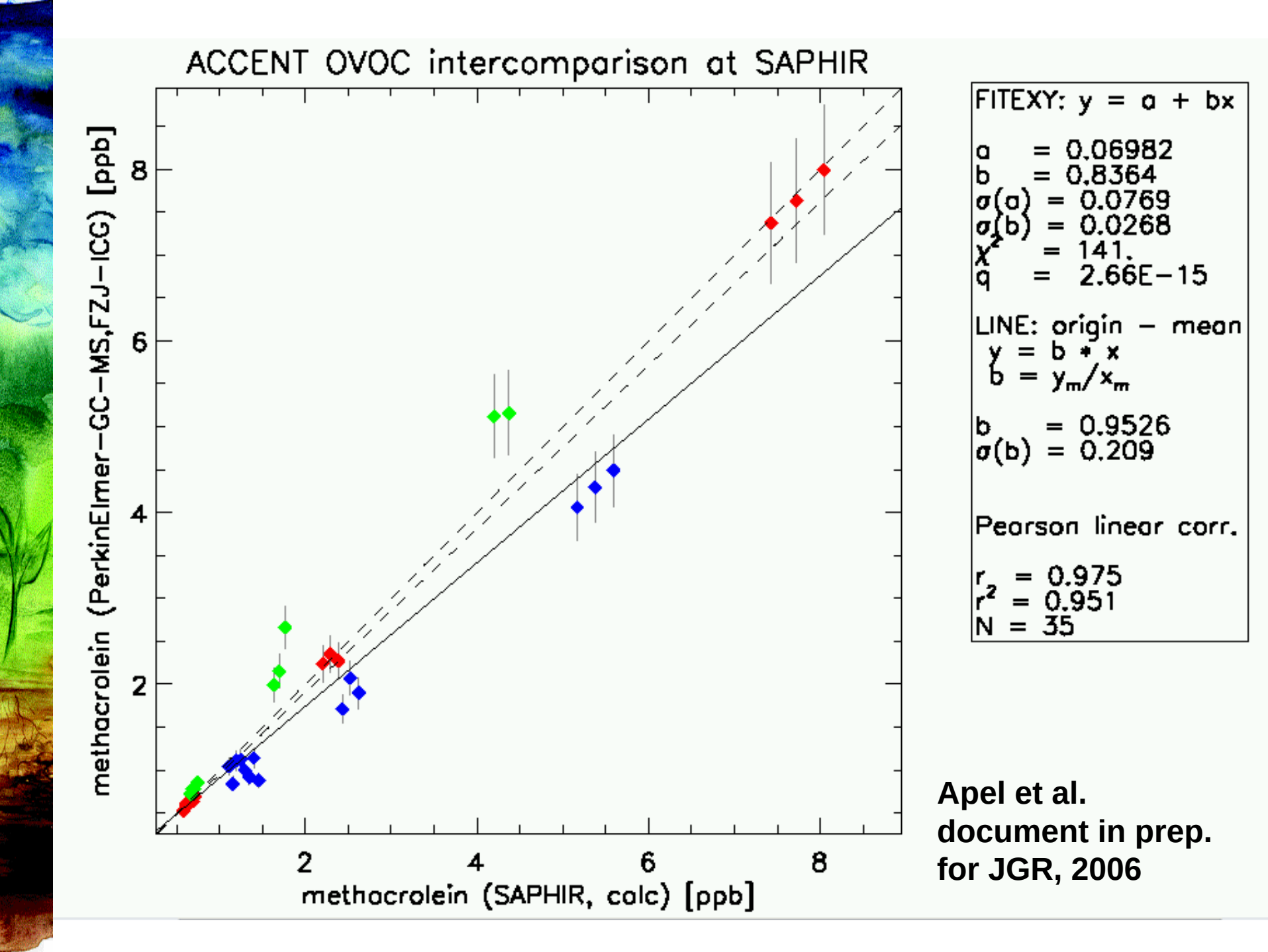
a = −0.5333
b = 0.9842
σ(a) = 0.0726
σ(b) = 0.0118
χ^2 = 1.03E+003
q = 0.00235

Pearson linear corr.

r = 0.945
r^2 = 0.894
N = 908

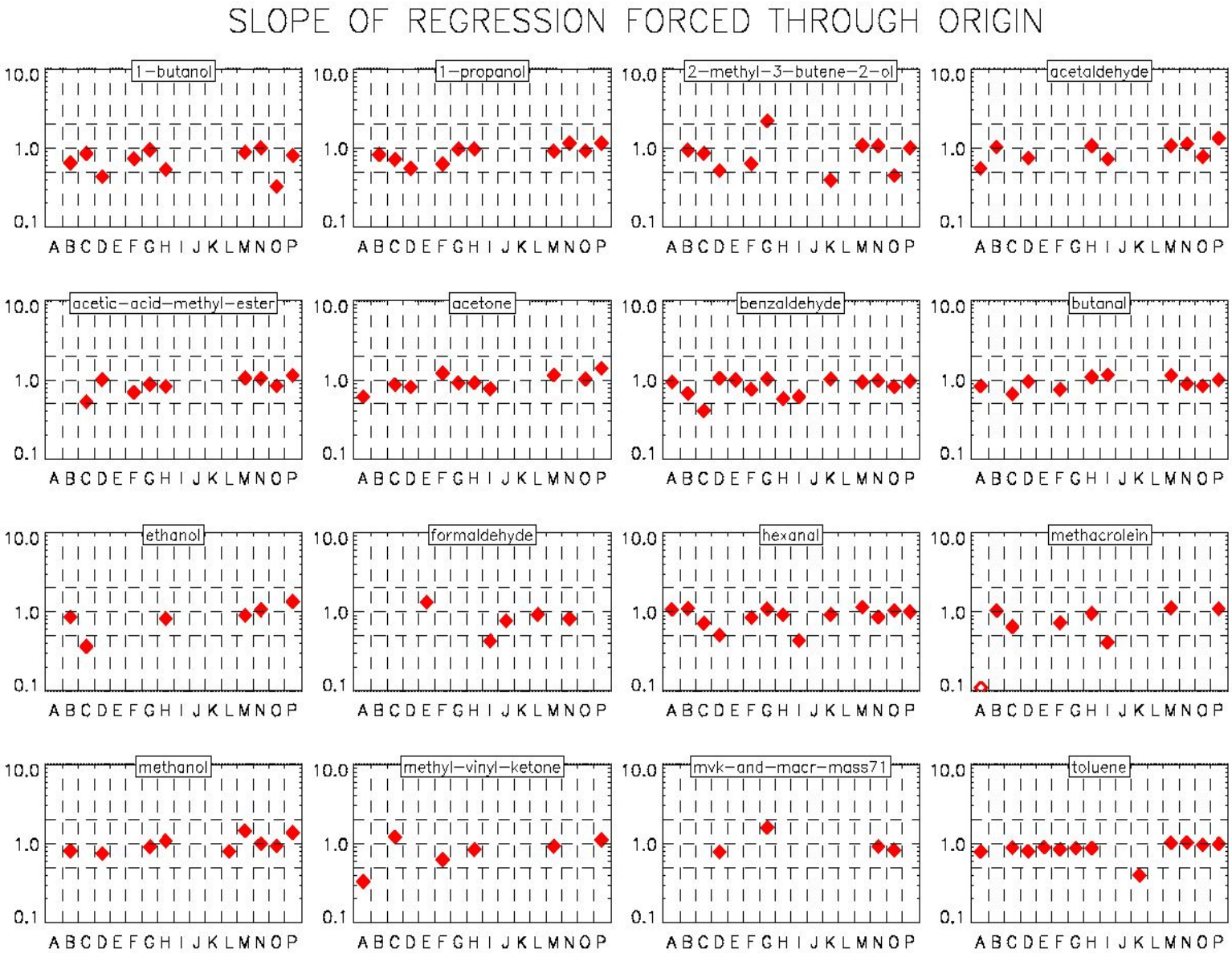
accuracies:
DOAS: 6%
LIF: 10%

Schlosser et al. 2006, JAC



Apel et al. document in prep. for JGR, 2006

OVOC intercomparison at SAPHIR

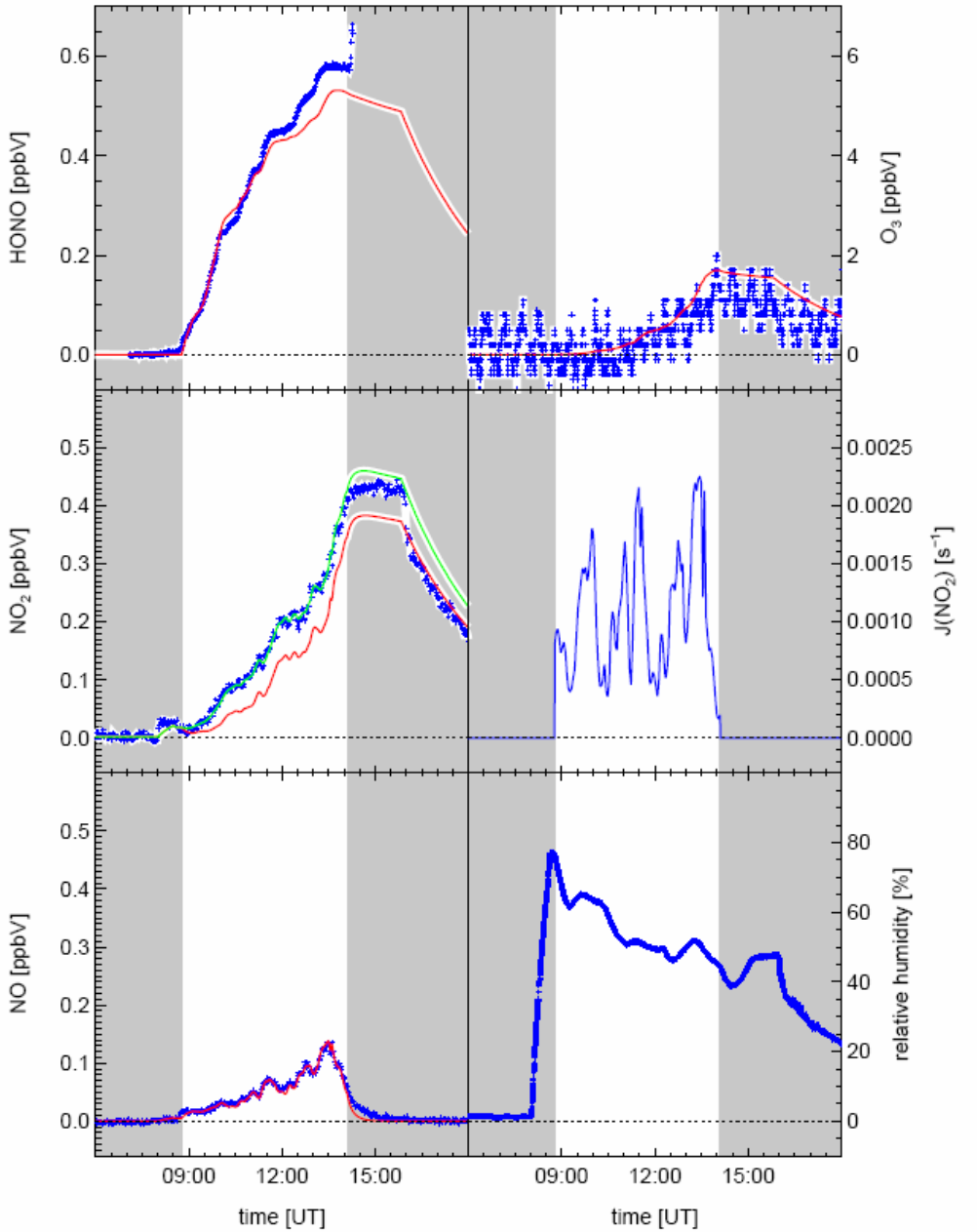


Apel et al., document in prep. for JGR, 2006

QA through standard or reference experiments

- ***"empty chamber" (+ light)***
  - HONO / NO formation
    FZJ, CEAM, PSI
  - HCHO formation
    FZJ, CEAM
  - particle formation
    PSI , FZK
- ***"well defined mixtures"***
  - ozone vs. tracer lifetime
  - NOx budget
  - ozonolysis of ethene as source of formaldehyde
  - tri-methyl-benzene + NOx + light
  - aerosol lifetime …

SAPHIR experiment: HONO source identification



- This experiment
  - Conditions:
    $J(O^1D) \approx 1\%$, $J(NO_2) \approx 30\%$
    of outside values
    CO = 500 ppm

- 25 different experiments
  - HONO source

    $S(HONO) = a \times J(NO_2)$

    $\times (1 + (RH/11.8\%)^2)$

    $\times \exp(-3950K / T)$

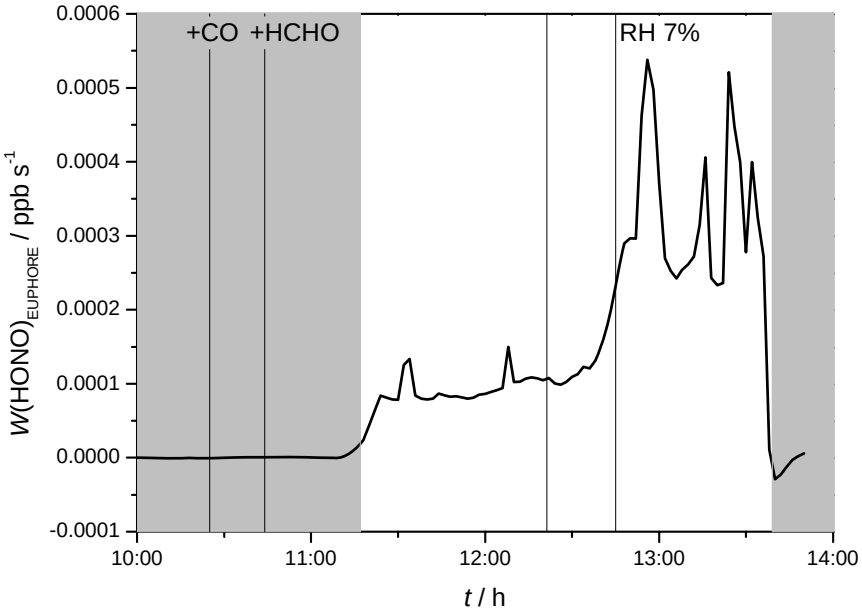
- published
  Rohrer et al. 2005 ACP

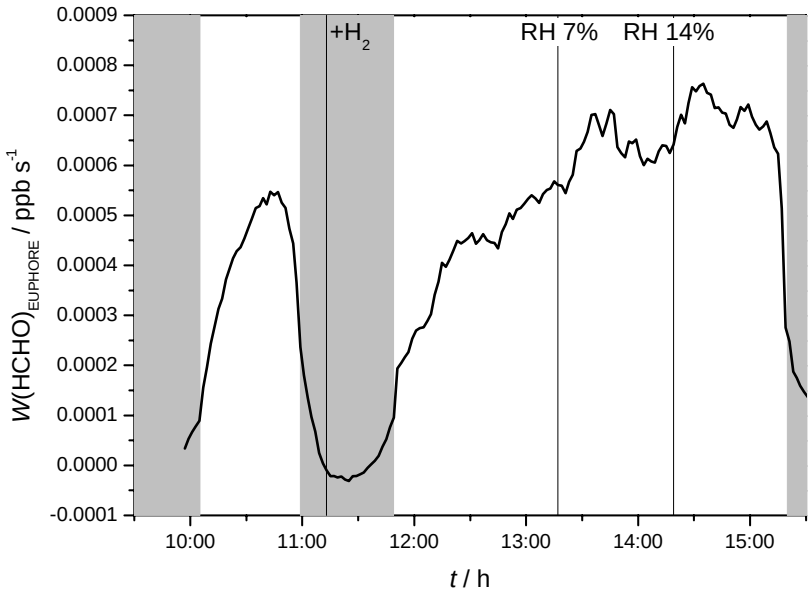
Chamber radical sources at EUPHORE

- Collaboration of CEAM and LEEDS, Zador et al, JAC, 2006
- 3 zero NOx experiments, coupled with rate of production analysis and local and global uncertainty analysis
- Production of HCHO and HONO related to wall processes. Rates:

$$W(HONO) = j_{NO2} \times (a + b \times RH^{1/2})$$

$$W(HCHO) = j_{NO2} \times c$$





EUROCHAMP Database Server

Introduction

Access Database GUEST

Access Database USERS

Access Database INSTITUTIONS

Useful Links to Partners

CEAM EUPHORE Lab.
FZJ-ICG-II Homepage
FZK AIDA Homepage
PC University of Wuppertal
UCC-CRAC Homepage
JRC-IES Ispra
CNRS-LCSR Orleans
PSI-LAC Villigen
University of Bayreuth
Uni. Leeds Chemistry
SP Borås
CNRS-LISA Paris

European Commission FP6
Project RII3-CT-2004-505968

Project Description

EUROCHAMP is a research project funded within the EC 6th Framework Programme, Section "Support for research Infrastructures - Integrated Infrastructure Initiative".

11 European Partners are the backbone of this project, a grid of environmental chambers designed for the the scientific investigation of atmospheric transformation processes. A number of associated research groups worldwide contribute to the project providing expert knowledge in specific fields of atmospheric science.

Database on Environmental Chamber Studies

The search engine will provide access to the data recorded during the experimental runs performed in the environmental simulation chambers of the participating institutes. There is a huge difference in size, sientific scope, technical capabilites and research topics treated among the groups providing the analysed data. The main objective is to give easy access to the data records and associated calibration files, with simple but specific search criteria and an easy to manage download facility.

Data base of chamber experiments

- part of EUROCHAMP (2004 – 2009) work plan

- structure
  - meta data base at CEAM, Valencia
  - http://80.24.165.149/wwweurochamp/Data_Base.htm
  - the data are not transferred to CEAM

- status
  - test phase successful
  - file format: tagged text files & pdf files with experiment description
  - comments and usage is welcomed

Summary and Conclusion

- (large) environmental cambers are widely used for **model tests**
- MCM key mechanism in use at SAPHIR and EUPHORE
- improvement of RACM → RACM-MIM → RACM2
- the EUROCHAMP data base of chamber experiments will provide a source of data for the community to **test models**

Thank you ...