5th Georgian – German School and Workshop in Basic Science

Photochemical Processes determine Air Quality and Climate

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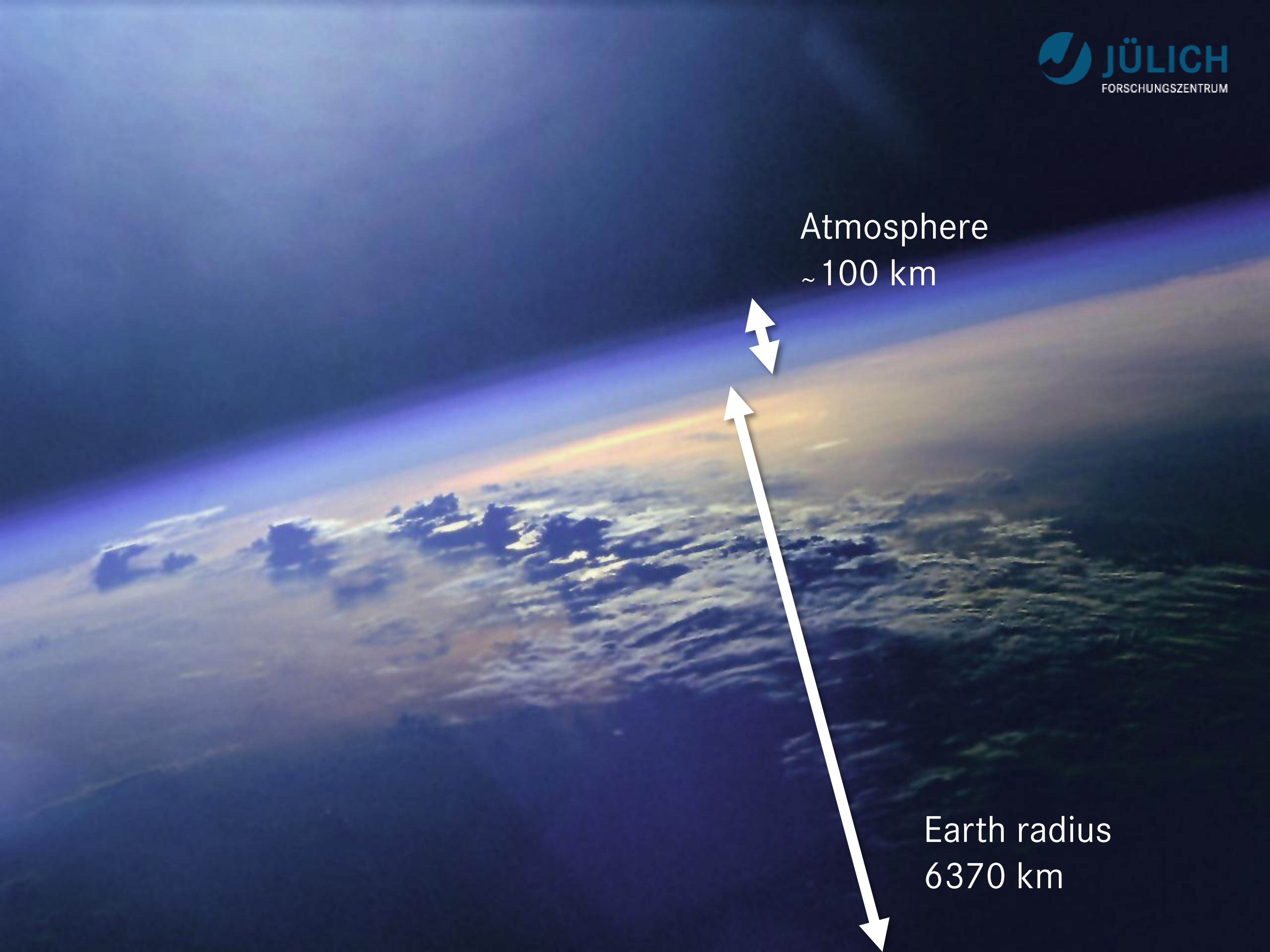
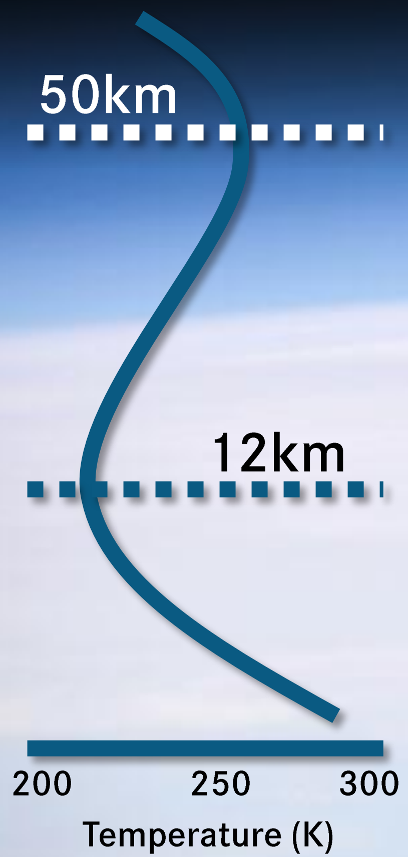
IEK-8: Troposphäre
Germany

GGSWBS'12, August 13 – 17, Batumi, Georgia


Atmosphere
~100 km
Earth radius
6370 km



Stratosphere — 18% air mass

Troposphere — 82% air mass

Composition: N_2 (78%), O_2 (20%), Ar (1%), H_2O (~1%)
trace gases (< 0.05 %)

Atmospheric Trace Gas Degradation by Oxidation

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Trace Gas	Global Emission (Million Ton per year)	Degradation by OH-radikals
CO	2800	85 %
Methan	530	90 %
Alkane	20	90 %
Isoprene	570	90 %
Terpene	140	50 %
NO_2	150	50 %
SO_2	300	30 %
$(CH_3)_2S$	30	90 %
$CFCl_3$	0,3	0 %

Trace Gas Oxidation in the Atmosphere

Oxidative Chemistry

OH, HO_2, NO_3, O_3, XO

- **Atmospheric Self-Cleaning**

  Oxidative removal of trace gases
  (CH_4, HCFCs, VOCs, CO, SO_2, NO_x)

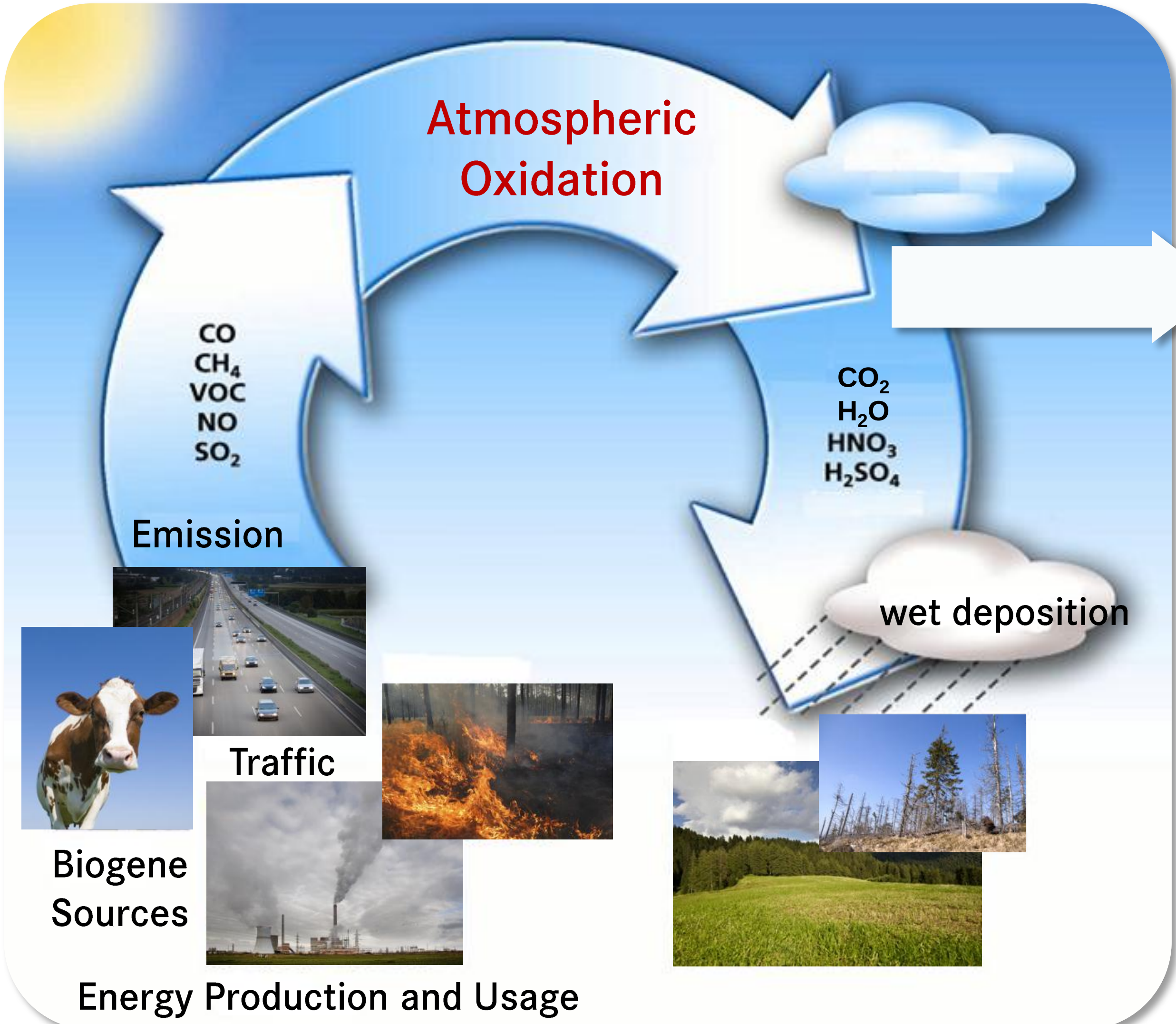
- **Chemical Transformation**

  Formation of secondary pollutants,
  gaseous + particulate phase
  (O_3, H_2O_2, HNO_3, H_2SO_4, OVOCs, SOA)

Air Quality
+
Climate
Impact

VOC	volatile organic compounds
OVOC	oxygenated VOC
SOA	secondary organic aerosol

Self Cleaning of the Atmosphere



secondary pollutants (O_3, HCHO, … aerosol)

Chemical Reactions in the Atmosphere

Earth atmosphere contains

main components (N_2, O_2, Ar, water vapor, ...)

+ complex mixture of **<u>reactive</u>** trace substances

➔ How do chemical transformations proceed ?

➔ What are the chemical products ?

➔ What are the time scales of chemical transformations ?

➔ What are the lifetimes of atmospheric components ?

Chemical Reactions in the Atmosphere

Earth atmosphere contains

main components (N_2, O_2, Ar, Wasserdampf, ...)

\+ complex mixture of **reactive** trace substances

Reactants

e.g.

CO

CH_4

NO

SO_2

$+ O_2$

→

somehow

Products

CO_2

$CO_2 + H_2O$

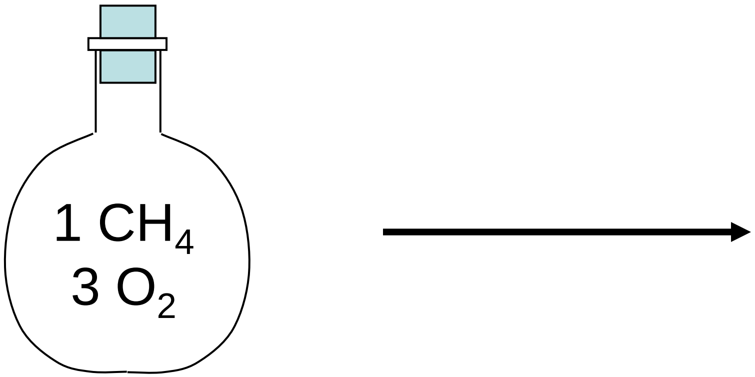
HNO_3

H_2SO_4

↓

Intermediates (O_3, H_2O_2 ...)

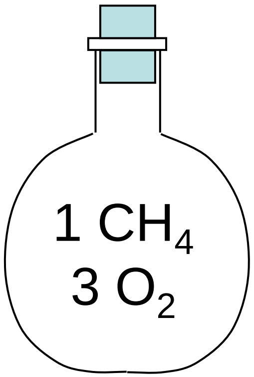
Activation of Chemical Reactions

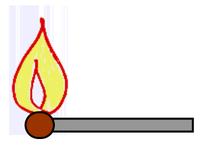


no chemical reaction

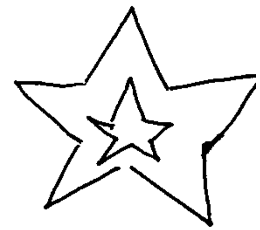
CH_4-lifetime $\rightarrow \infty$

Activation of Chemical Reactions





Activation

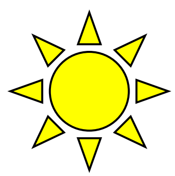


Explosion
$CO_2 + H_2O$

fast
oxidation
~ 10^{-6} s

Atmosphere:

1.7×10^{-6} CH_4
0.21 O_2



UV-radiation

$CO_2 + H_2O$

slow
oxidation
~ 8 years

Chemical Reaction Kinetics

Reaction-
mechanisms

Reaction rates
= f (concentrations)
= f (temperature)
= f (radiation $h\nu$)

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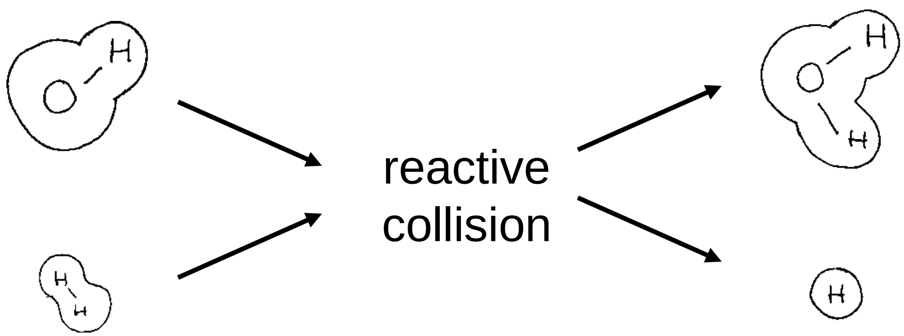
Reaction Mechanisms

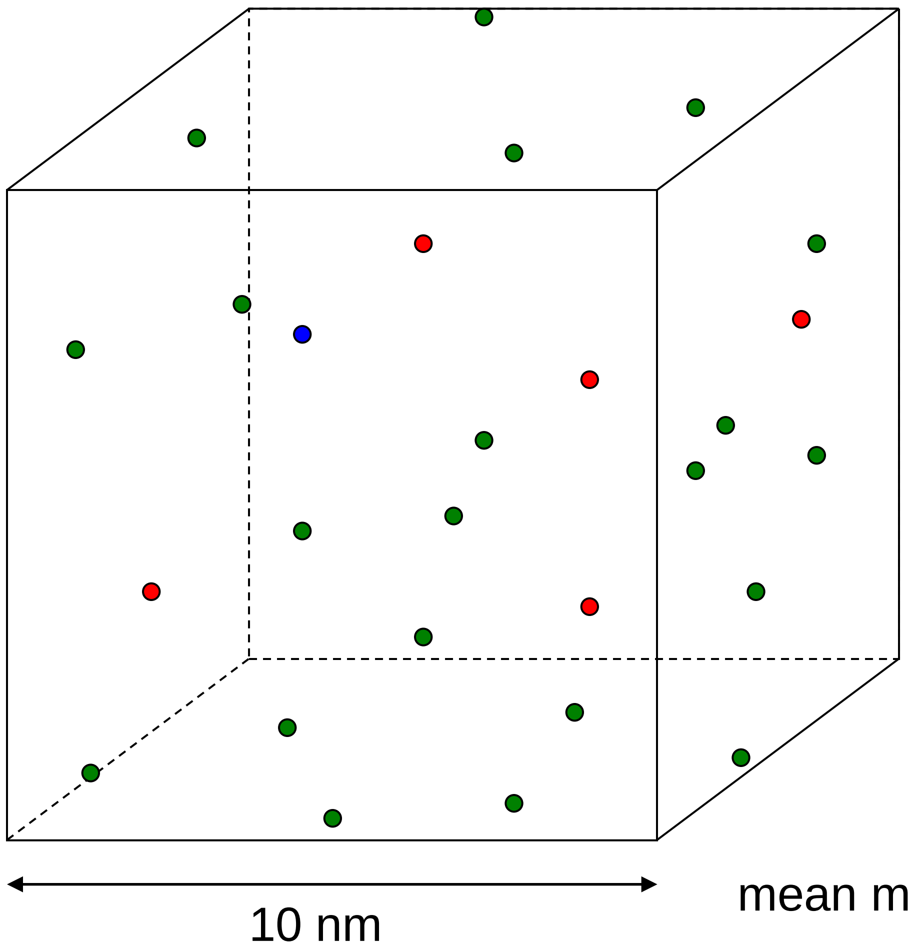
Elementary reactions
= reactive collisions between molecules
or decomposition of molecules

Example :

$$OH \quad + \quad H_2 \qquad \rightarrow \quad H_2O \quad + \quad H$$



Reaction dynamics



Air volume element at 1 atm, 25°C

- N_2
- O_2
- O_3

in total 25 molecules

mean molecular velocity ≈ 475 m/s

mean free pathlength ≈ 100 nm (10 boxes)

40 ppb O_3 → 1 molecule O_3 in 1 million boxes

Elementary Reactions

are named according to their molecularity

(= number of involved collision partners) :

uni-molecular:	A	$\rightarrow$	Prod.

$CH_3CO(O_2)NO_2 \rightarrow CH_3CO(O_2) + NO_2$

bi-molecular:	A + B	$\rightarrow$	Prod.

$O_3 + NO_2 \rightarrow NO_3 + O_2$

ter-molecular:	A + B + M	$\rightarrow$	Prod.

$O(^3P) + O_2 + M \rightarrow O_3 + M$

$(M = O_2, N_2)$

Reaction Mechanisms

Composite complex reactions
proceed on a molecular level via several elementary reactions (sequential and/or parallel)

Example :

Reaction mechanism

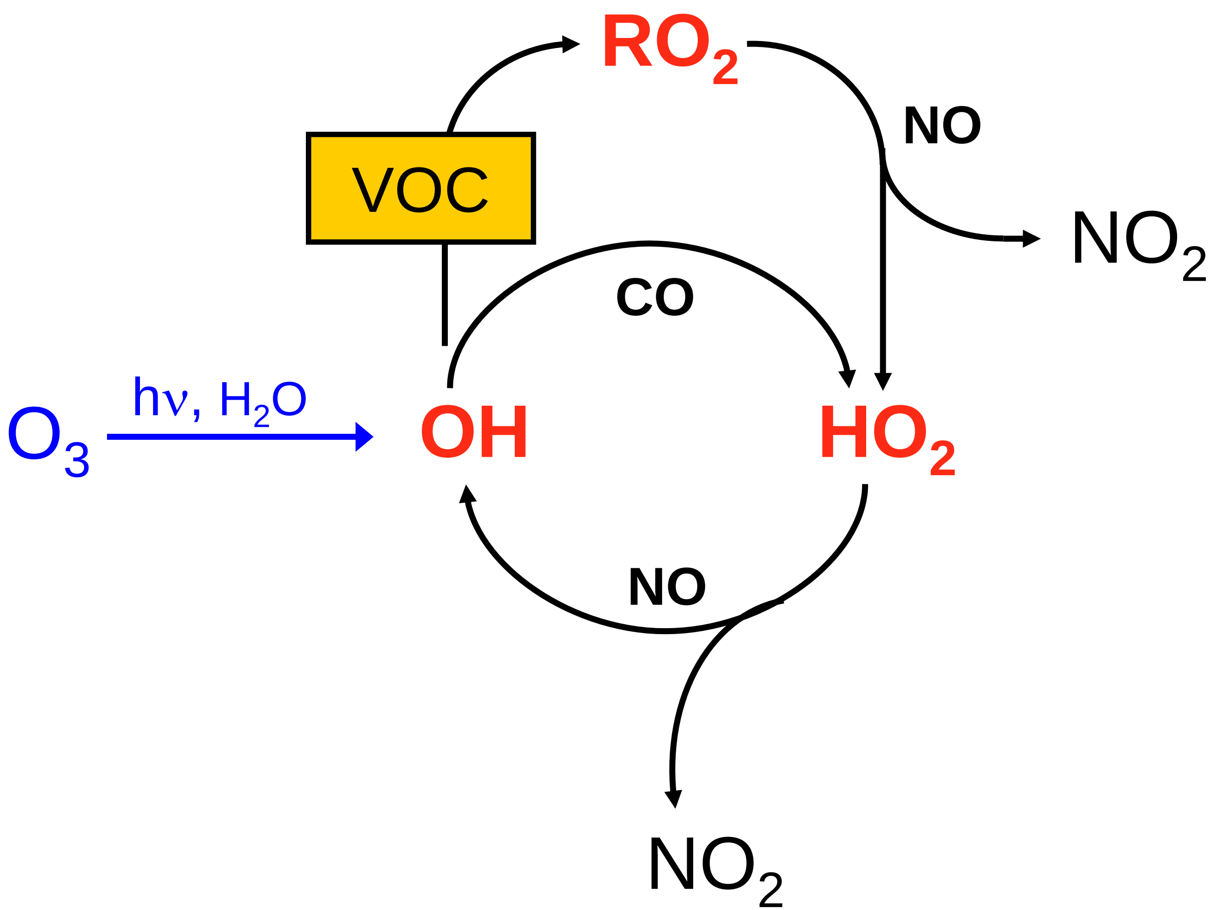
$$O_3 + h\nu \rightarrow O_2 + \cancel{O(^1D)} \qquad \lambda \leq 340\ \text{nm}$$

$$\cancel{O(^1D)} + H_2O \rightarrow OH + OH$$

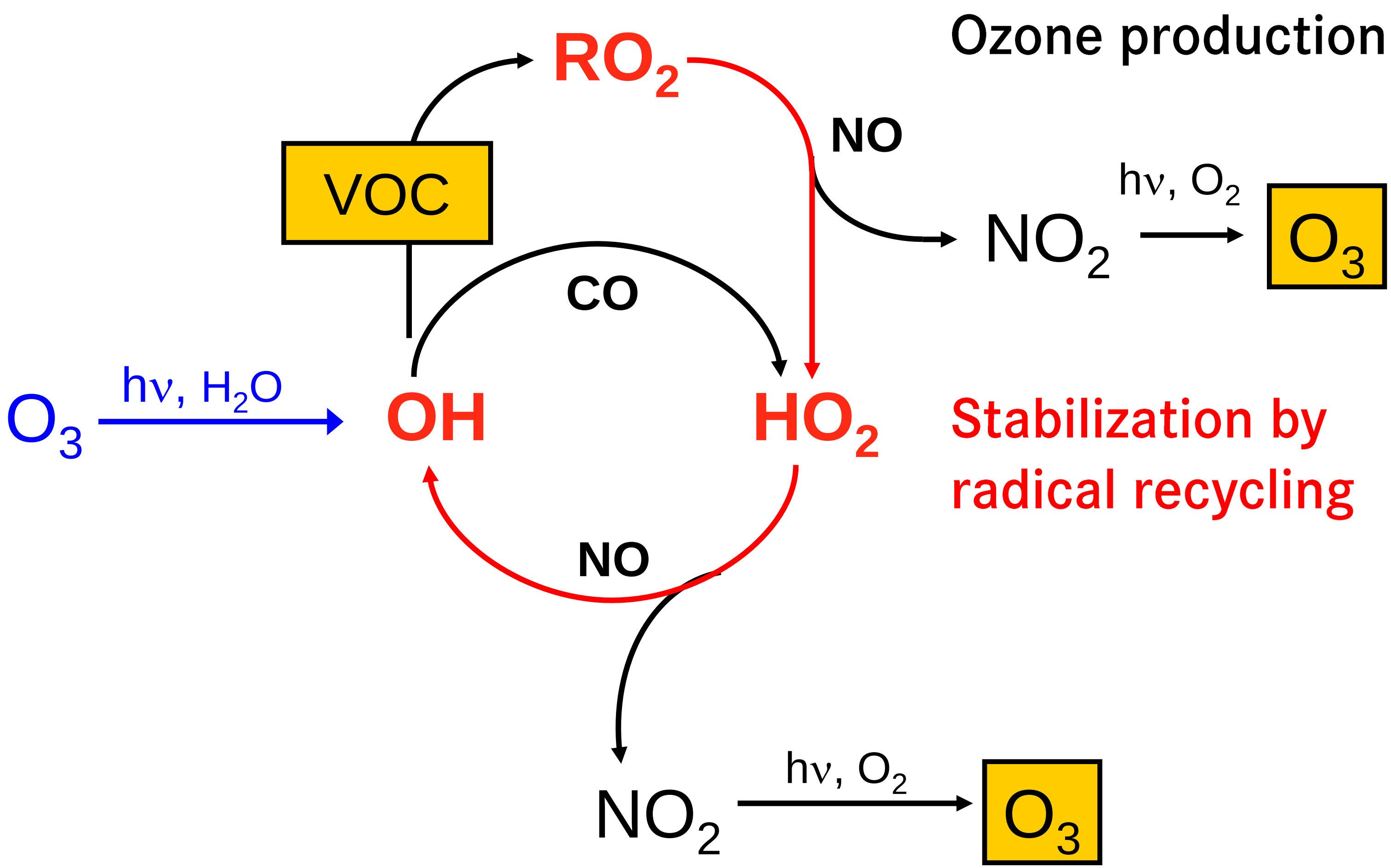
$$O_3 + H_2O + h\nu \rightarrow 2\,OH + O_2 \qquad \lambda \leq 340\ \text{nm}$$

Net reaction

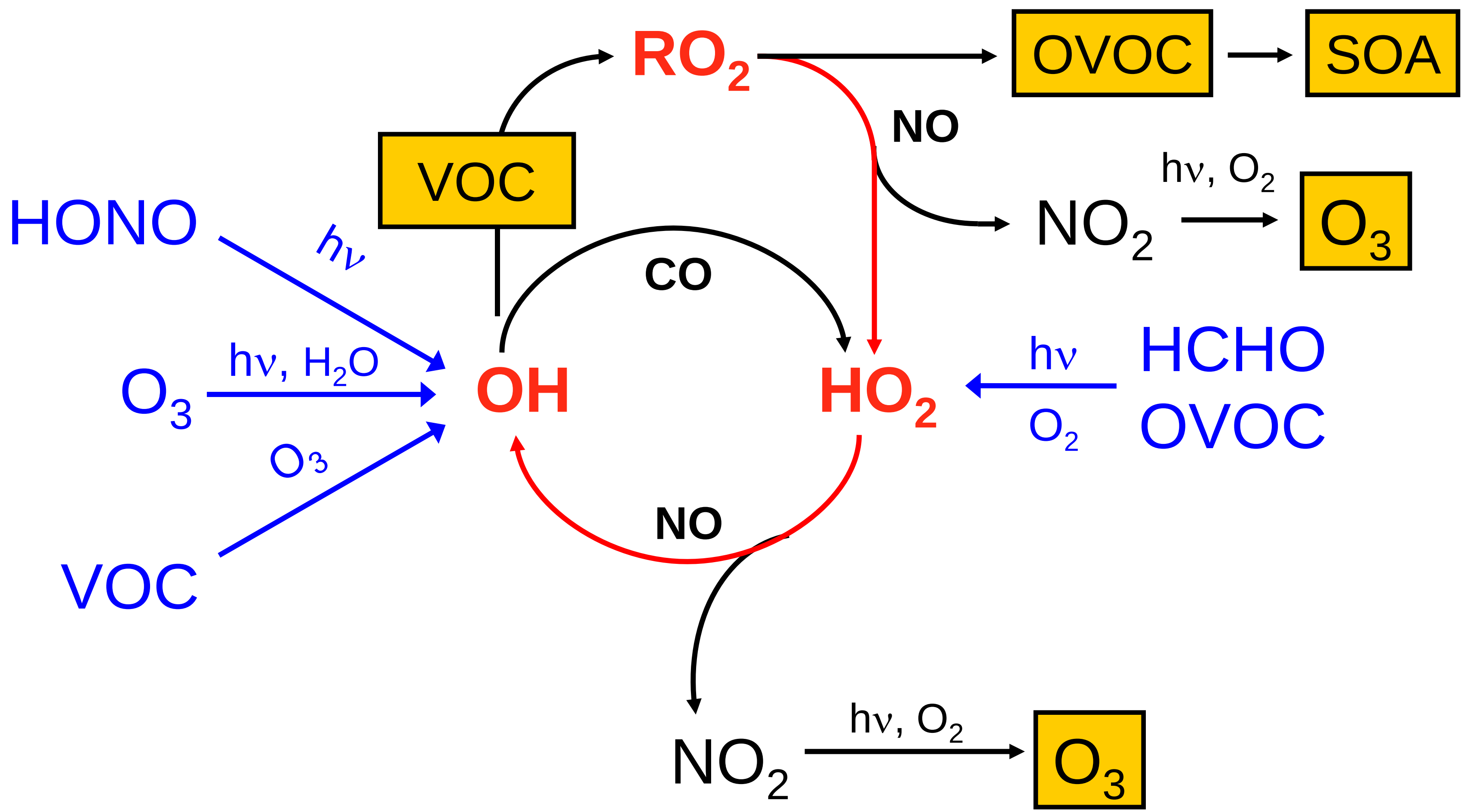
Oxidative Chemistry
Radical Perspective



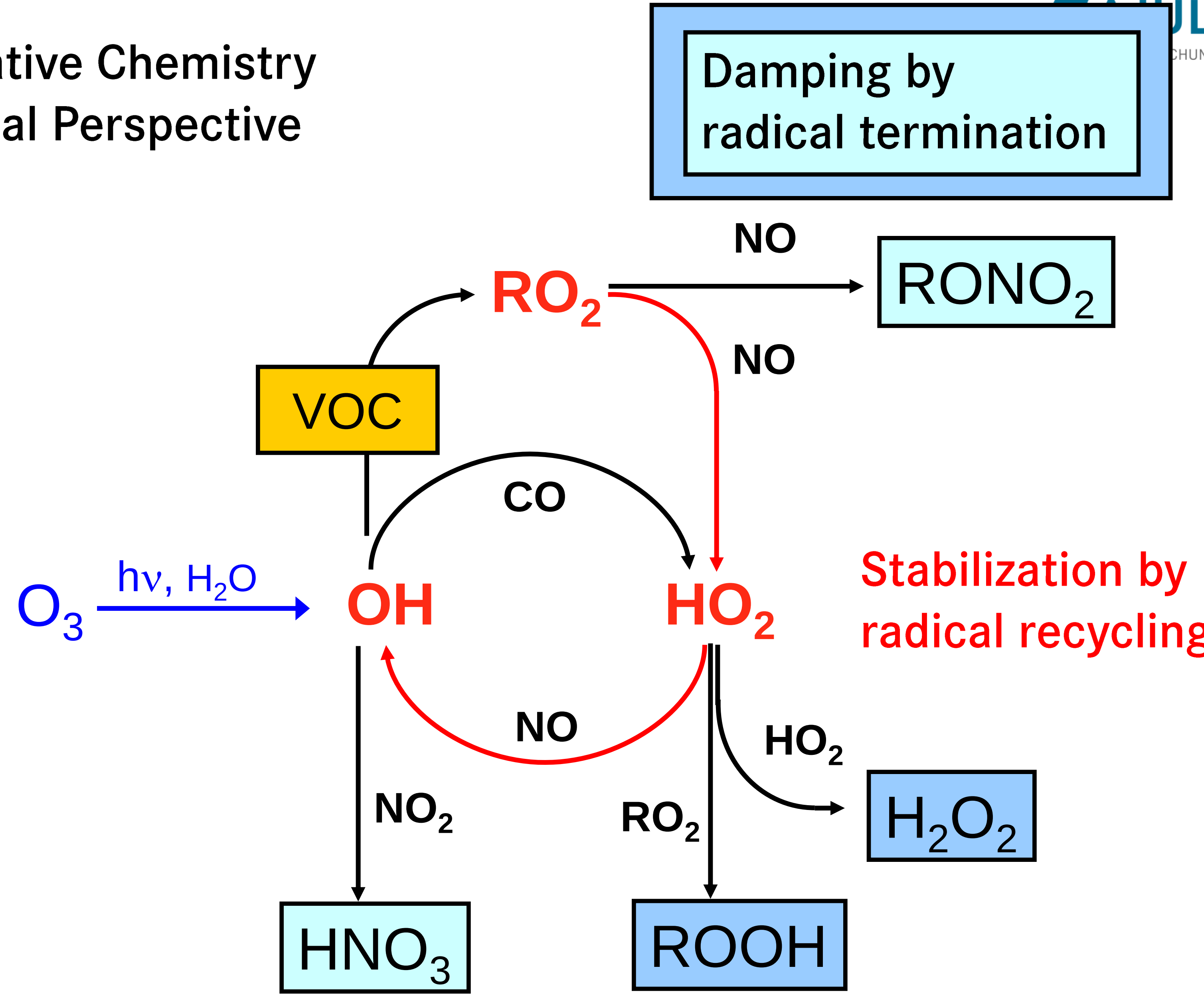
Oxidative Chemistry
Radical Perspective



Oxidative Chemistry
Radical Perspective



Oxidative Chemistry
Radical Perspective



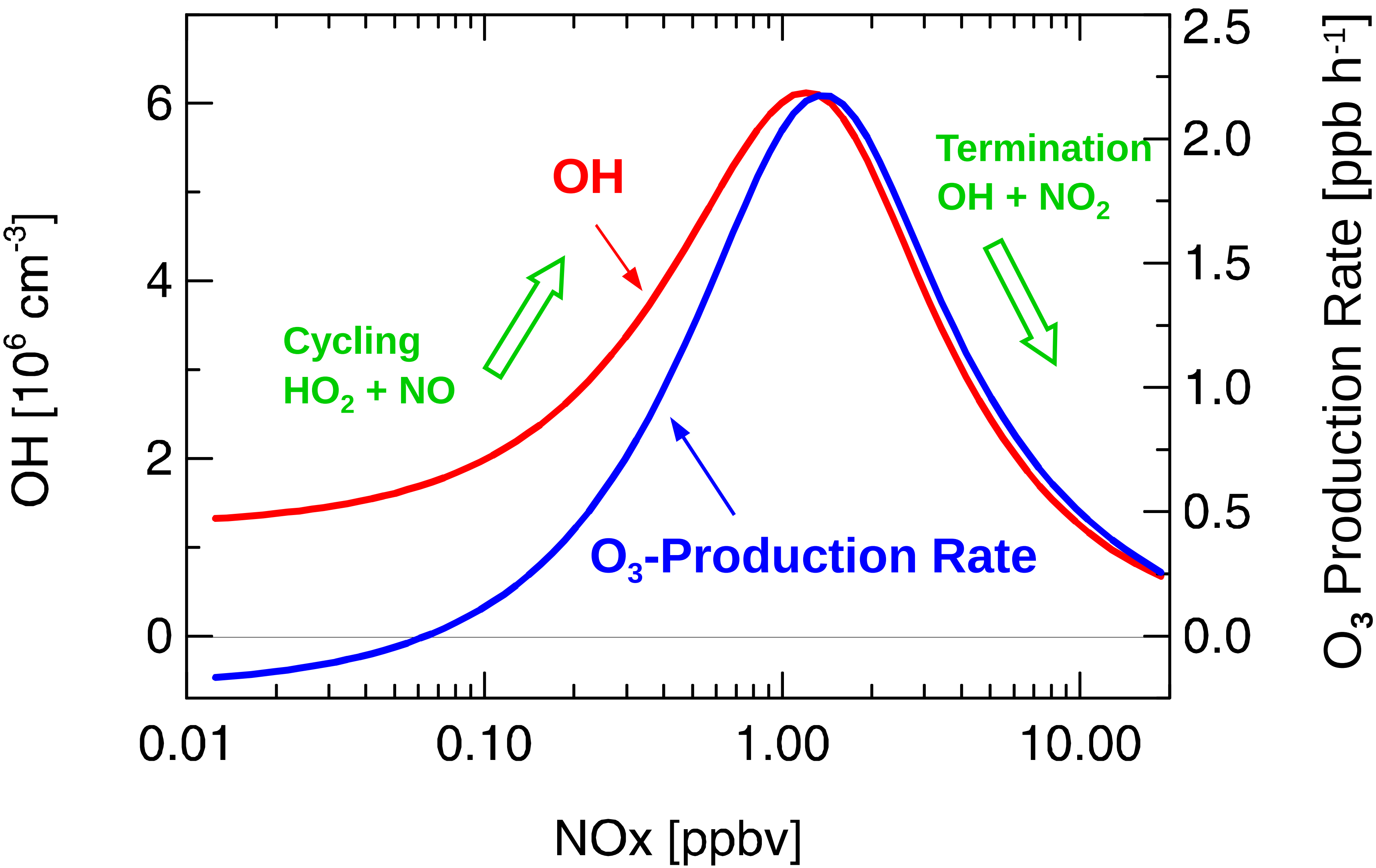
Oxidative Chemistry
Radical Perspective

- Photodissociation reactions (primary sources) "power" OH radical chemistry

- Cycling reactions with NO
  → stabilize OH
  → generate O_3 (+ OVOC)

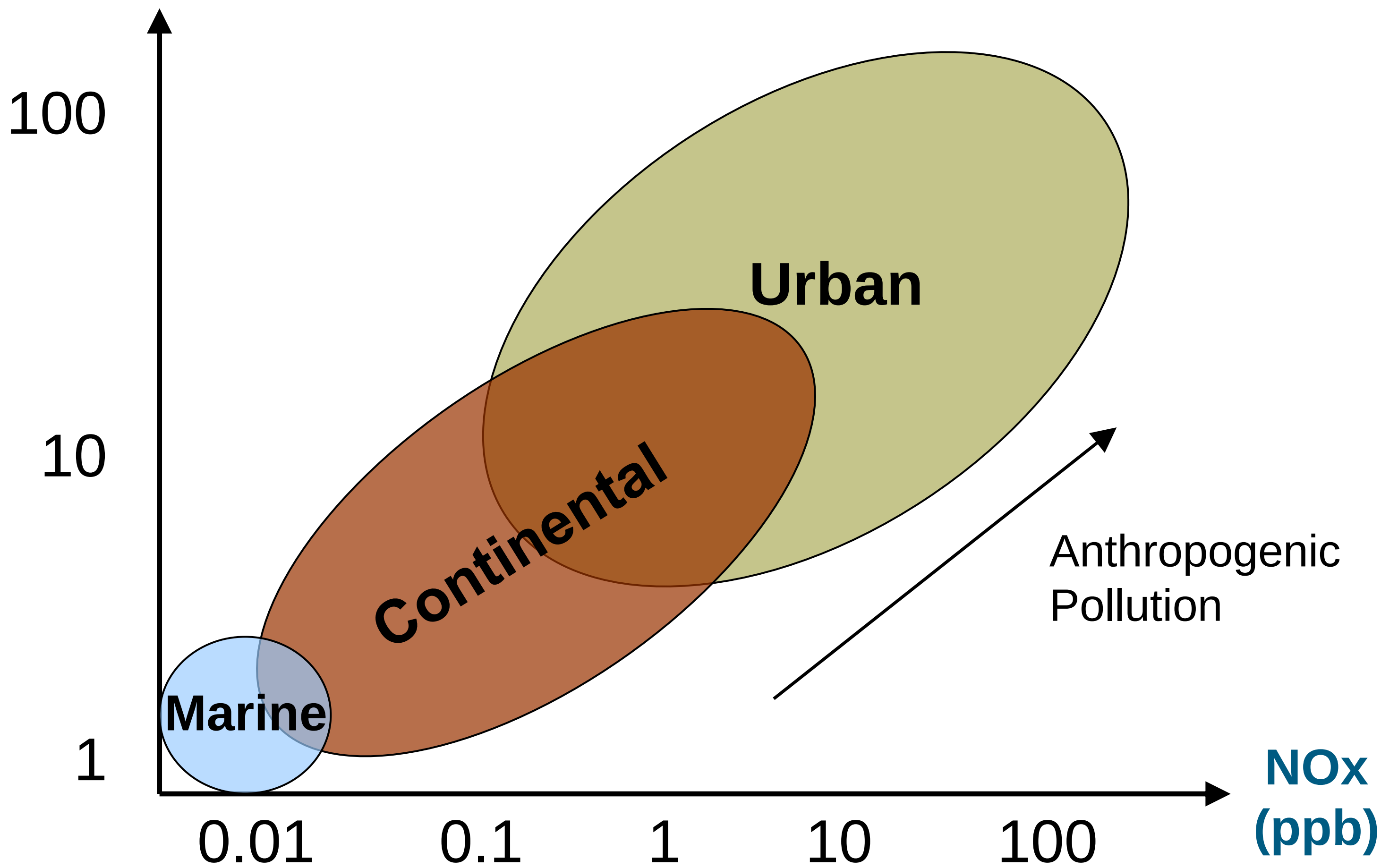
- Termination reactions with NOx
  → damp OH oxidation
  → reduce ozone production rate

NO_x Dependence of OH (model prediction)
(" classical theory ")

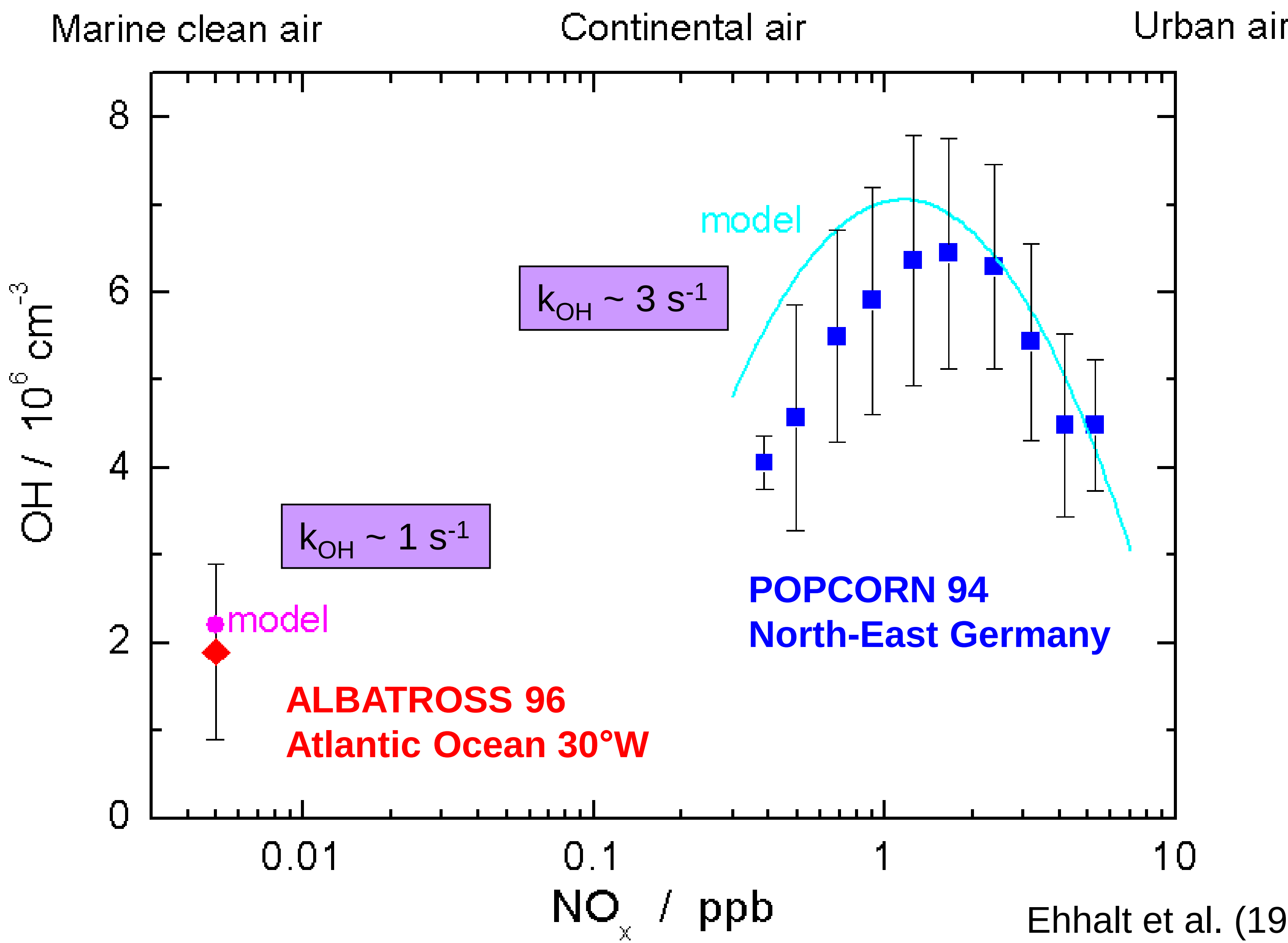


Chemical Coordinates

VOC reactivity (s^{-1}) $k_{OH} = \Sigma\, k_{OH+Xi}\, [\, X_i\,]$



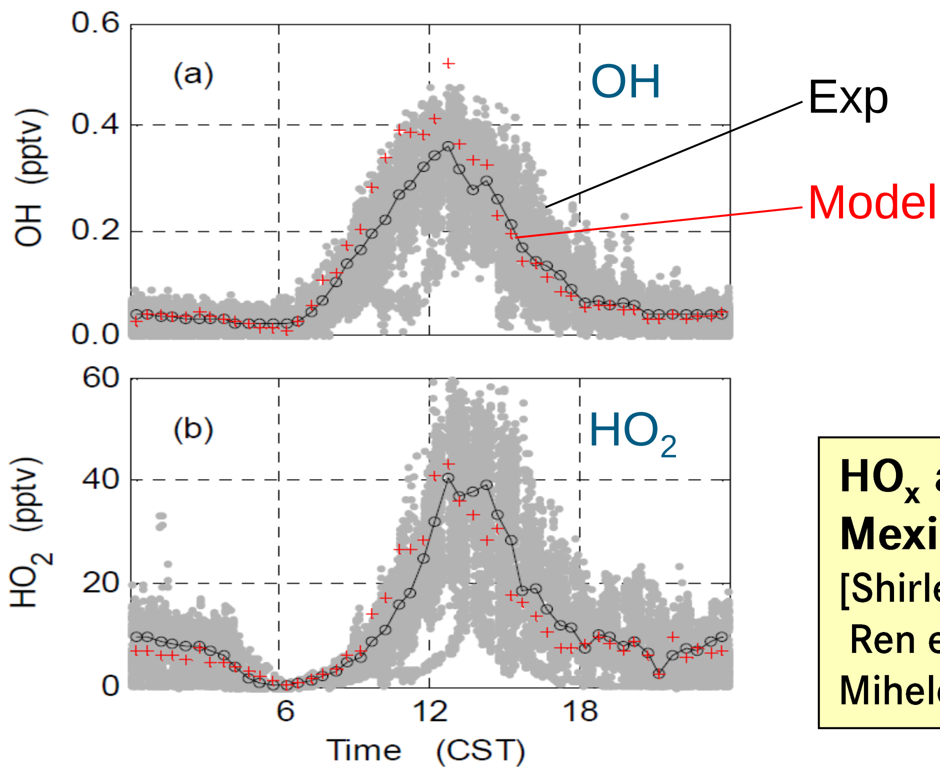
Field Observations at Low VOC



Ehhalt et al. (1999)
Brauers et al. (2001)

Field Observations at High VOC, High NOx

Mexico City 2003



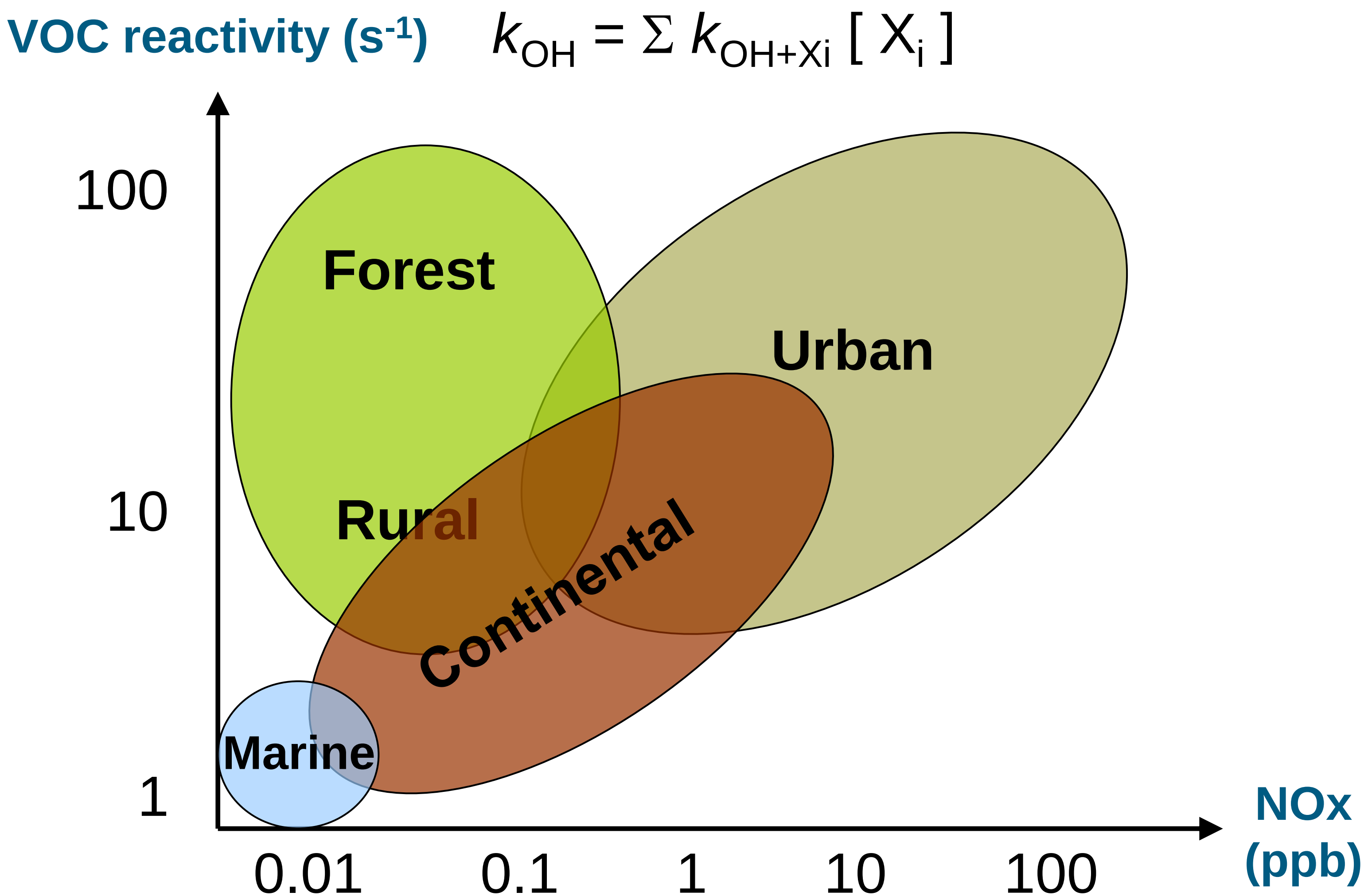
Shirley et al. (2006)

Highly Polluted Air

k_{OH} = 10 – 200 s^{-1}
NO_x = 1 – 200 ppb

HO_x agreement within factor 2
Mexico City, New York, Tokyo, Berlin
[Shirley et al., 2006; Dusanter et al., 2009; Ren et al., 2006; Kanaya et al., 2007; Mihelcic et al., 2003]

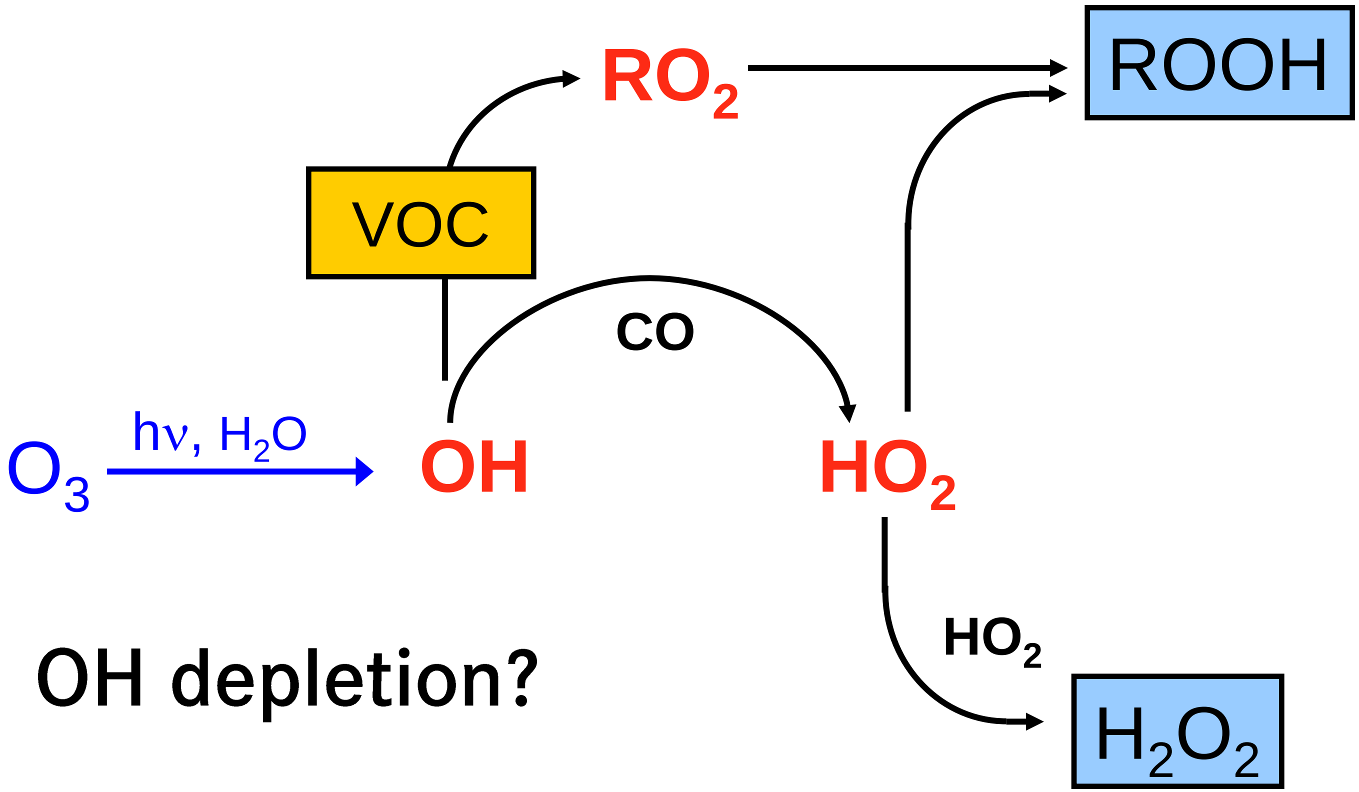
Chemical Coordinates



What happens in chemical regimes at low NOx with high VOC load?

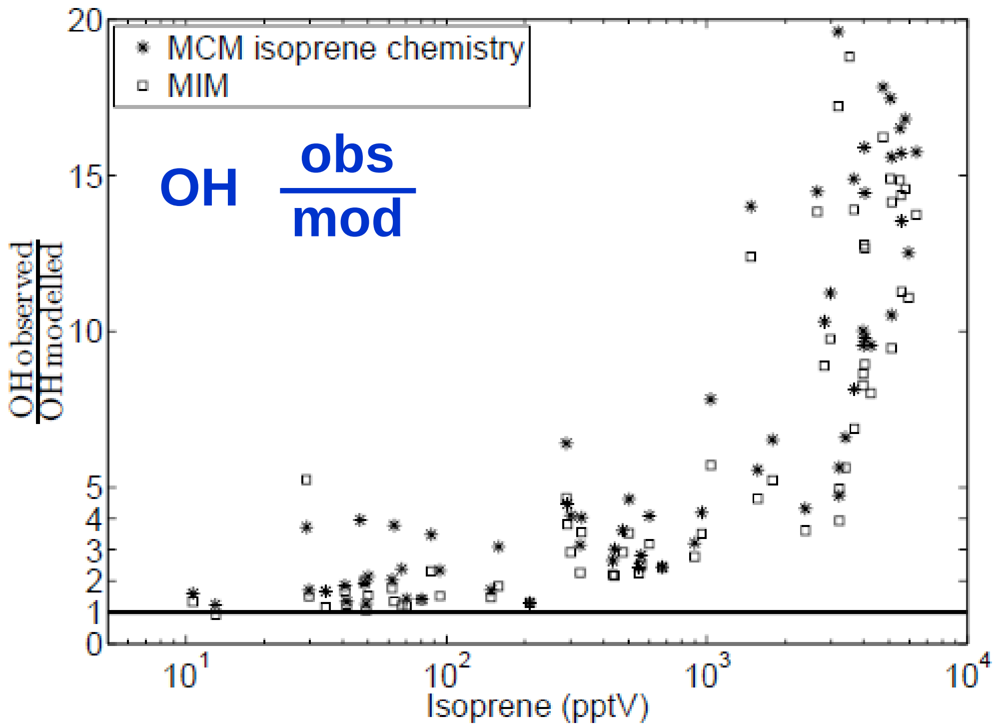
Oxidative Chemistry
Radical Perspective

What happens at low NO_x and increasing VOCs ?



OH depletion?

Underpredicted OH over Tropical Rainforest (pristine conditions)



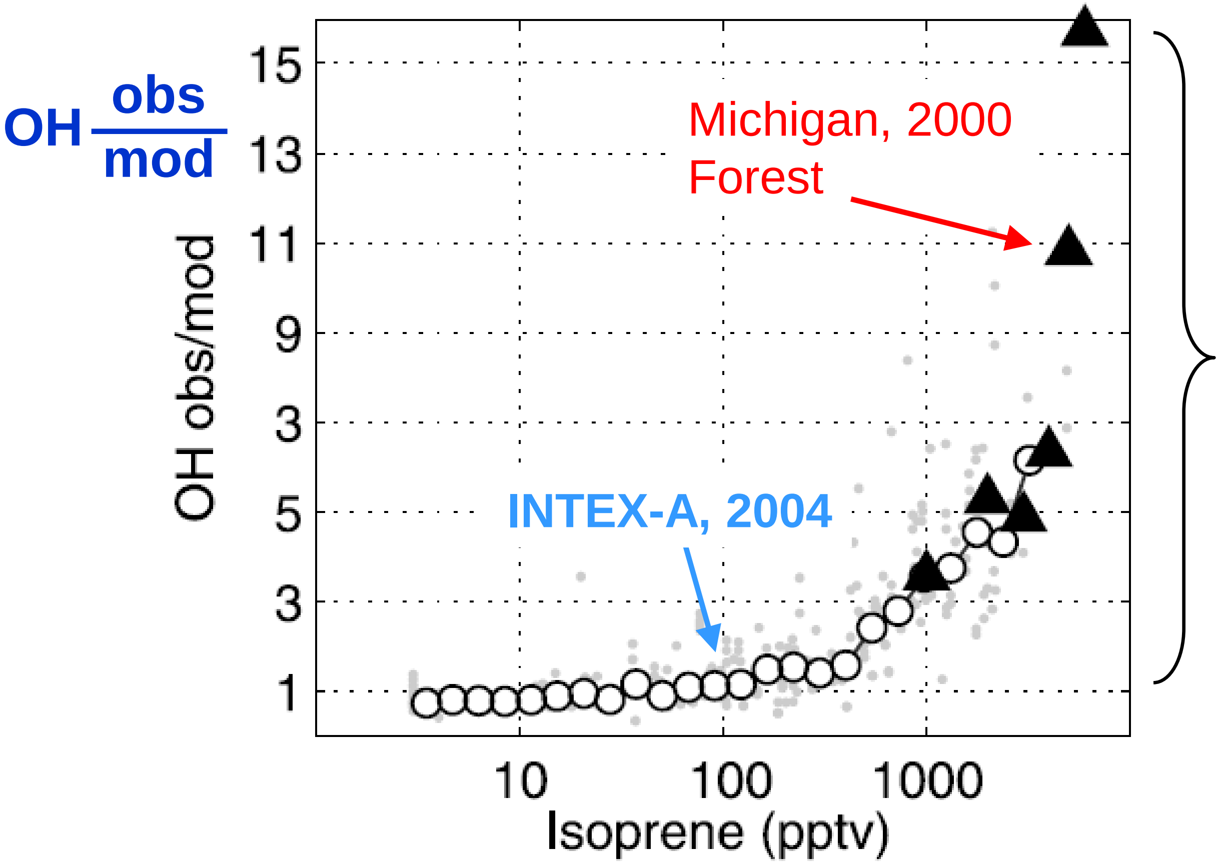
Low NO (~ 20 pptv)
High Isoprene (~ 2 ppbv)

Airborne measurements over the **Amazonian rainforest** 2005

Lelieveld et al. (2008)

Similar observations in the **rainforest of Borneo**
Pugh et al. (2010)

Underpredicted OH in Forested Regions in US



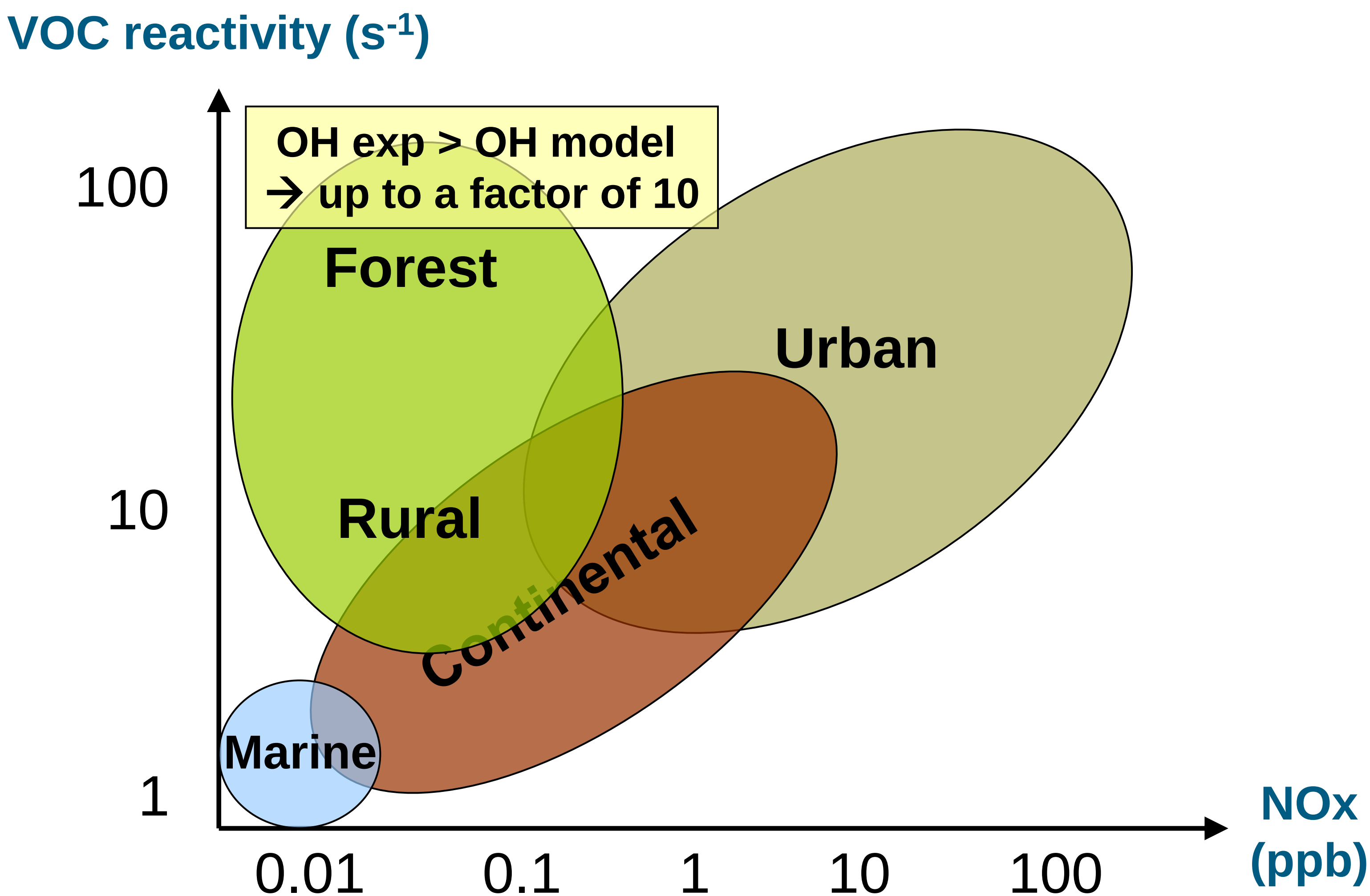
Factor > 10 !!

Ren et al. JGR 2008

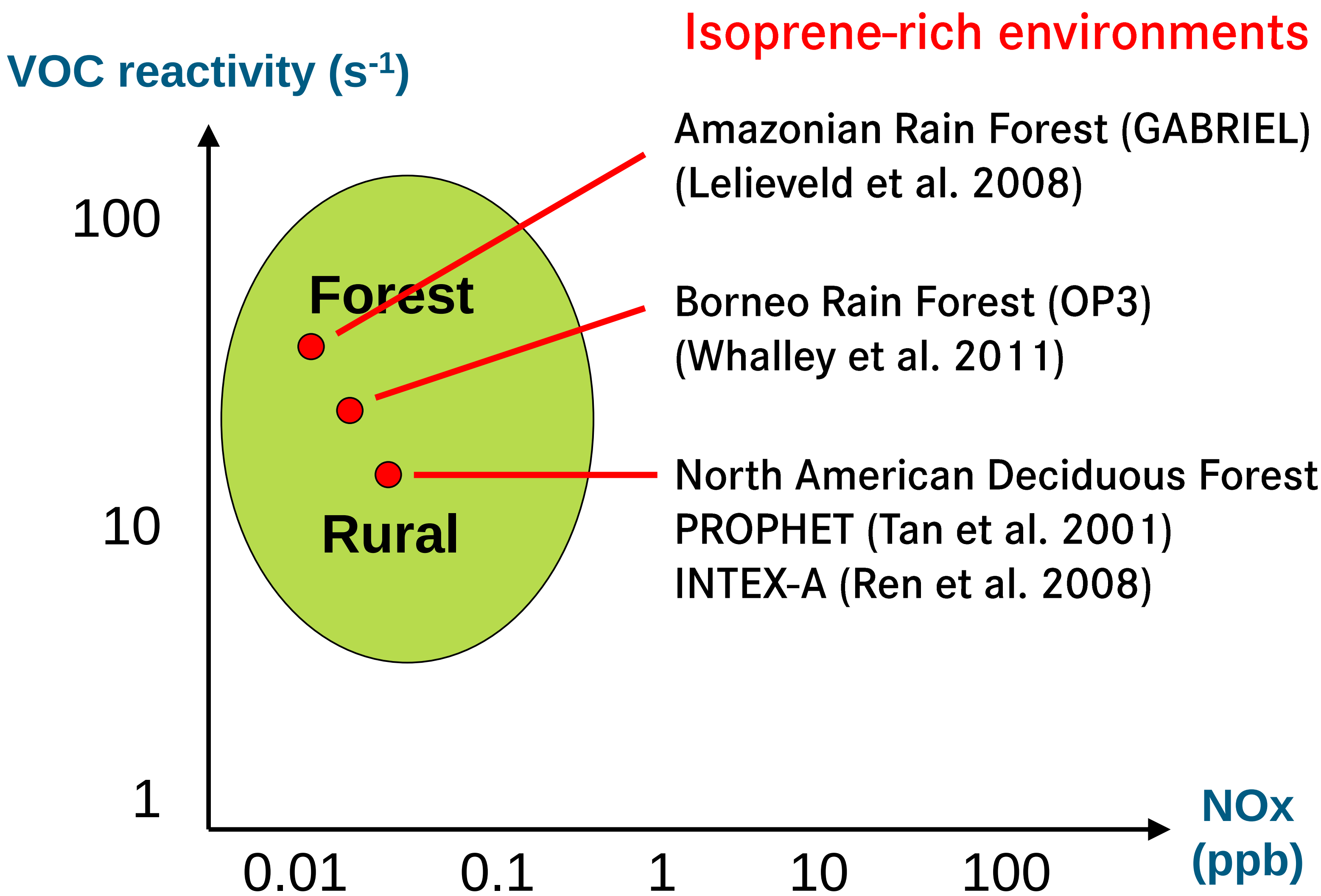
INTEX-A 2004 -> airborne measurements

Michigan 2000 -> groundbased measurements

Chemical Coordinates

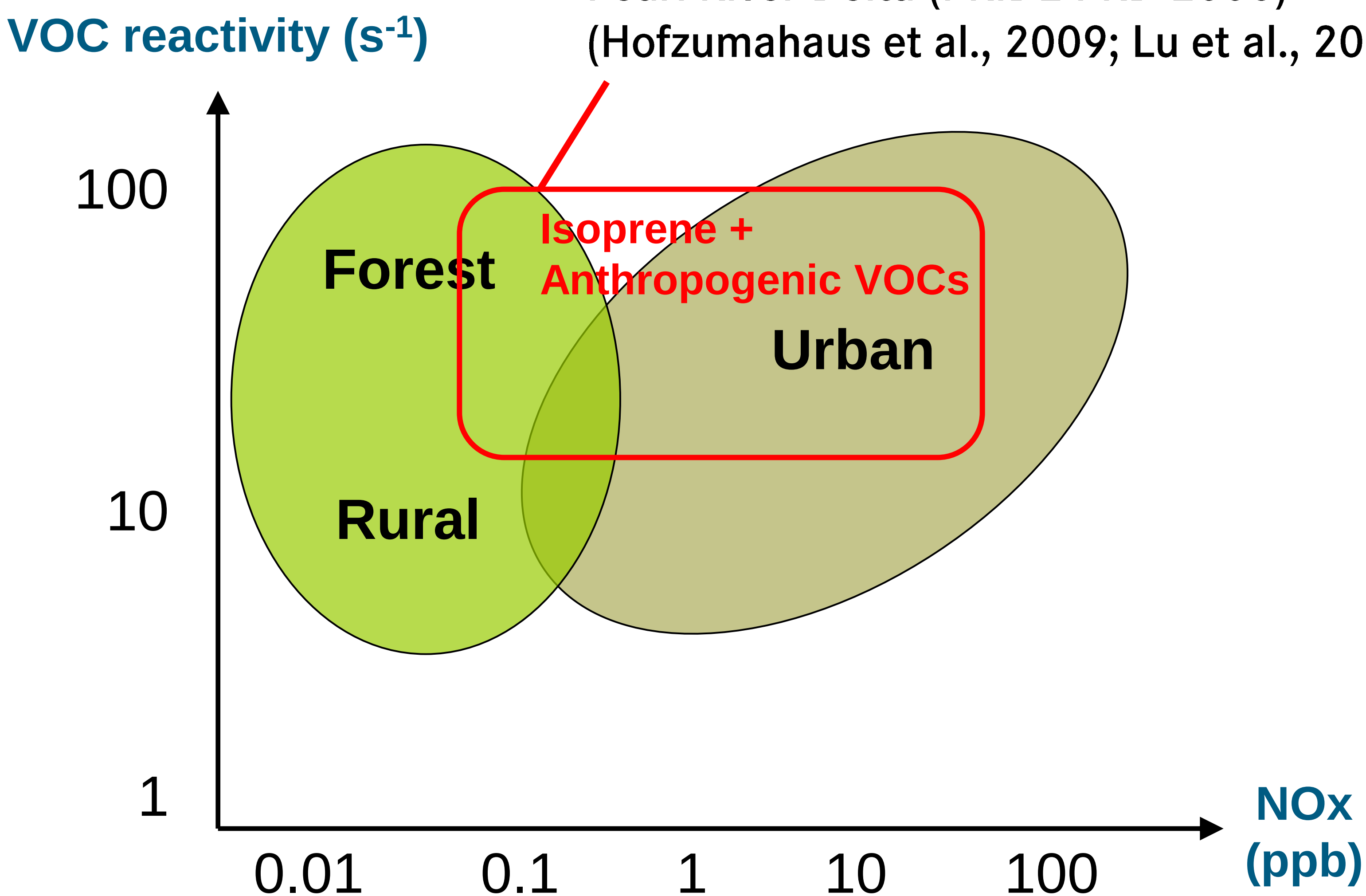


Chemical Coordinates

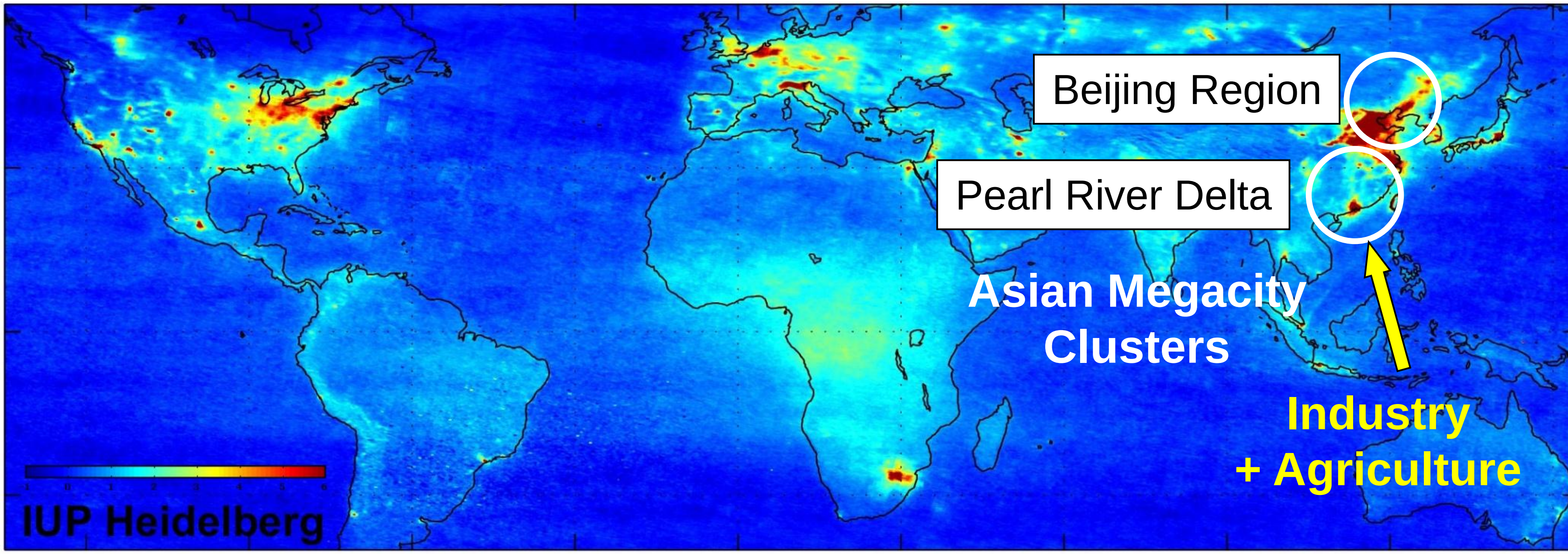


Chemical Coordinates

Pearl River Delta (PRIDE-PRD 2006)
(Hofzumahaus et al., 2009; Lu et al., 2011)



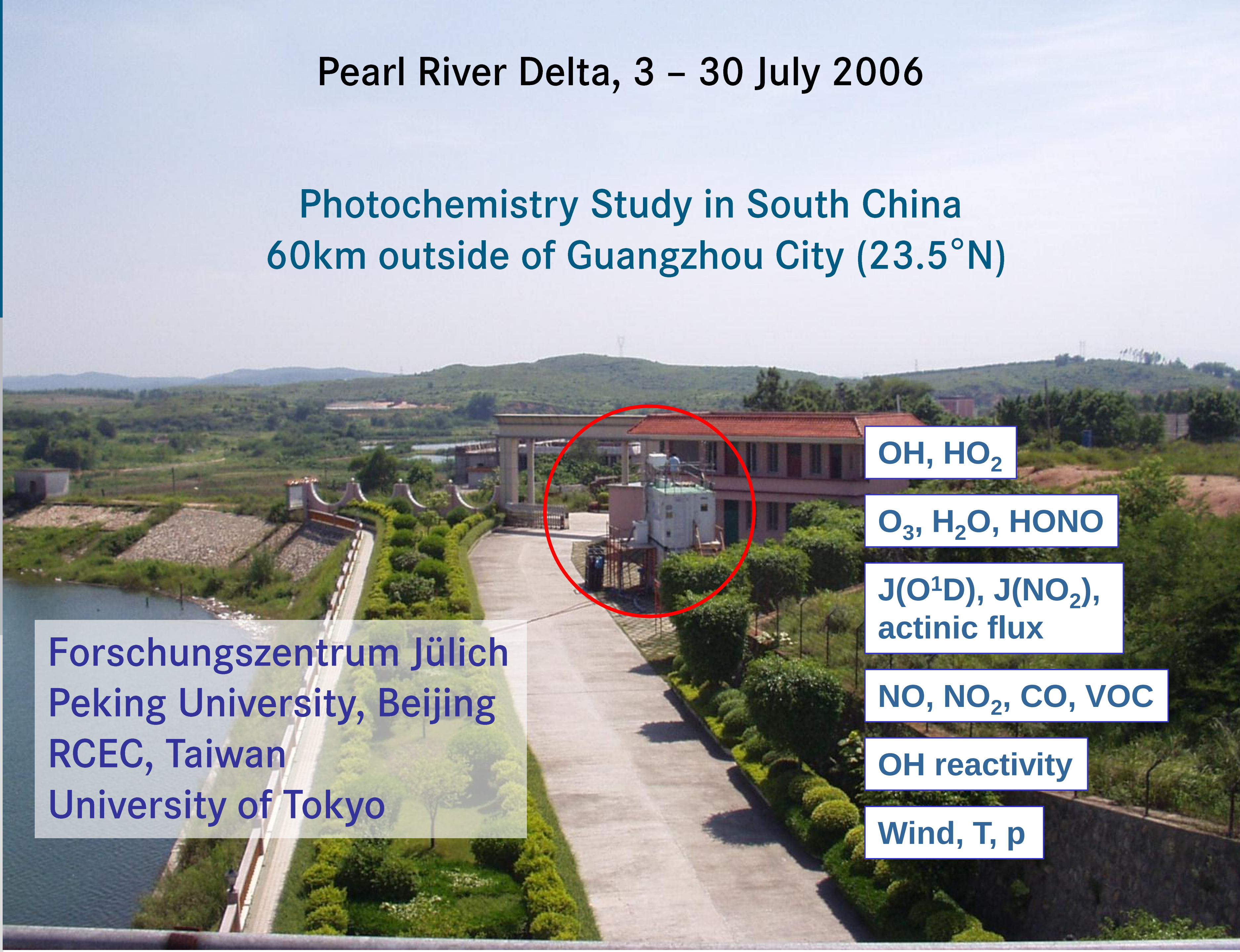
Hot Spots of Air Pollution



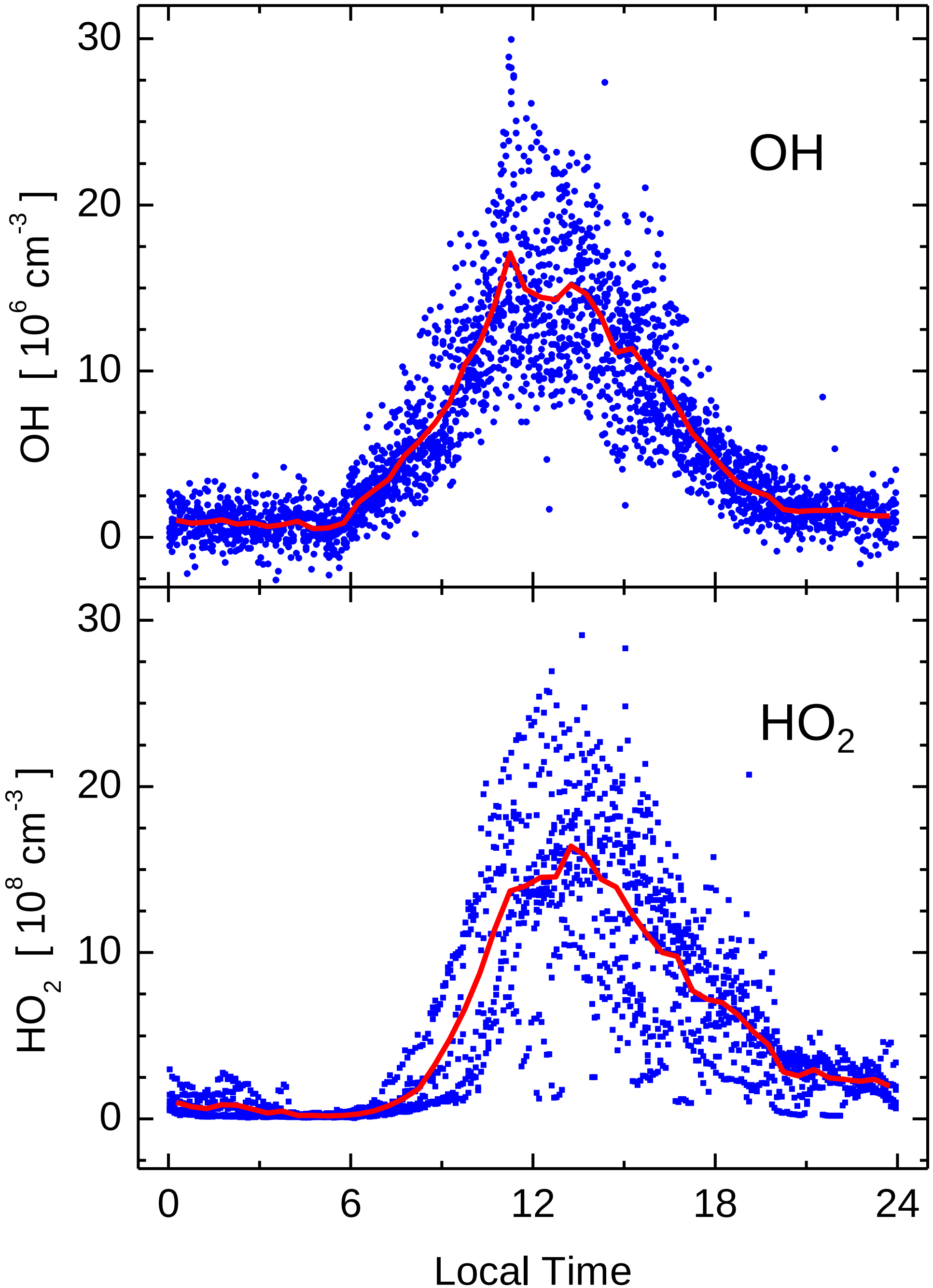
Satellite measurement of tropospheric NO_2 as seen by SCIAMACHY

Pearl River Delta, 3 – 30 July 2006

Photochemistry Study in South China
60km outside of Guangzhou City (23.5°N)



Forschungszentrum Jülich
Peking University, Beijing
RCEC, Taiwan
University of Tokyo



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Mean Diurnal Profiles

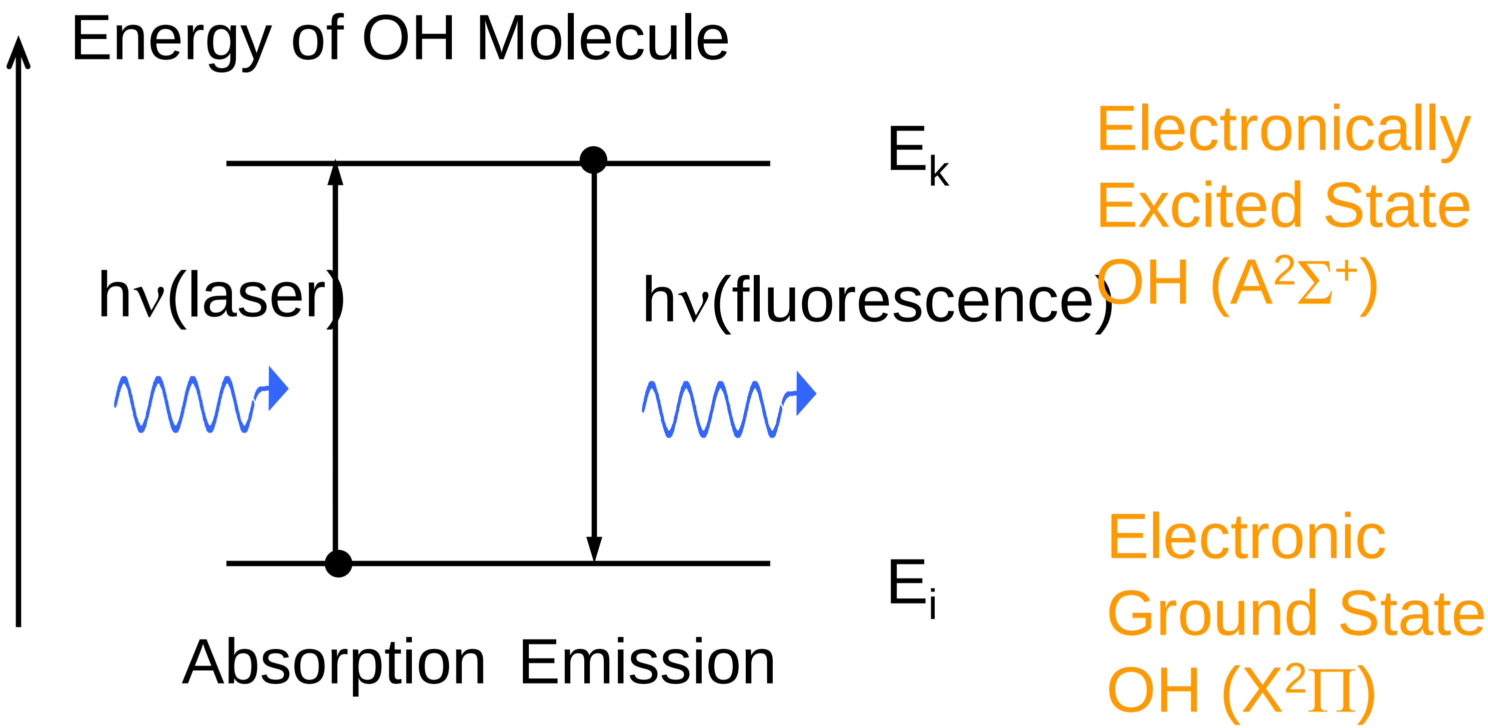
OH peak values
2 x 10^7 molecules / cm^3
~ 0.8 pptv

High photochemical activity !

HO_2 peak values
~ 80 pptv

(red line)	mean diurnal profiles
(dot)	individual data points

Laser Detection of OH Radicals



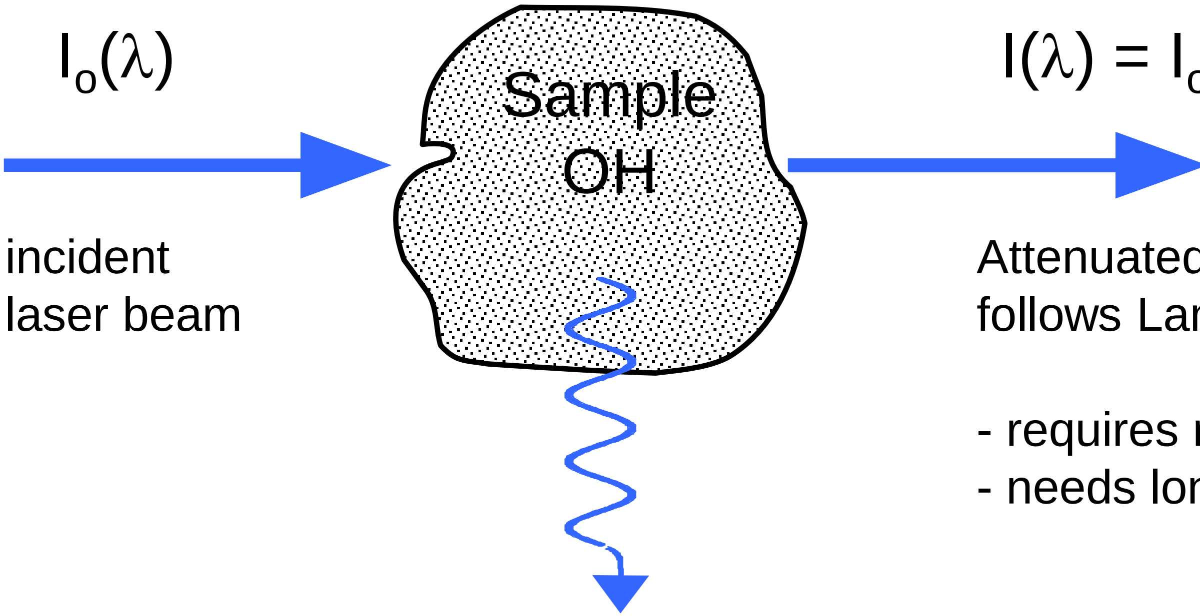
$$E_k - E_i = h\nu_{ik} = hc / \lambda_{ik}$$

h Planck's constant
c light velocity
ν frequency
λ wavelength

Laser Detection of OH Radicals

$I_o(\lambda)$

incident
laser beam



$I(\lambda) = I_o(\lambda)\, e^{-\sigma[OH]L}$

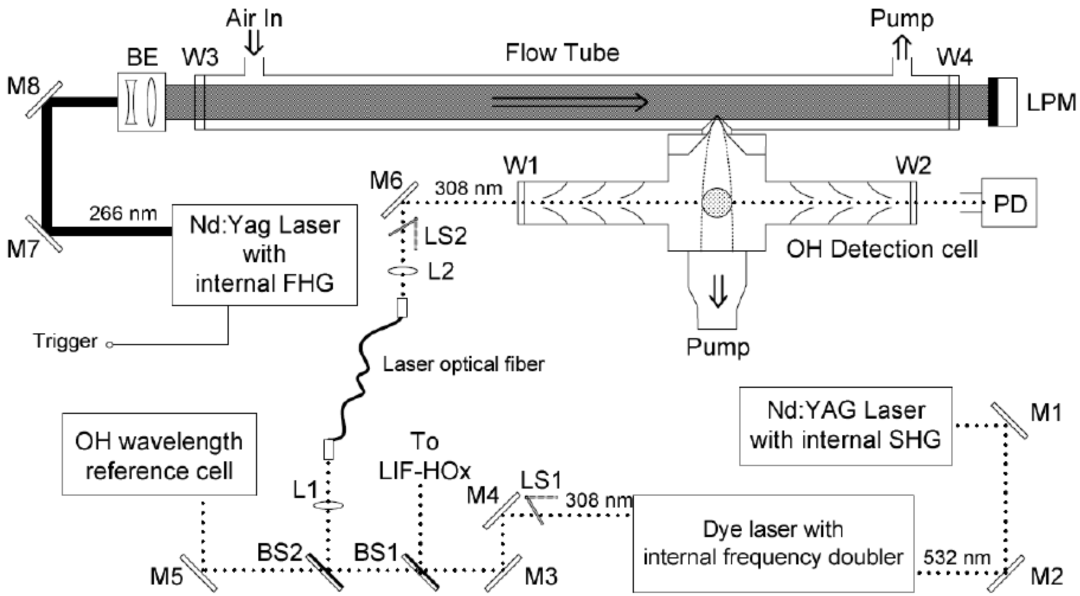
Attenuated laser beam
follows Lamber-Beer's law

- requires no calibration
- needs long light path (~ 1km)

Fluorescence $\Delta I \sim [OH]$

- requires calibration
- small detection volume (~ 1cm)

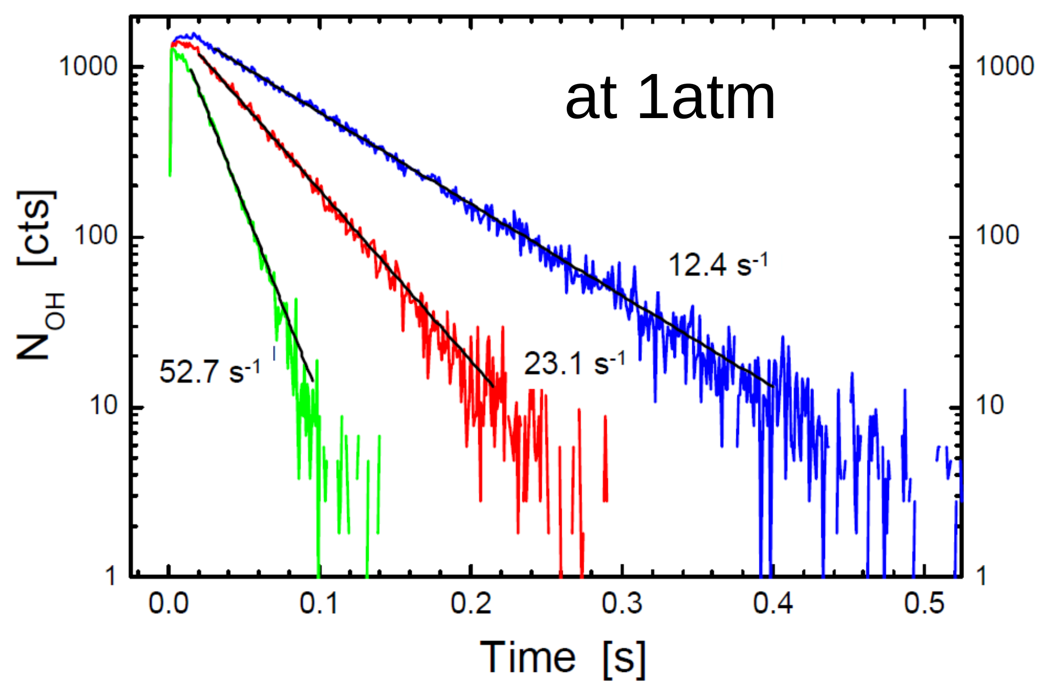
OH Reactivity Measurement in Ambient Air



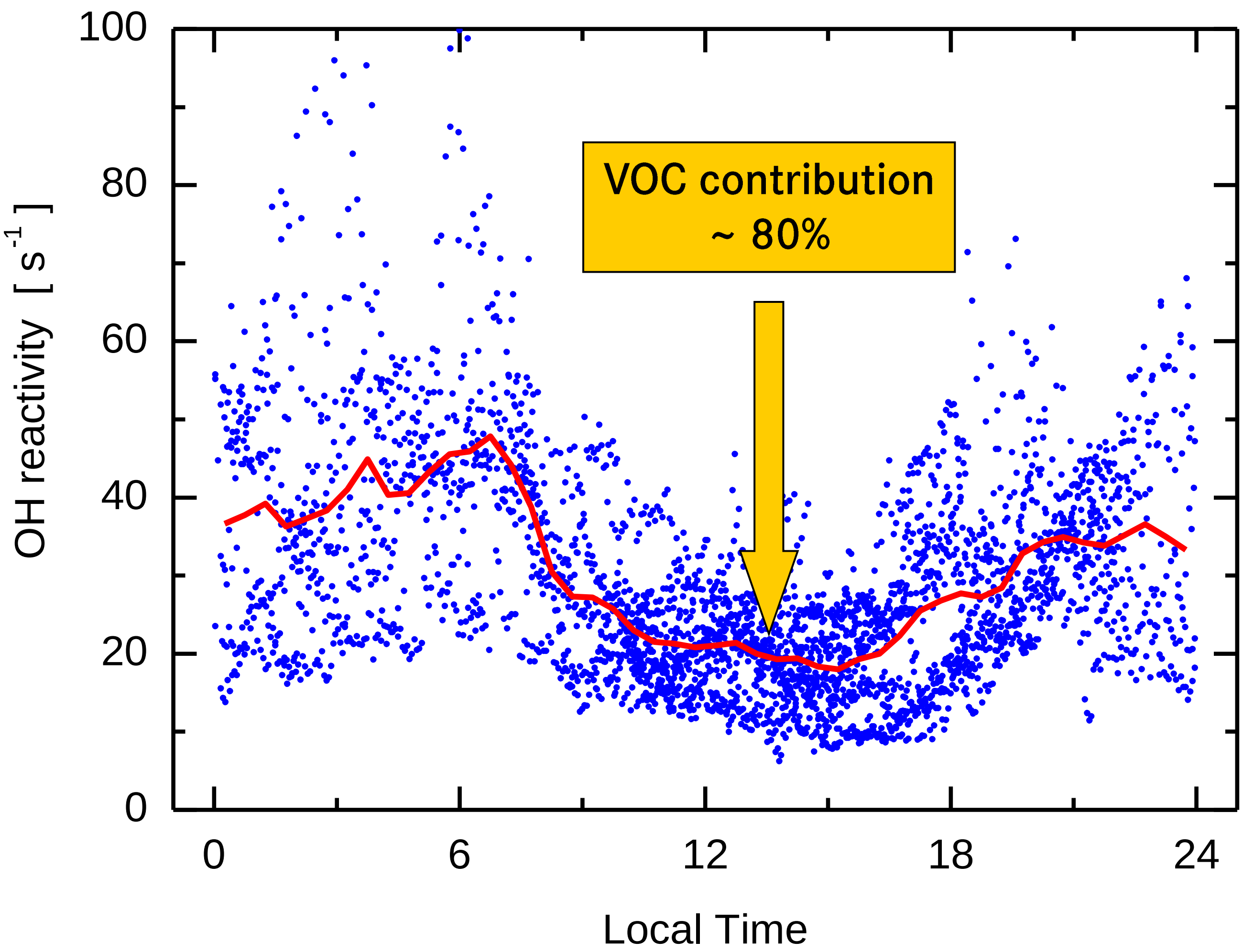
$$k_{OH} = \frac{1}{\text{OH lifetime}}$$

Laser-Flash Photolysis of O_3

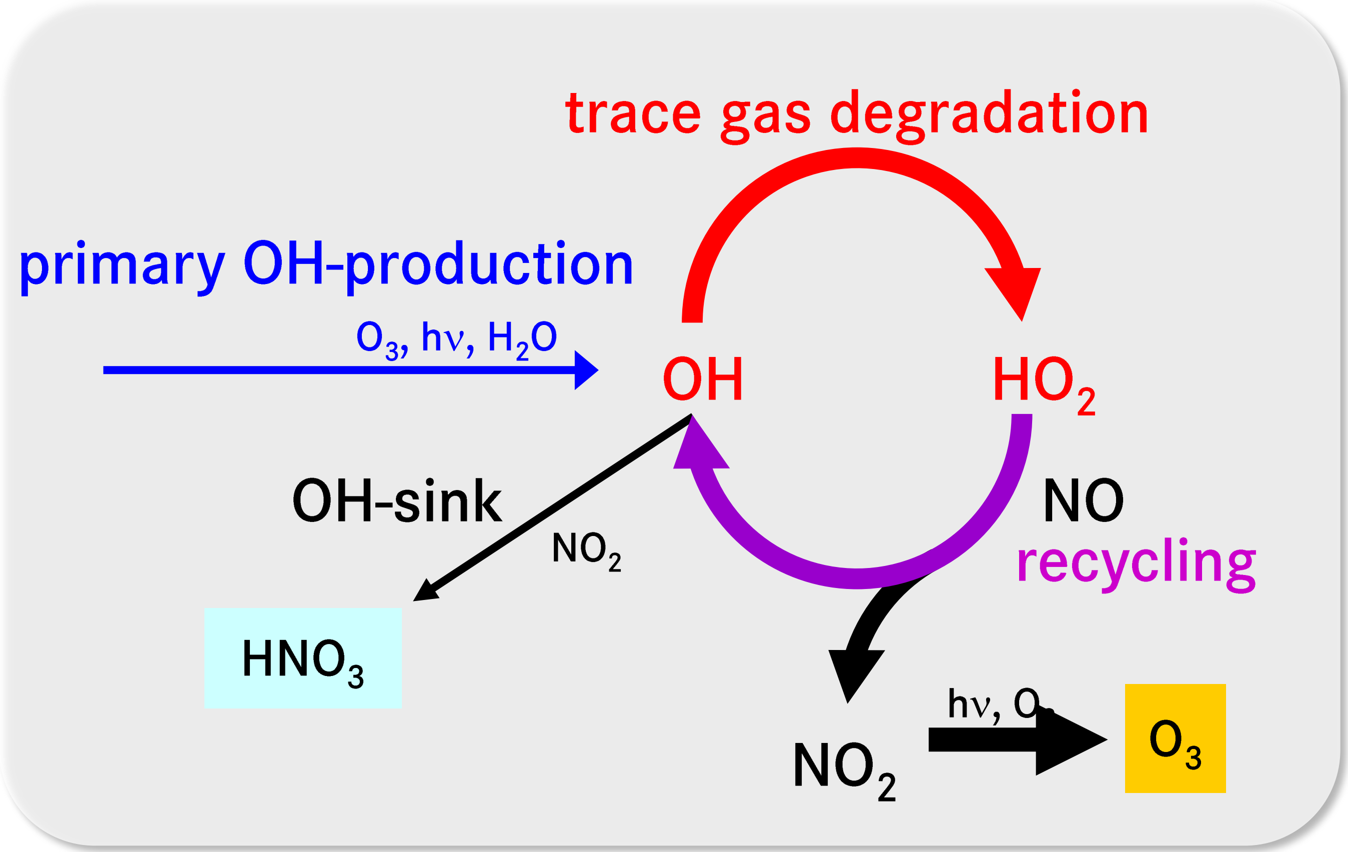
LIF Detection of OH Decay



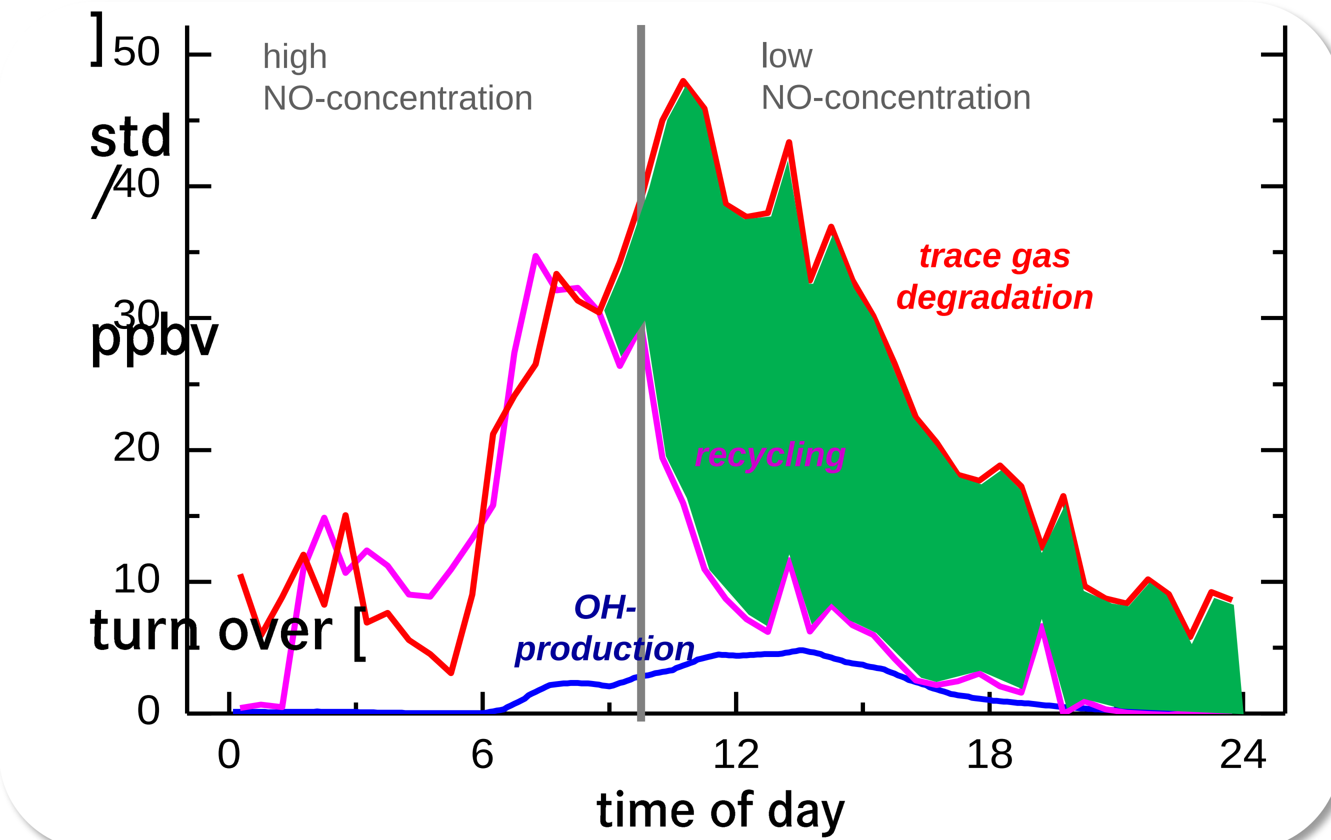
OH Reactivity Measured at PRD



Trace gas degradation in the troposphere (simplified)



Measurements:
balance not closed !



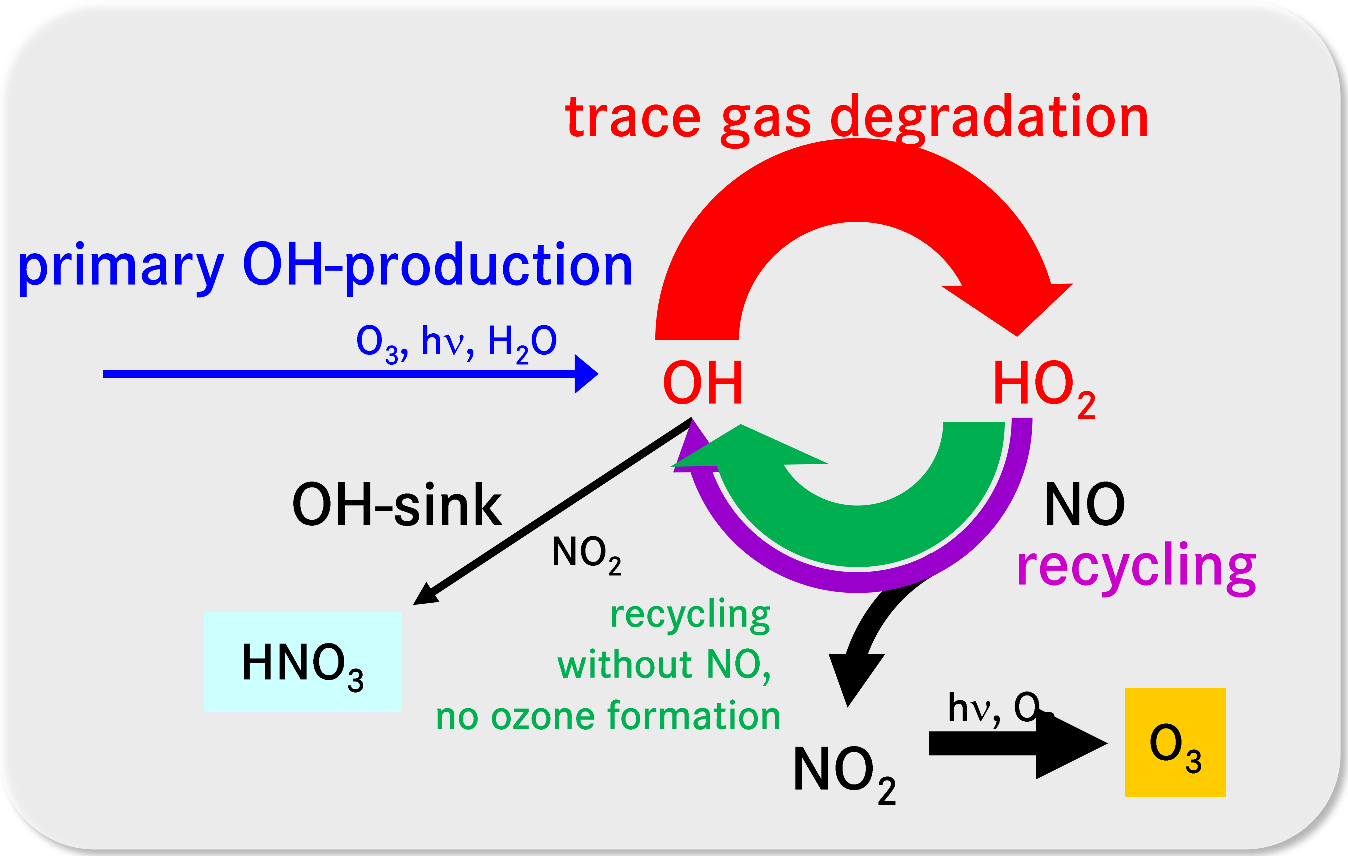
closed balance!

missing OH-formation !

Science magazine

Hofzumahaus et al., Science 324, 2009

Trace gas degradation in the troposphere new results (simplified)

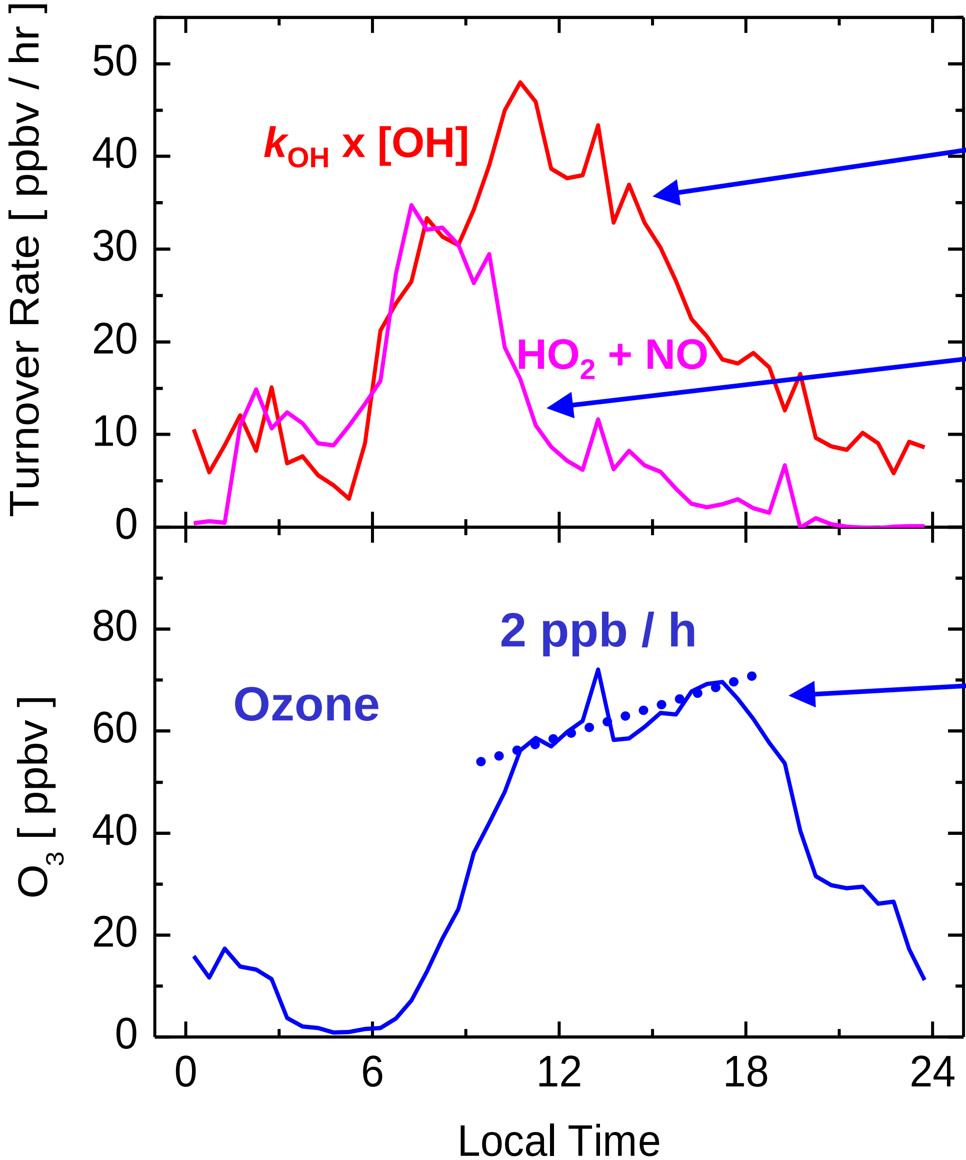


- increased trace gas degradation
- less ozone formation

in biogenic dominated regions

new understanding → climate, global air quality

Photochemical Ozone Formation



Expected ozone production from VOC oxidation rate ~ 60 ppb/h

$\Sigma(RO_2 + NO) + (HO_2 + NO)$ ~ 10 ppb/h

Observed ozone trend ~ 2 ppb/h

The unknown recycling seems to produce not much ozone !

Quantitative Experiments in Atmosphere-Simulation-Chamber

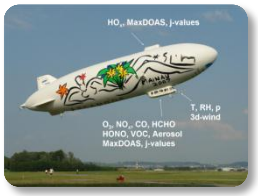
SAPHIR

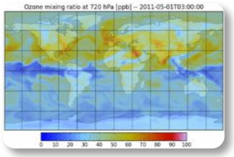
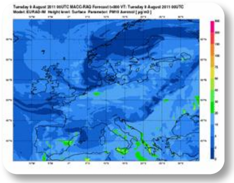
Atmospheric Research

- Future energy supply:
  supply, resources, protection of nature and climate, economy
- Impact of energy production and usage on air quality and climate

Observation	Simulation / Prozess Understanding	Modell






Scientific basis for societal and political decisions: Energy options, mitigation- and adaption strategies

Acknowledgments

Contributions to the PRIDE-PRD 2006 campaign

Forschungszentrum Jülich

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University of Tokyo

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