Chemical oxidation of greenhouse gases

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(representing a lot of work here in Chemistry)

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NERC SCIENCE OF THE ENVIRONMENT

National Centre for Atmospheric Science
NATURAL ENVIRONMENT RESEARCH COUNCIL

SEE – Chem meeting
5th January 2017 - Chemistry

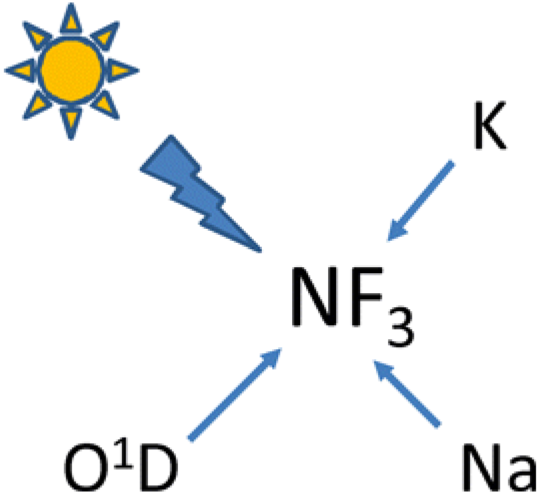
Oxidants

(initiators of removal under atmospheric conditions)

- OH
- O_3 (O_2 only for unstable radicals)
- NO_3 (night)
- Cl atoms
- Criegee intermediates
- $O(^1D)$
- $h\nu$
- Metals, Metals $^+$
- Other positive Ions (O^+, O_2^+)
- Redox-chemistry in solution (Cu^{2+}, Fe^{3+}, H_2O_2…..) (not today)

Much of the research here in Chemistry focusses on understanding the abundance and behaviour of these oxidants

“Unconventional” oxidants



Removal can mainly be in the mesosphere

Mesospheric removal of NF_3
Totterdill et al., JPC A, 2014

Lifetime = 550 years (excluding mesosphere)

Below 60 km removal dominated by reaction with O(^{1}D) and photolysis at $\lambda < 190$ nm

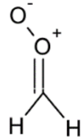
Above 60 km dominated by photolysis at $\lambda = 121.1$ nm, reactions with metal atoms less important

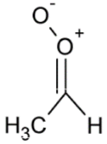
100 yr Global Warming Potential = 10,800 – 17,000 years

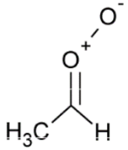
Going to restrict things to the troposphere (BL)

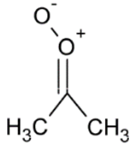
Newly discovered oxidant Criegee Intermediates

Dan Stone's NERC Fellowship


Formaldehyde oxide


Syn-acetaldehyde oxide


Anti-Acetaldehyde oxide


Acetone oxide

Novelli et al., ACPD, 2016

Formed from O_3 + alkenes, a source of OH

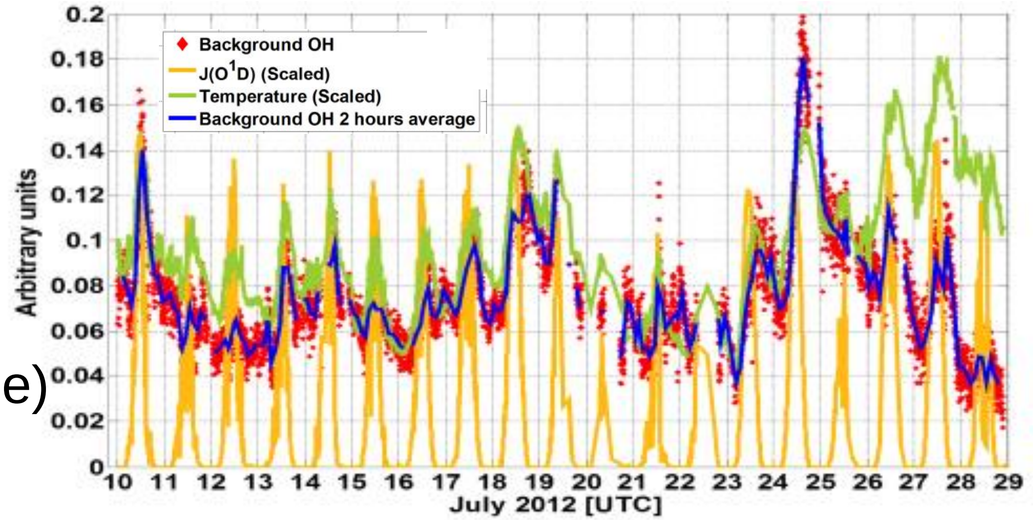
$CH_2OO + SO_2 \rightarrow HCHO + SO_3 \longrightarrow H_2SO_4$ (particle nucleation)

$CH_2OO + (H_2O)_2 \rightarrow HO\text{–}CH_2OOH + H_2O$ $k = (4.0\pm1.2)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}

Stone et al., PCCP, 2014; Lewis et al., PCCP 2015

Field measurement of Criegee intermediates in Boreal forest in Finland?

[Criegee] ~ 5×10^4 cm^{-3} (+/- big range)



Novelli et al., ACPD,. 2016

Scientists flag new causes for surge in methane levels
Paul Voosen (December 22, 2016)
Science **354** (6319), 1513. [doi: 10.1126/science.354.6319.1513]

Heavy rains in recent years may have boosted microbial production of methane in tropical wetlands.

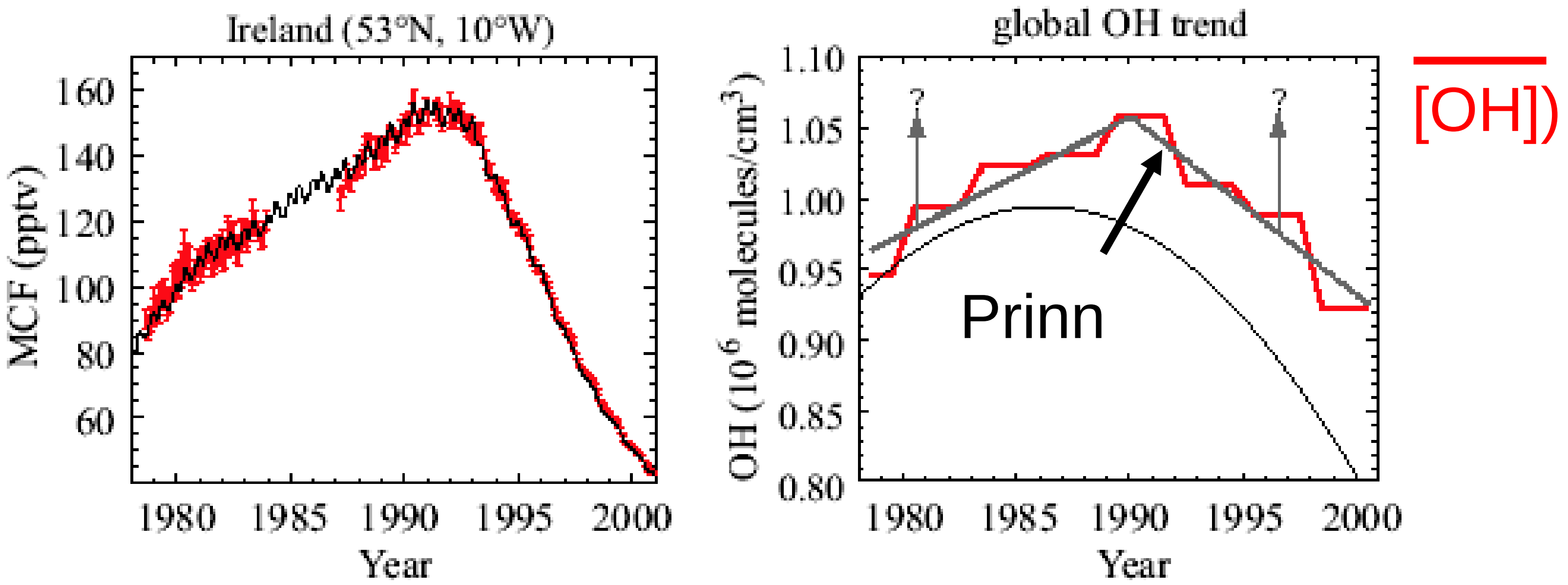
ATMOSPHERIC CHEMISTRY

Scientists flag new causes for surge in methane levels

Swelling tropical wetlands and a decline in a natural atmospheric detergent are leading suspects

Are global levels of OH going down?
(Joey’s talk)

Global mean [OH] since 1978 – estimated using CH_3CCl_3

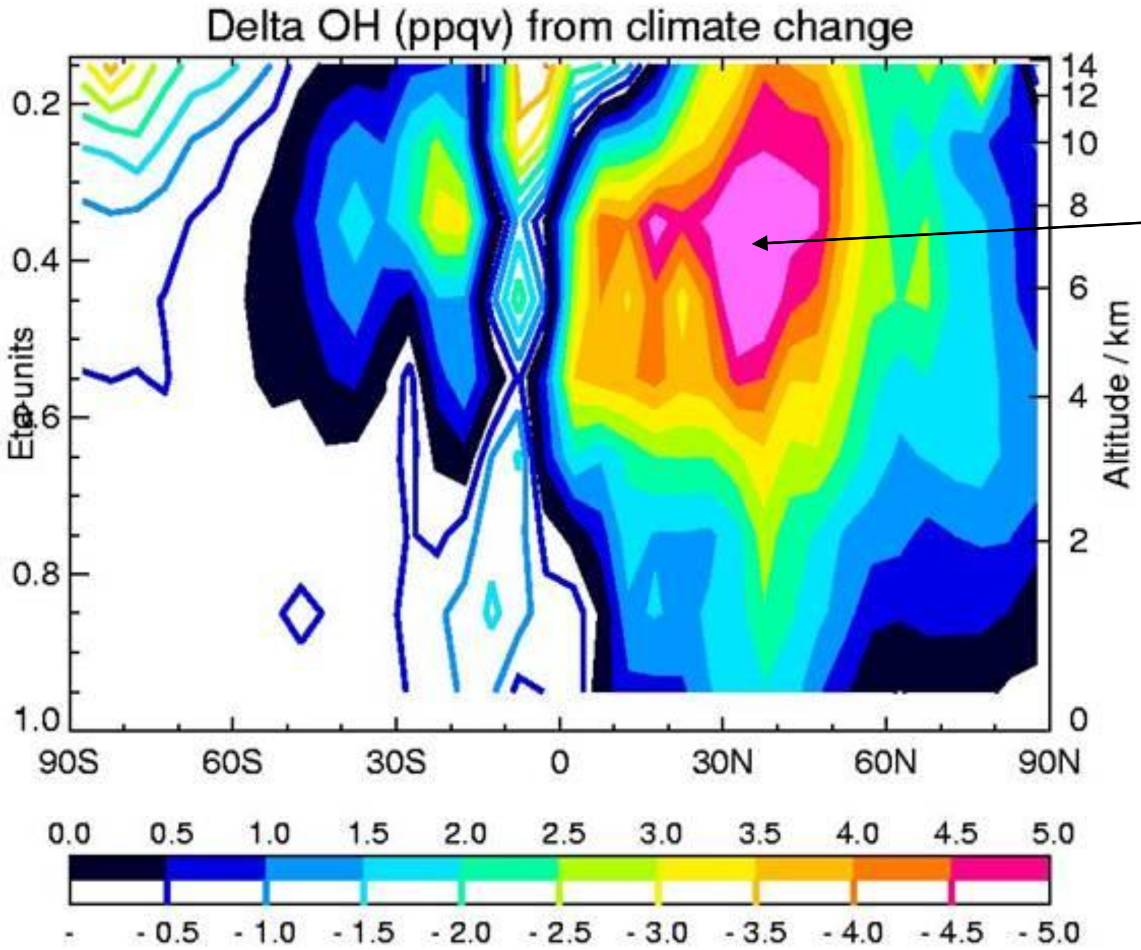


Leilieveld et al., *ACP,* **4**, 2337 (2004)

No <u>significant</u> global change in OH concentrations for ~ 20 years

It is getting harder to use this method as methyl chloroform was banned by the Montreal Protocol to protect the ozone layer – and its concentration is getting lower and lower

How will climate change affect global OH?



Δ(OH) = 0.005 ppt

~7x10^4 cm^{-3} at 5 km

Zonal mean change in [OH] from 1990s – 2020s
(Model run with climate change – run with fixed climate)

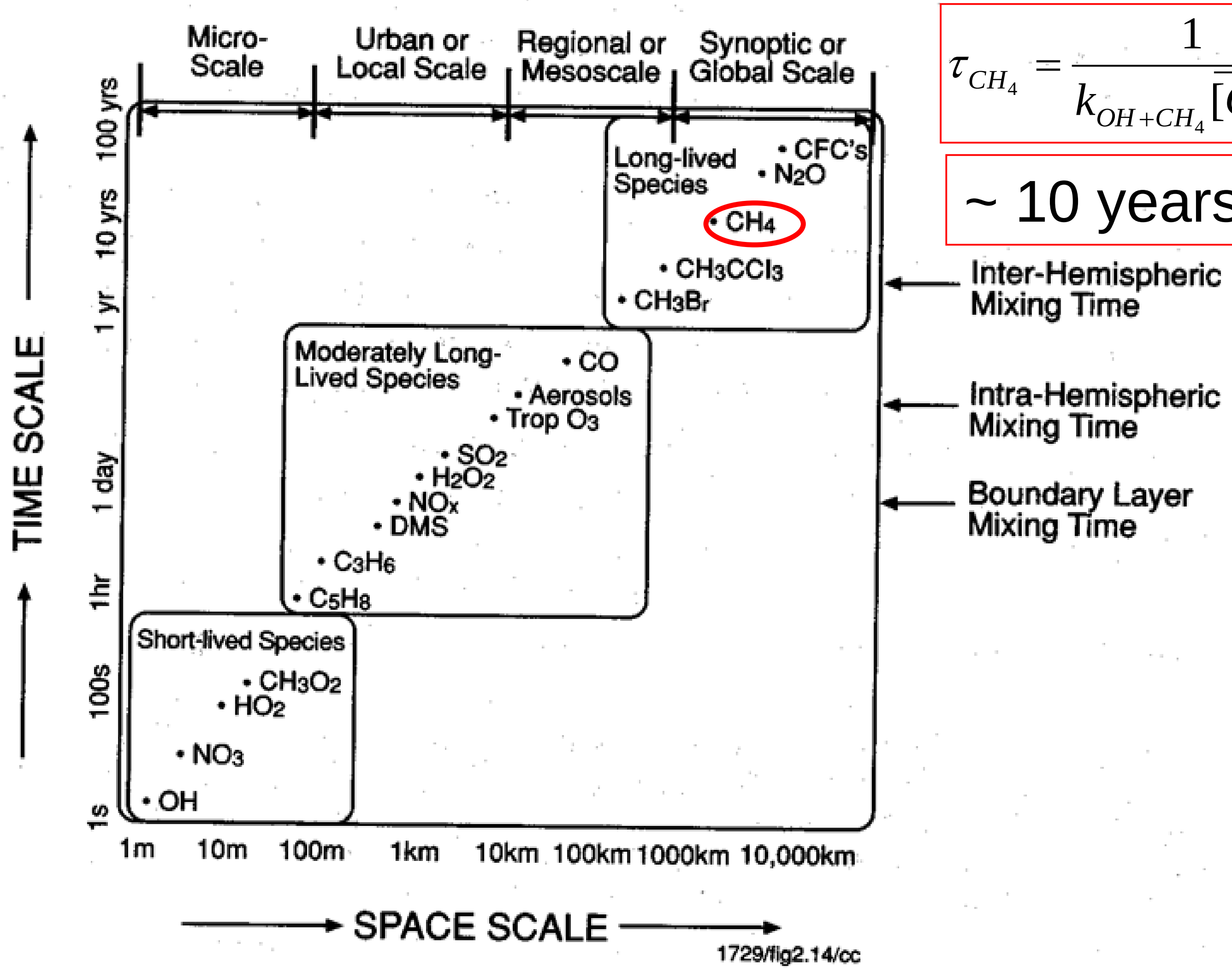
Stevenson et al., *Faraday Disc*. 130, 41 (2005)

ATMOSPHERIC LIFETIME

For many trace gases removed by OH,

$$\tau_X = \frac{1}{k_{OH+X}\overline{[OH]}}$$

Figure 3.15. *The spatial and temporal scales of variability for atmospheric constituents in the atmosphere (courtesy of W. L. Chameides).*

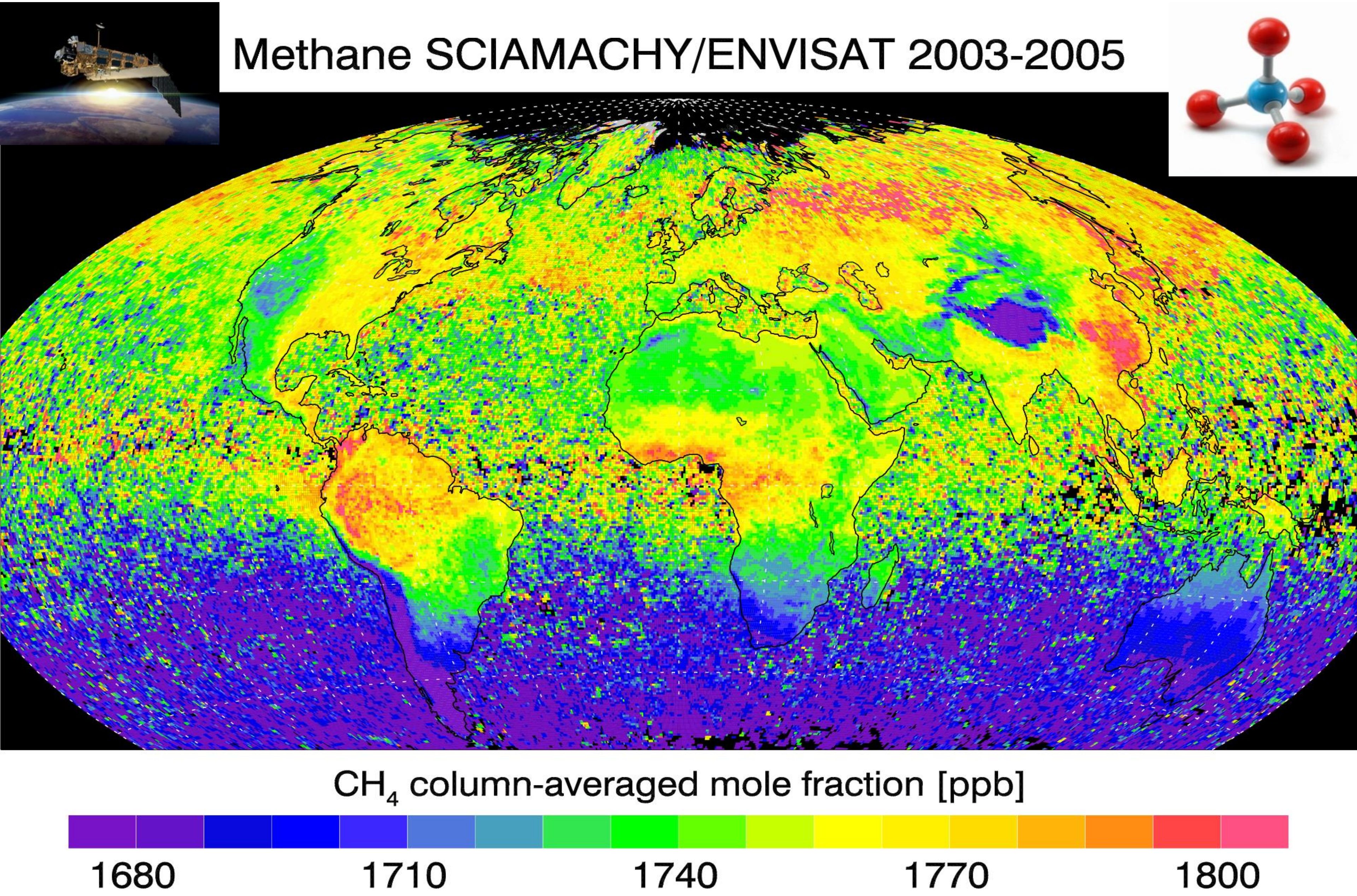


$$\tau_{CH_4} = \frac{1}{k_{OH+CH_4}\overline{[OH]}}$$

~ 10 years

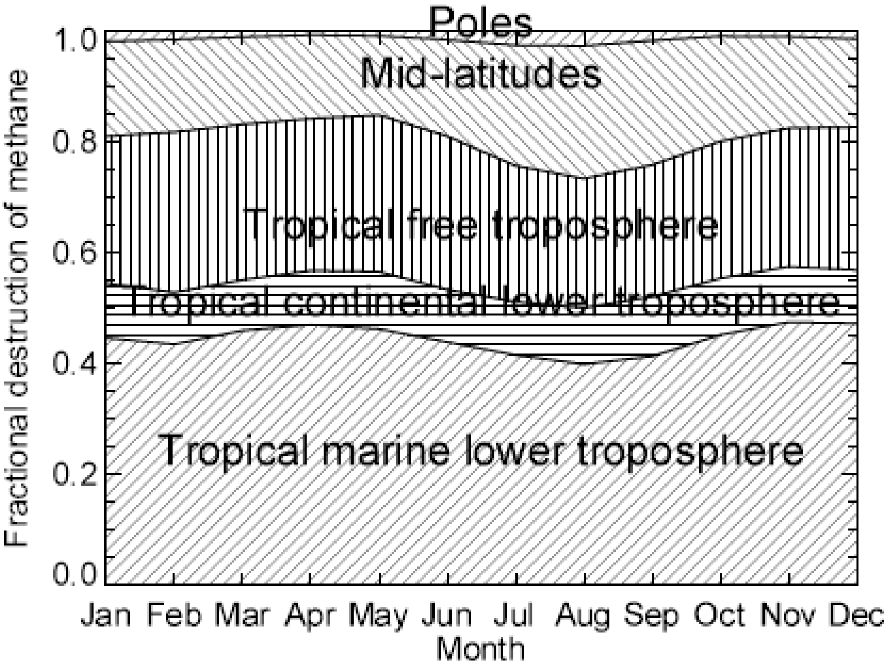
See Ravishankara, JCS Faraday Trans., 90, 2159 (1994)

Methane SCIAMACHY/ENVISAT 2003-2005



Methane removal

Dominant – reaction with OH (>80%)



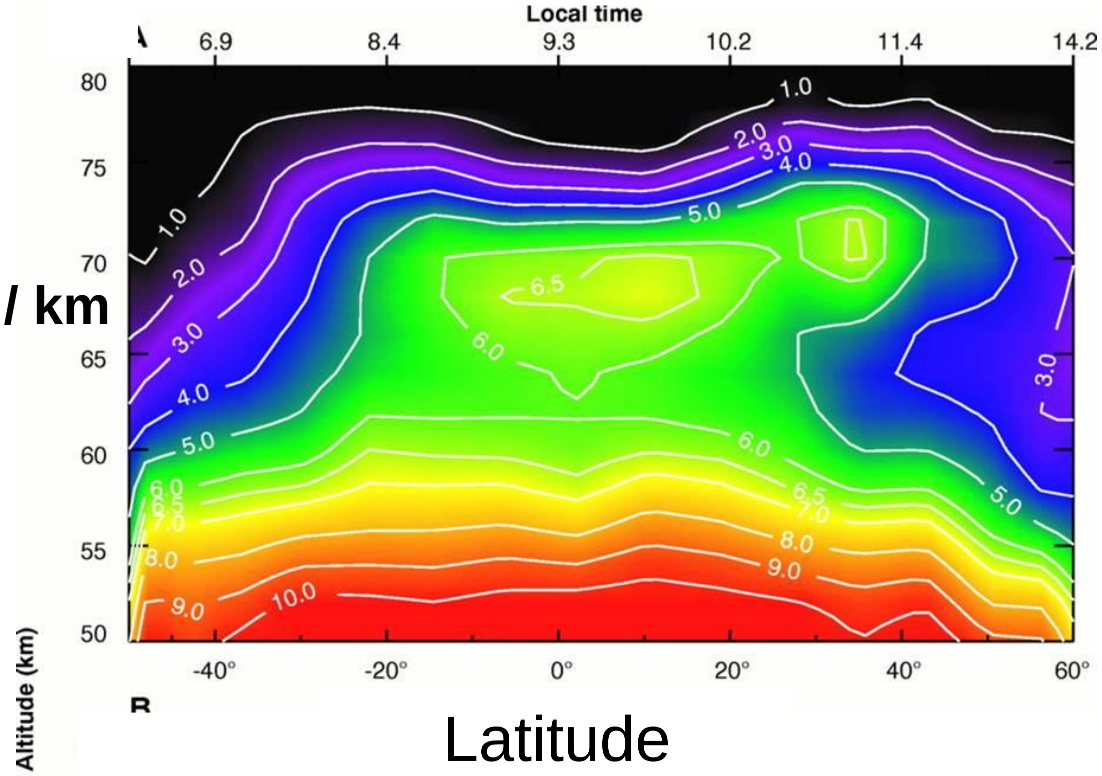
Bloss et al., *Faraday Trans*. **130**, 425 (2005)

So need to understand distribution of OH, and what controls its production and loss

Minor sinks:
(1) Cl atoms, lifetime ~ 50 years
(2) Stratosphere (also O^1D)
(3) Soils

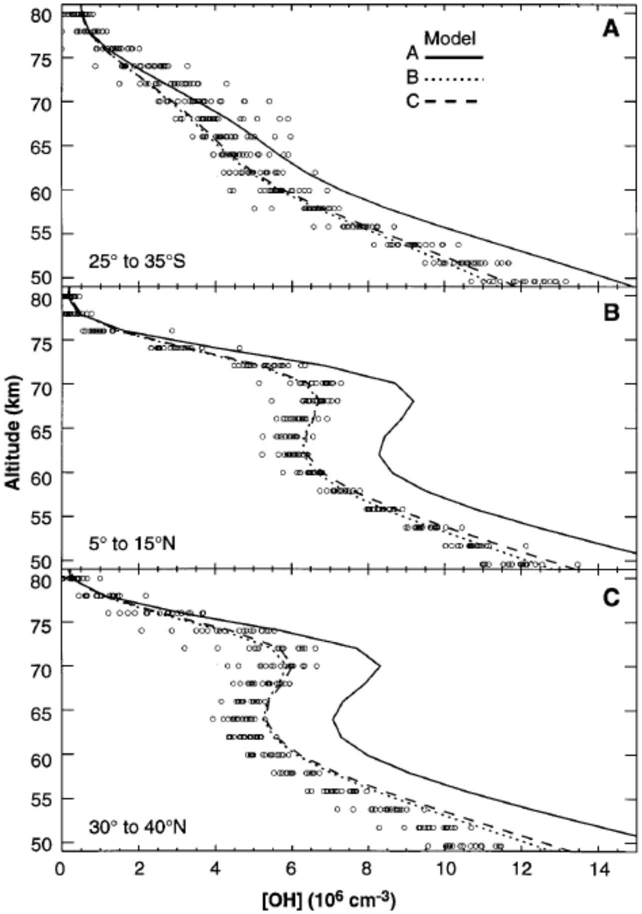
Satellite global measurements of OH – only at higher altitudes

MAHRSI OH number density (units of 10^6 cm^{-3}) on 5 November 1994



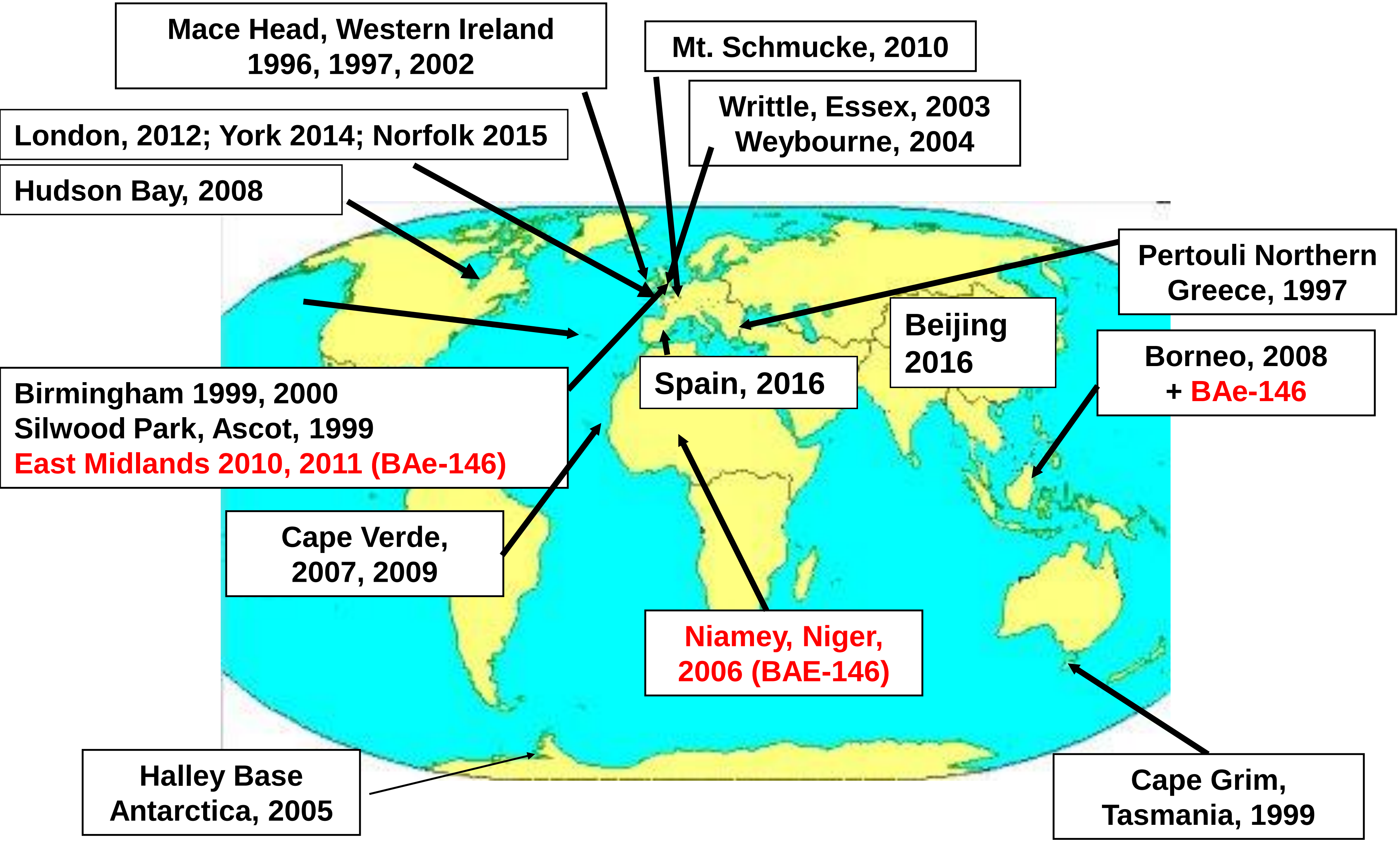
z / km

Latitude



Summers et al., Science (1997)

Surface OH measurements (by Leeds)



Mace Head, Western Ireland
1996, 1997, 2002

Mt. Schmucke, 2010

Writtle, Essex, 2003
Weybourne, 2004

London, 2012; York 2014; Norfolk 2015

Hudson Bay, 2008

Pertouli Northern
Greece, 1997

Beijing
2016

Borneo, 2008
+ BAe-146

Spain, 2016

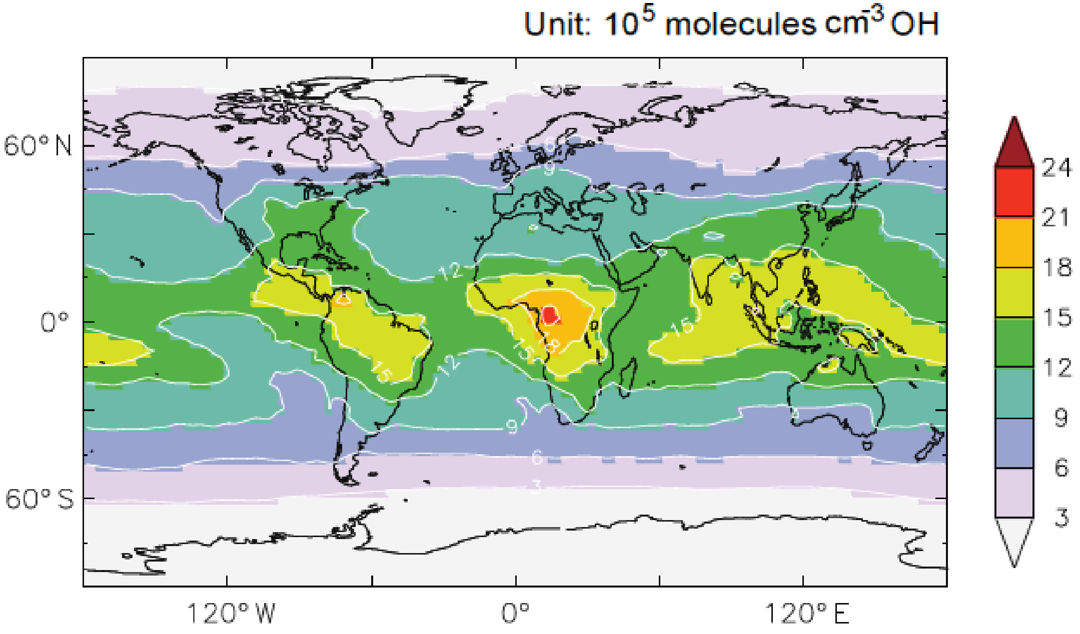
Birmingham 1999, 2000
Silwood Park, Ascot, 1999
East Midlands 2010, 2011 (BAe-146)

Cape Verde,
2007, 2009

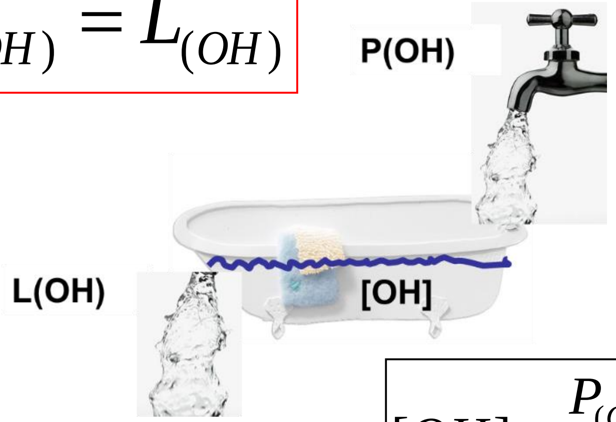
Niamey, Niger,
2006 (BAE-146)

Halley Base
Antarctica, 2005

Cape Grim,
Tasmania, 1999



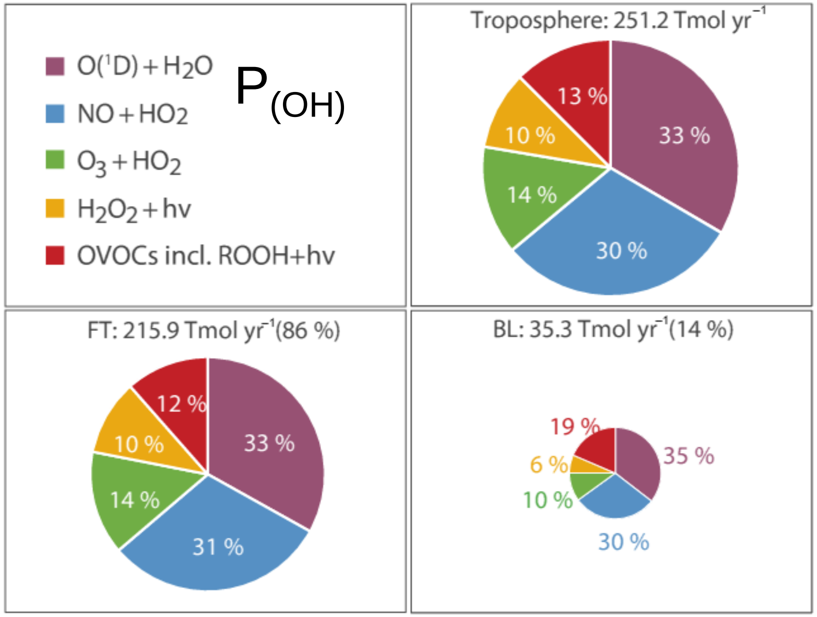
$$\boxed{P_{(OH)} = L_{(OH)}}$$

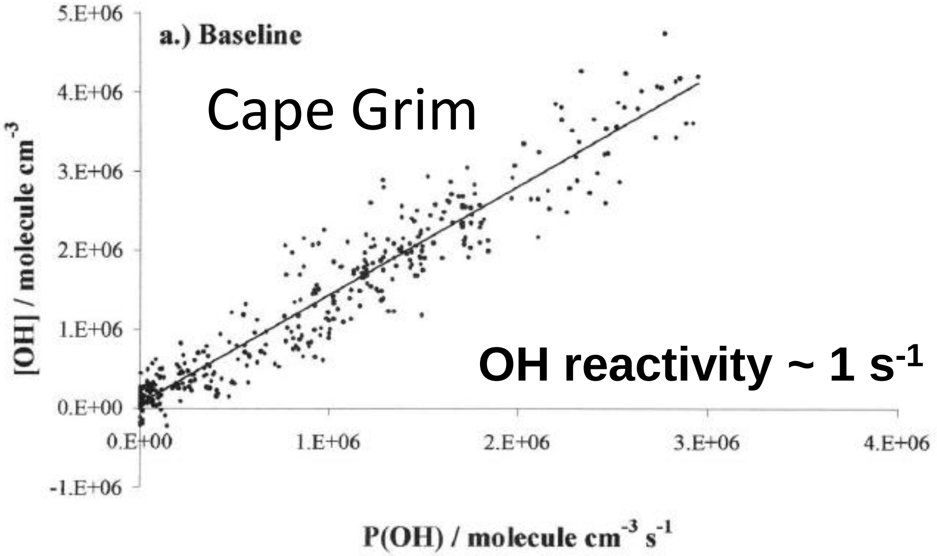


$$L(OH) = [OH] \times k'_{OH}$$

$$\boxed{[OH] = \frac{P_{(OH)}}{k'_{OH}}}$$

OH reactivity





Cape Grim

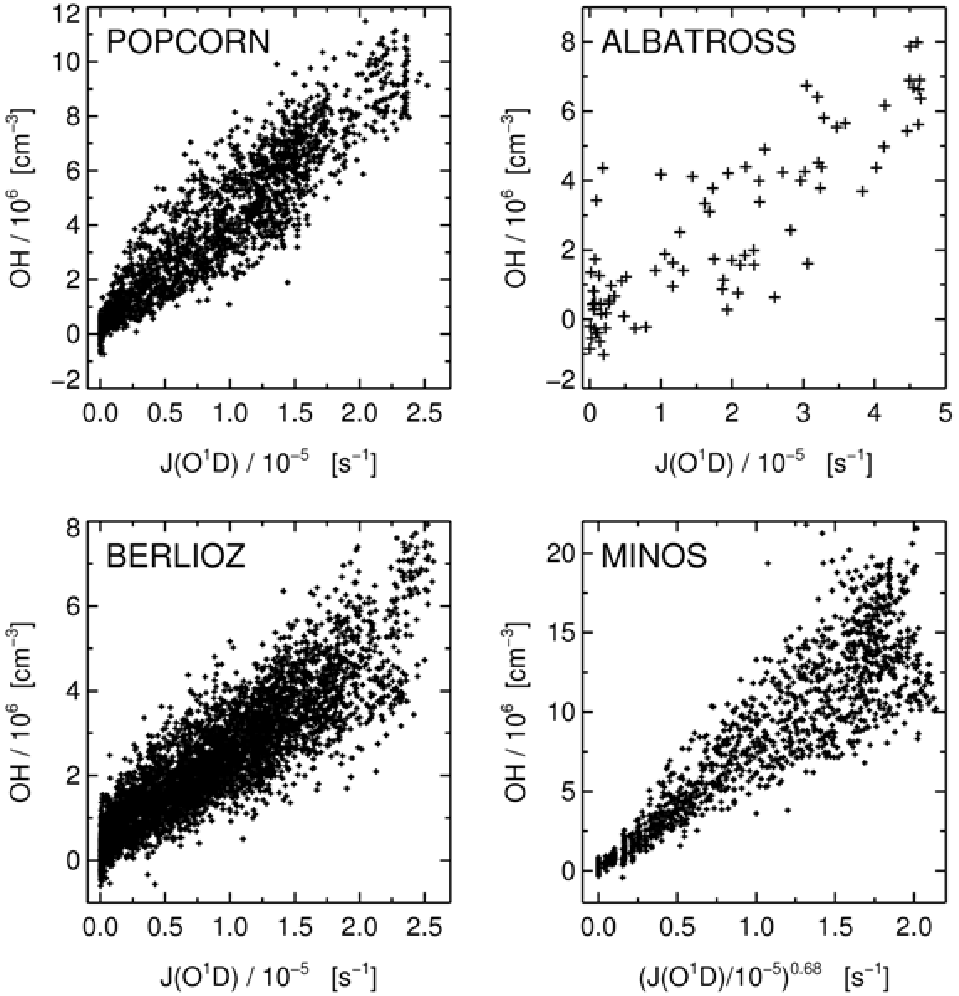
OH reactivity ~ 1 s^{-1}

Lelieveld et al., ACP 2016

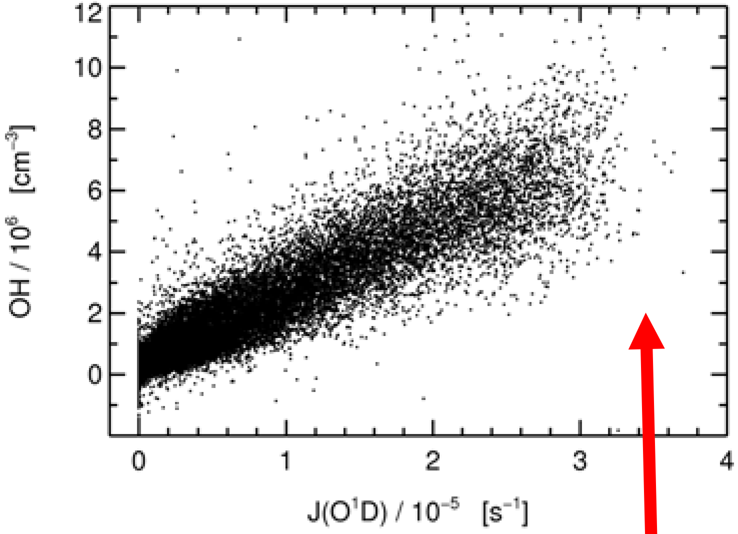
Creasey et al JGR, 2003

Can we parameterise OH for use in global models?

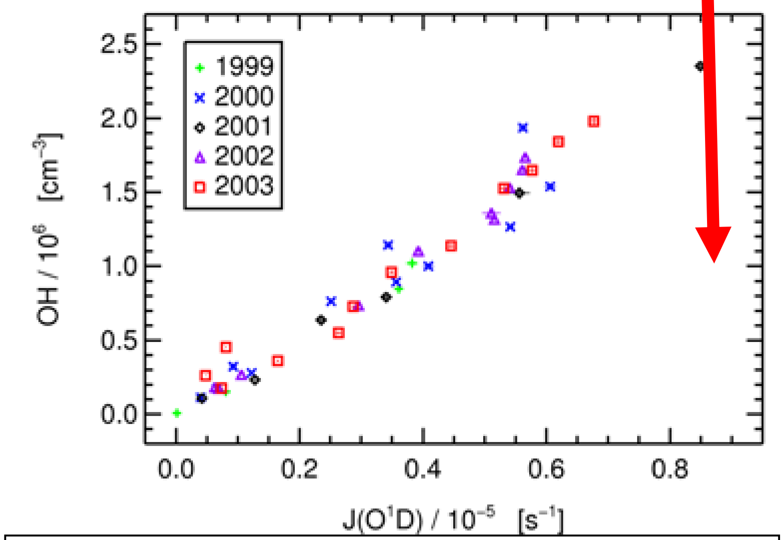
Rohrer and Berresheim,
Nature, 442, 184, 2006



$$[\mathrm{OH}] = a \times \{ j(\mathrm{O^1D}) / 10^{-5}\ \mathrm{s^{-1}} \}^{b} + c$$

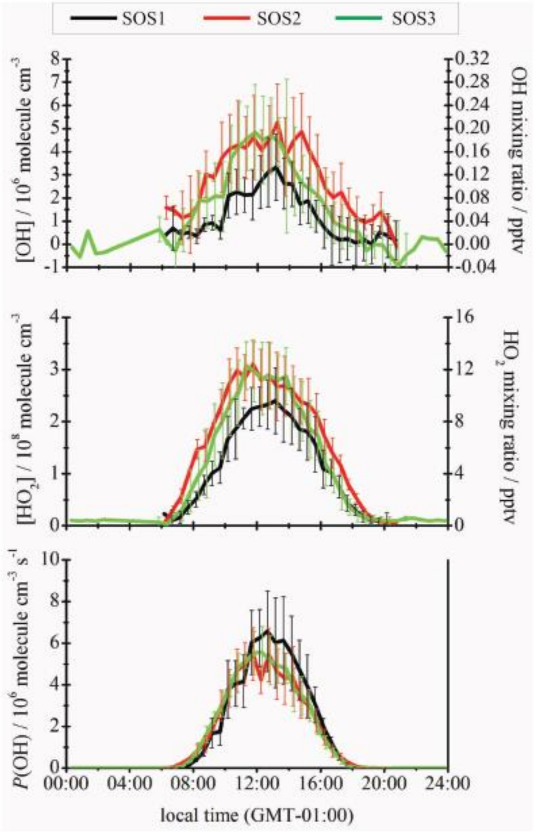


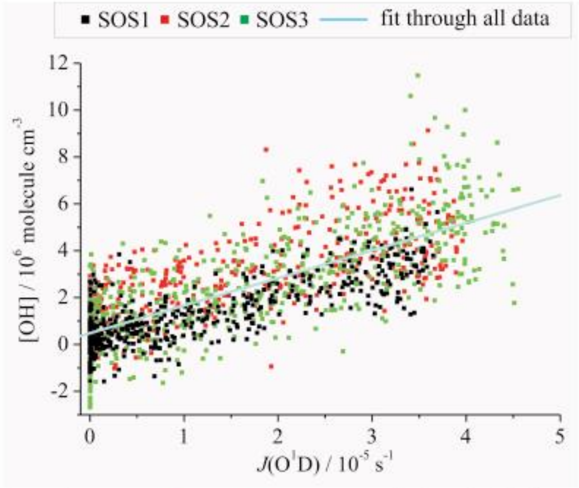
5 year study in
Southern Germany

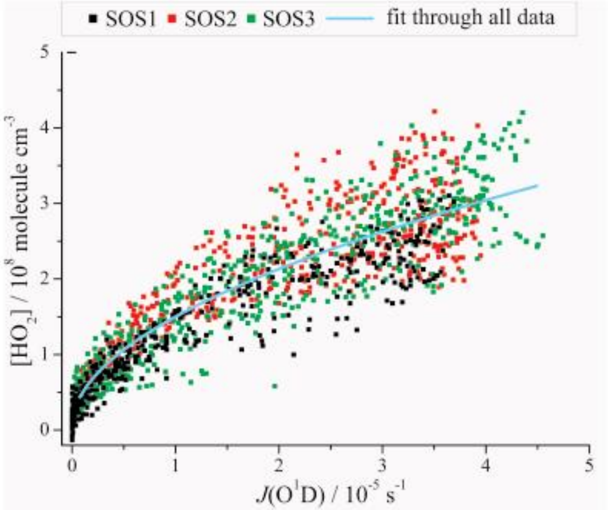


There is no 5 year OH trend

Seasonal observations of HOx at Cape Verde (Vaughan et al., ACP, 2012)





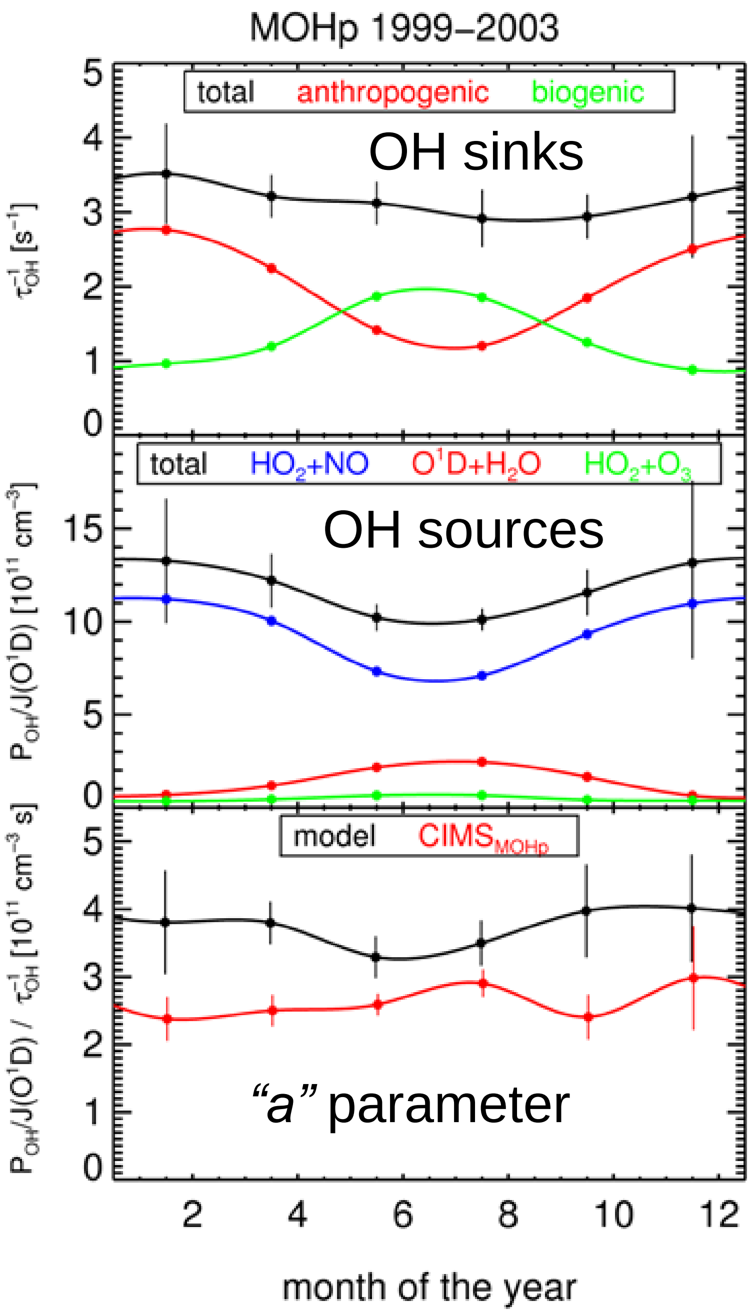


Richard Honrath was interested in establishing long term OH measurements at Pico (Azores)

$$[\mathrm{OH}] = a \times \{\, j(\mathrm{O}^{1}\mathrm{D}) / 10^{-5}\ \mathrm{s}^{-1}\}^{b} + c$$

	a	*b*	*c*
OH / 10^5 cm^{-3}			
Halley, Antarctica	**2.52 ± 0.16**	**0.74 ± 0.04**	**1.06 ± 0.12**
Brauers *et al*. (2001) ALBATROSS, Tropical Atlantic	13.7	1 (fixed)	0 (fixed)
Holland *et al*. (2003) BERLIOZ – Rural Germany	20[1]	1 (fixed)[1]	0 (fixed)[1]
Smith *et al*. (2006) NAMBLEX, Mace Head, Ireland	14.7	0.84 ± 0.05	4.4
Rohrer & Berresheim (2006) Hohenpeissenberg Observatory	24	1	1.3

Although all datasets fit equation reasonably well, the values of *a, b* and *c* are site-dependent, and are not known *a priori*



Rohrer and Berresheim,
Nature, 442, 184, 2006

$$\boxed{[\mathrm{OH}] = a \times \{ j(\mathrm{O^1D}) / 10^{-5}\ \mathrm{s^{-1}}\}^{b} + c}$$

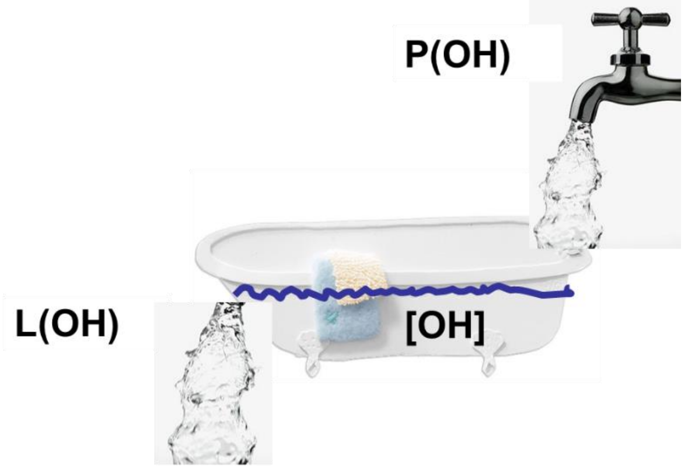
Southern Germany

It is surprising that 5 years of data (what an achievement!) fit this simple equation and that each season can be represented by the same set of parameters (There is no 5 year OH trend)

However, at this site there is a balancing out of sources and sinks during the year.

We need measurements of [OH] in a wide variety of environments in order to define an "OH index" of a, b, and c

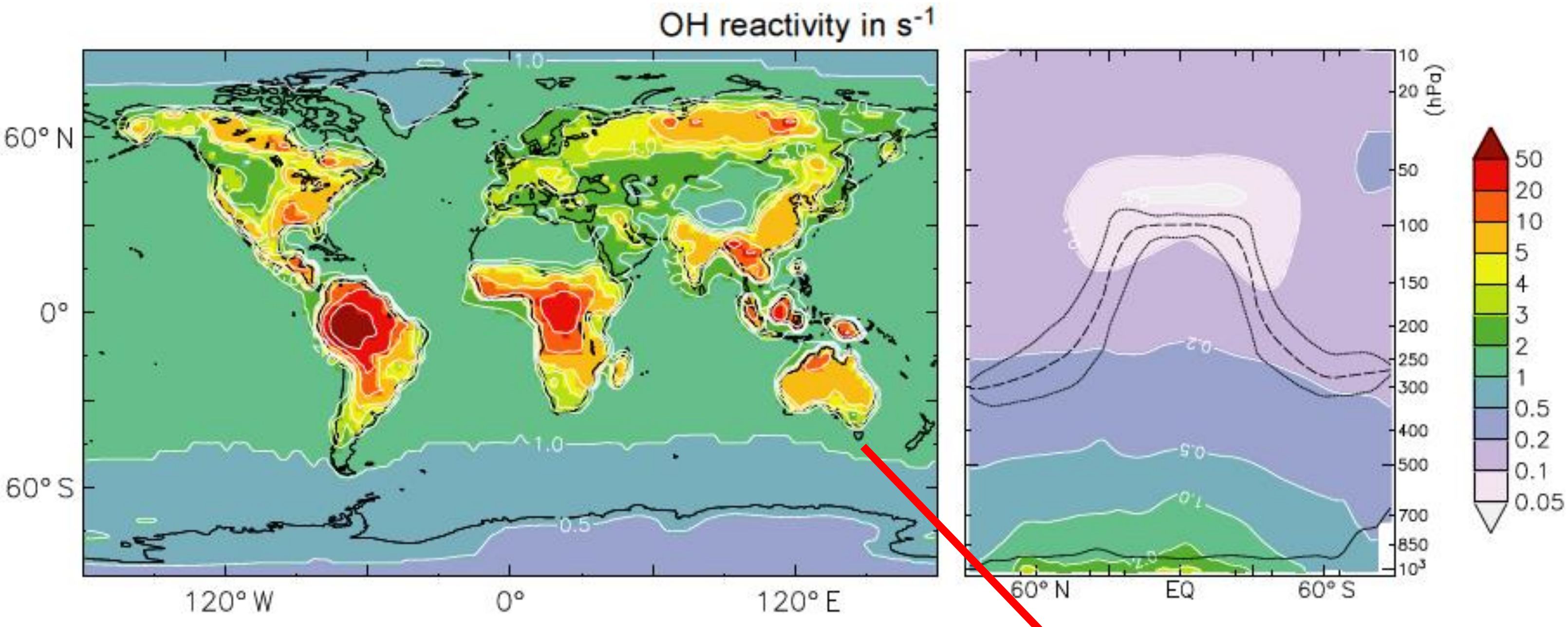
More about OH sinks



OH reactivity, k'_{OH}

$k'_{OH} = \Sigma_X k_{OH+X}[X]$

$$L(OH) = [OH] \times k'_{OH}$$

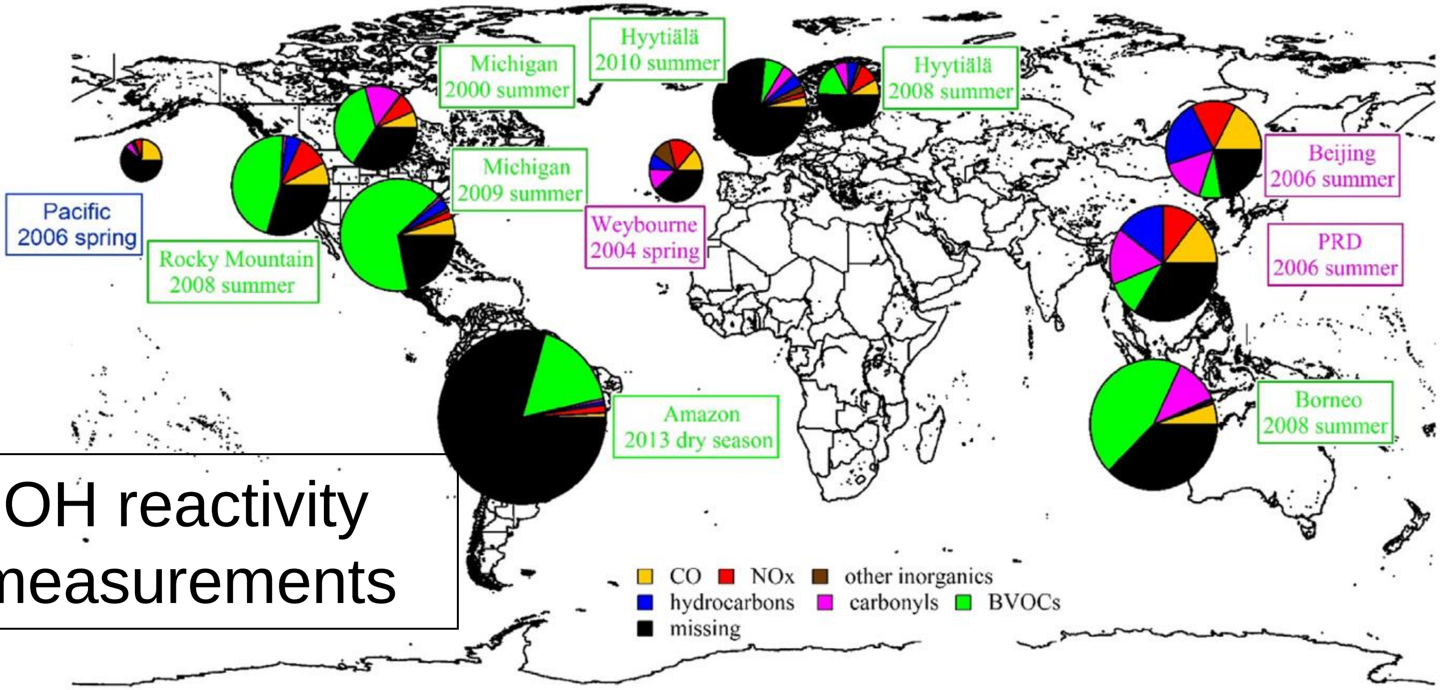


Lelieveld et al., ACP 2016

Cape Grim
OH lifetime ~ 1s

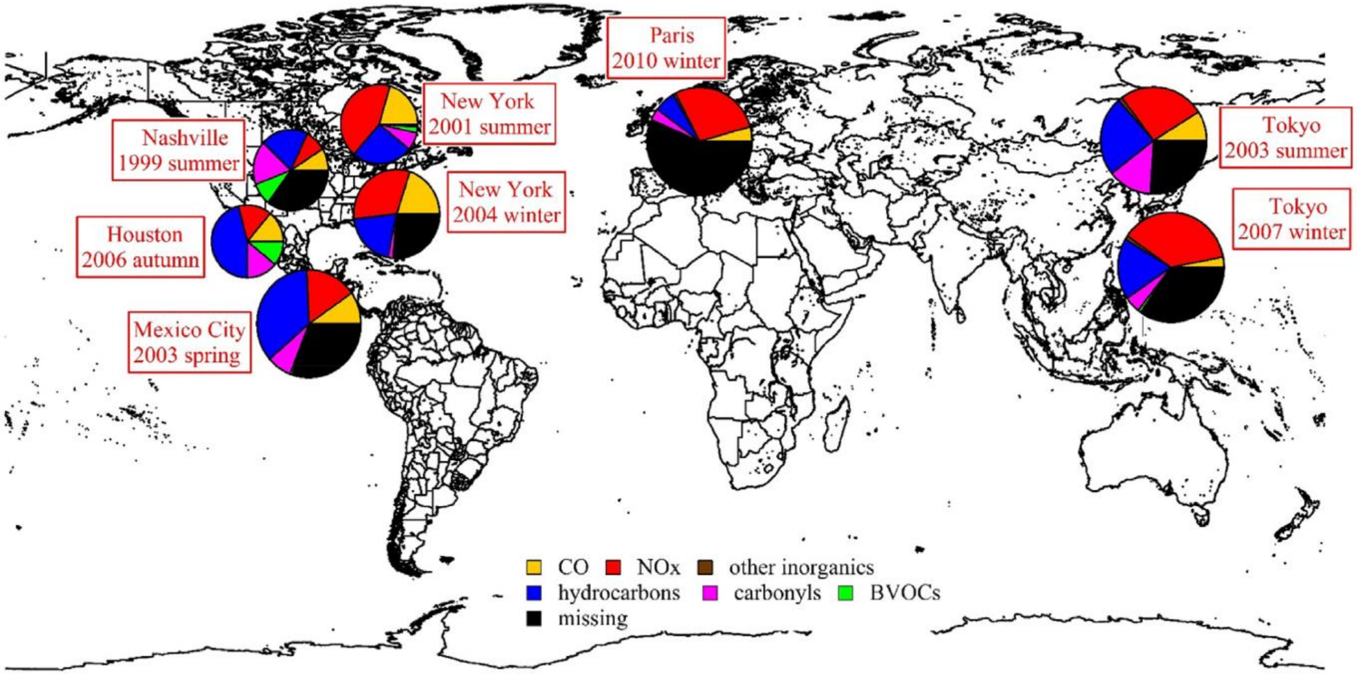
OH reactivity measurements

“Clean” sites



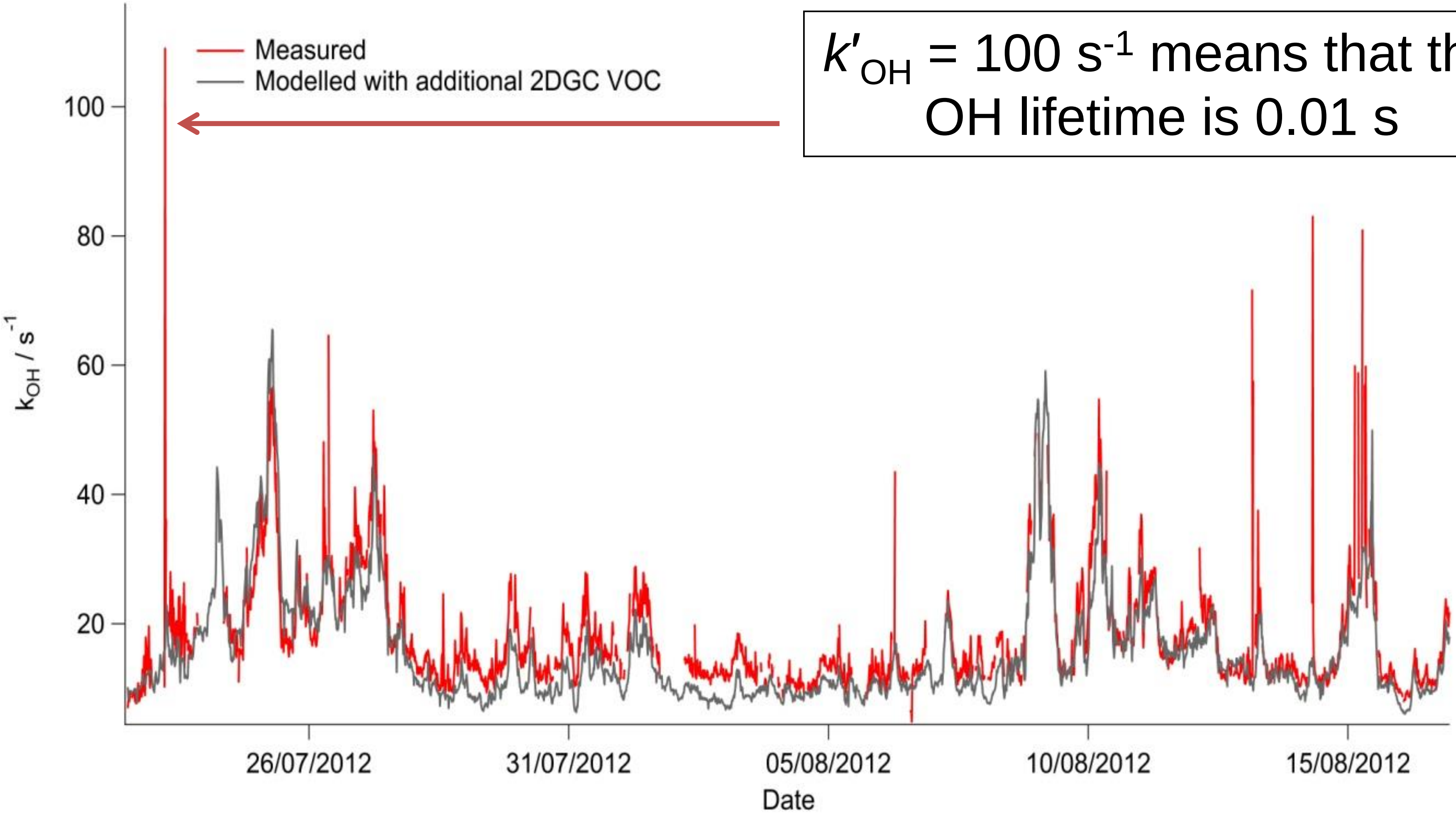
Yang et al.
Atm. Env.,
2016

Urban sites



OH reactivity $k'_{OH} = \Sigma_X k_{OH+X}[X]$

Measurements and model (MCM v3.2)

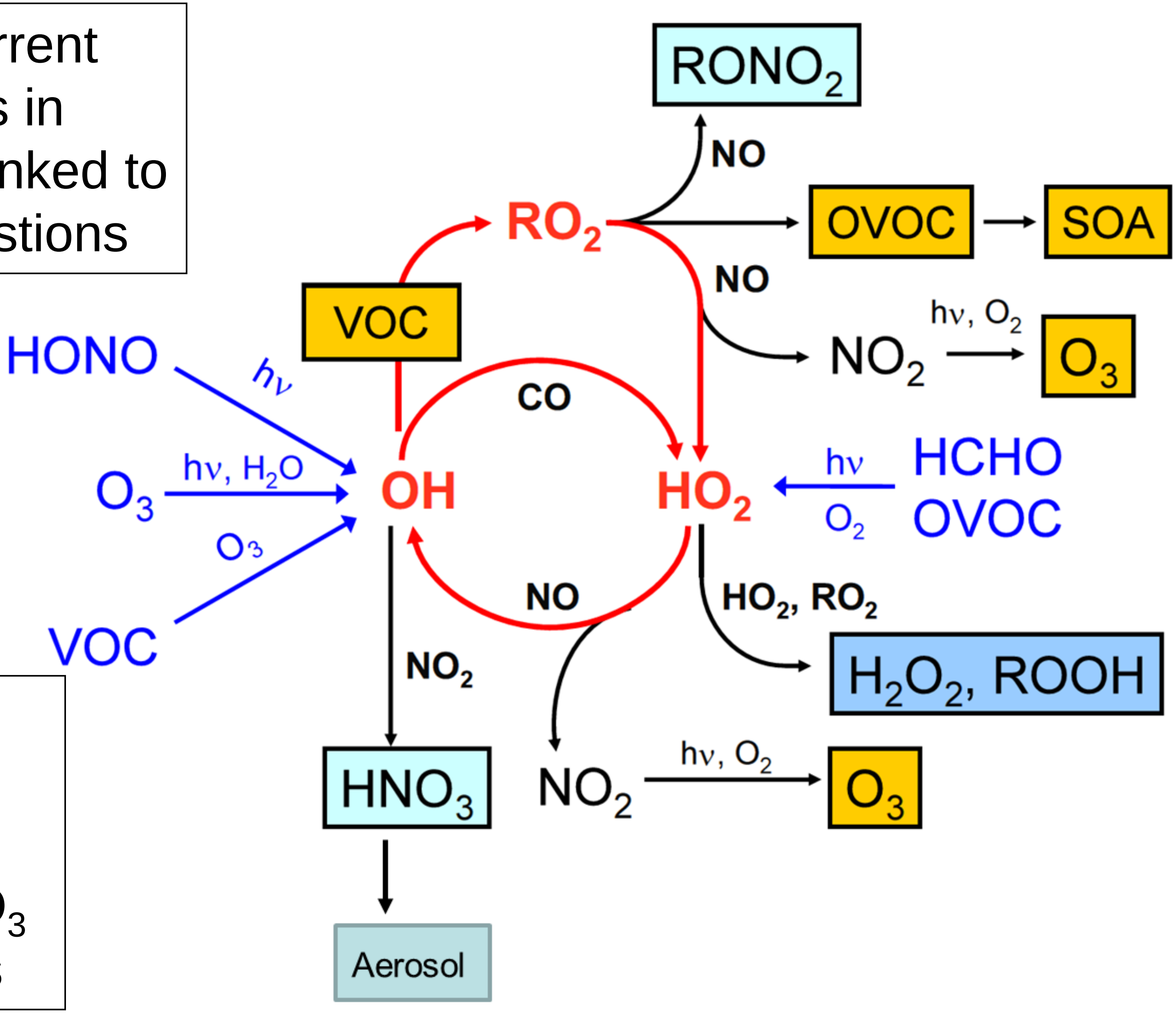


k'_{OH} = 100 s^{-1} means that the OH lifetime is 0.01 s

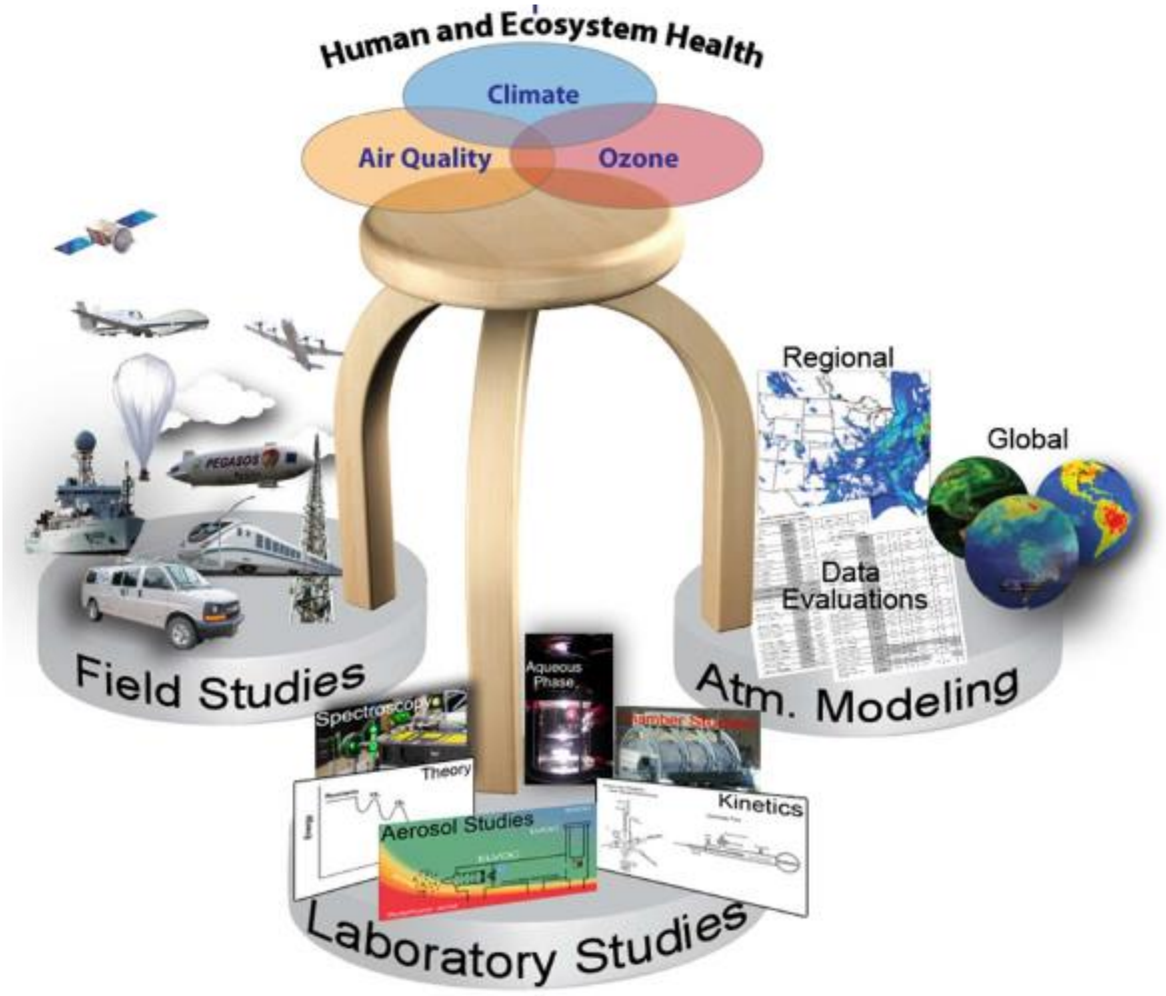
Whalley et al., ACP, 2016

More Detail – what controls OH (and HO_2, RO_2) and how can we measure them?

Many current projects in Chemistry linked to these questions



CH_4
O_3
SOA
H_2SO_4, HNO_3
Halocarbons



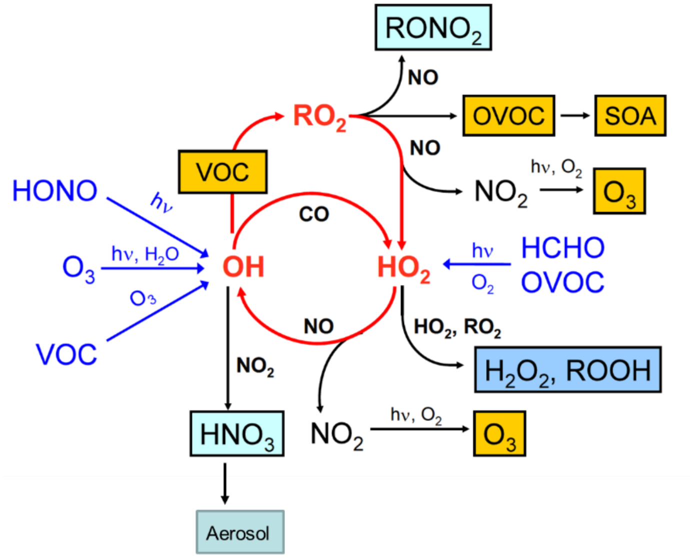
Burkholder et al., JGR, submitted 2016

Approaches (1)

Process studies at the individual reaction

- Laboratory studies k(T,P), $\phi_{photolysis}(\lambda, P, T)$, γ(RH, T, composition)
- Identification of products
- T range 38 K – 1000 K
- Pressure range 1 Torr – 10 atmospheres
- Quantum theory to calculate energies of transition states and intermediates
- Kinetic rate theory to calculate *k(T,P)* and product channels (MESMER)
- Gas phase or at surface/within aerosols
- Values then used as input to models thereby improving their accuracy (SEE collaborations)
- Development of new technology and detection methods: laser-induced fluorescence, mass spectroscopy (PIMS, PTR), cavity-ring down, long-path absorption (QCL), frequency comb (?)

Individual reactions (very selective)



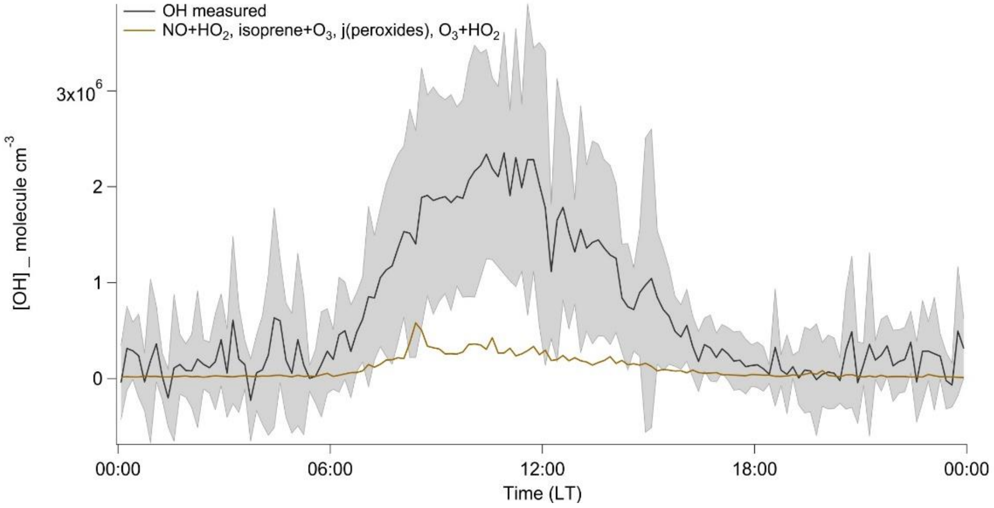
Dainton and Challenger Laboratories

Aerosol laboratory

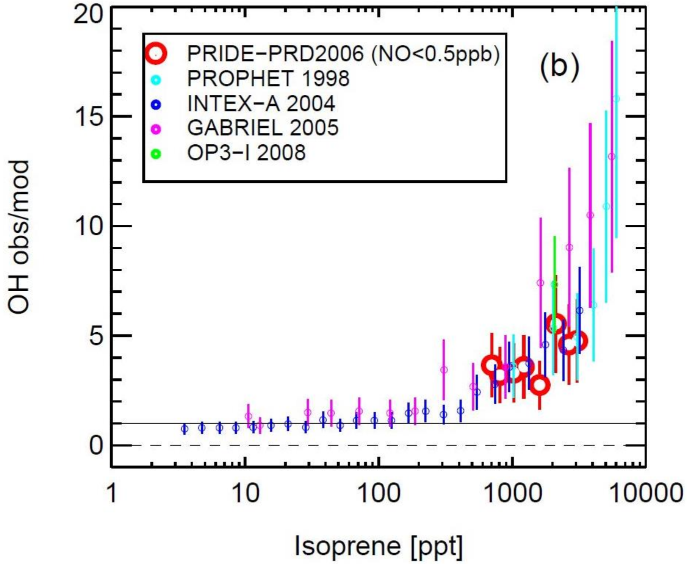
If you'd like a process studied, talk to us!
k(NO+O$_3$) at low T?

- Criegee radical kinetics (alternate oxidant, and source of OH at night)
- Photolysis of acetone (with SEE), glyoxal
- HO$_2$ uptake on aerosol (salts, organics, SOA, dust, cosmic dust, TiO$_2$, role of surfactants, transition metals, viscosity) [CO, O$_3$ Arctic]
- Production of radicals on aerosols (e.g. TiO$_2$)
- Heterogeneous sources of HONO from aerosols (poorly understood), e.g. pNO$_3^-$ photolysis
- Photolysis of RO$_2$ (e.g. isoprene) to give OH
- Photolysis of HPALD (isoprene product)
- OH + amines (CCS) k(T) and products
- OH + isoprene → OH recycling
- OH + biofuels (DME, DEE, furans)
- OH + SO$_2$, glyoxal k(T,P)
- OH + acetylene (OH recycling)

Higher than expected OH in forested regions
Danum Valley, Malaysian Borneo, 2008



Model agreement gets worse at higher levels of isoprene

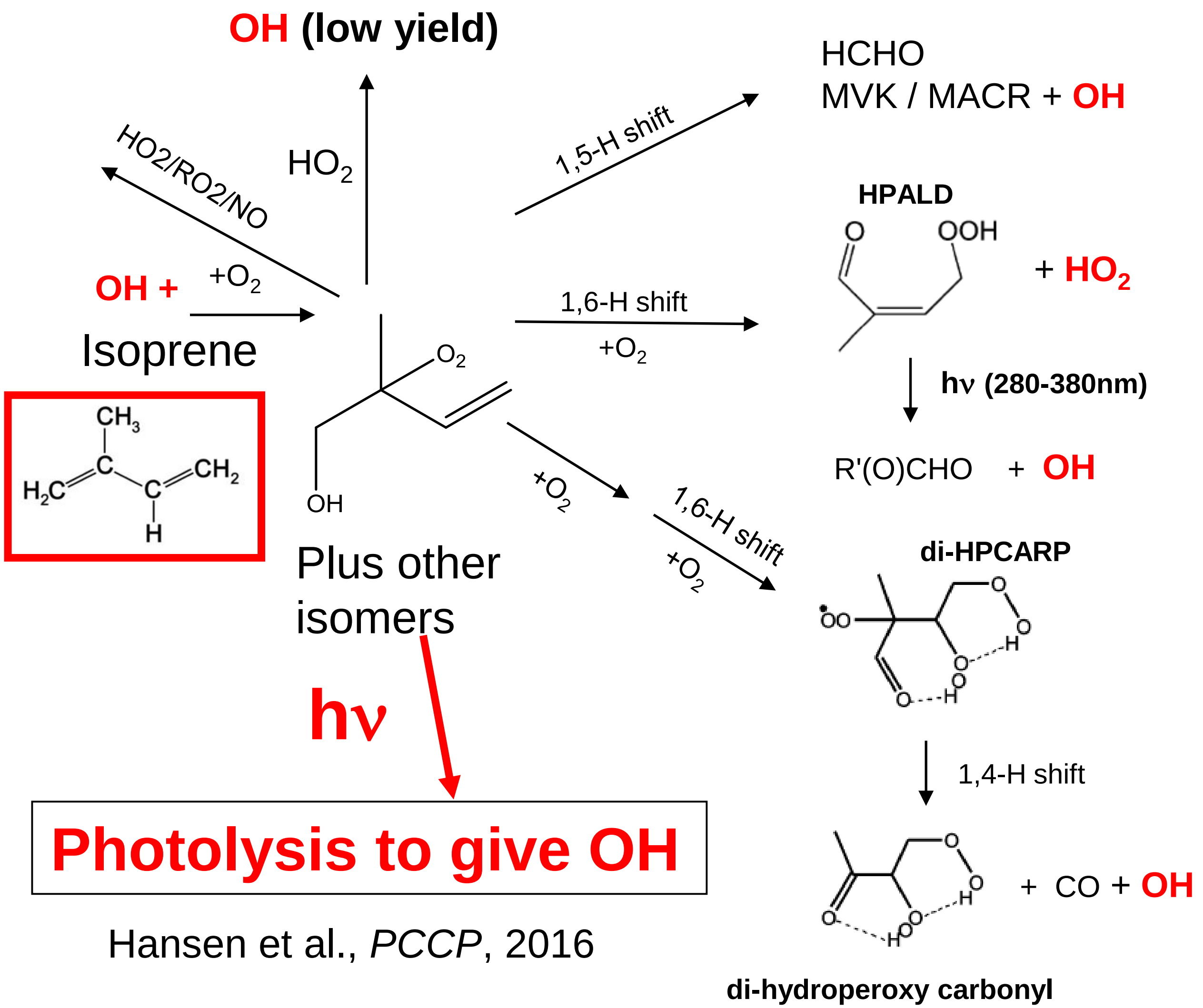


Whalley *et al.*, *ACP*, 2011

Stone et al., *ACP*, 2011; Lu et al., ACP, 2012

New routes from RO_2 back to OH?

LIMx, Peeters et al., 2009, 2010, 2014



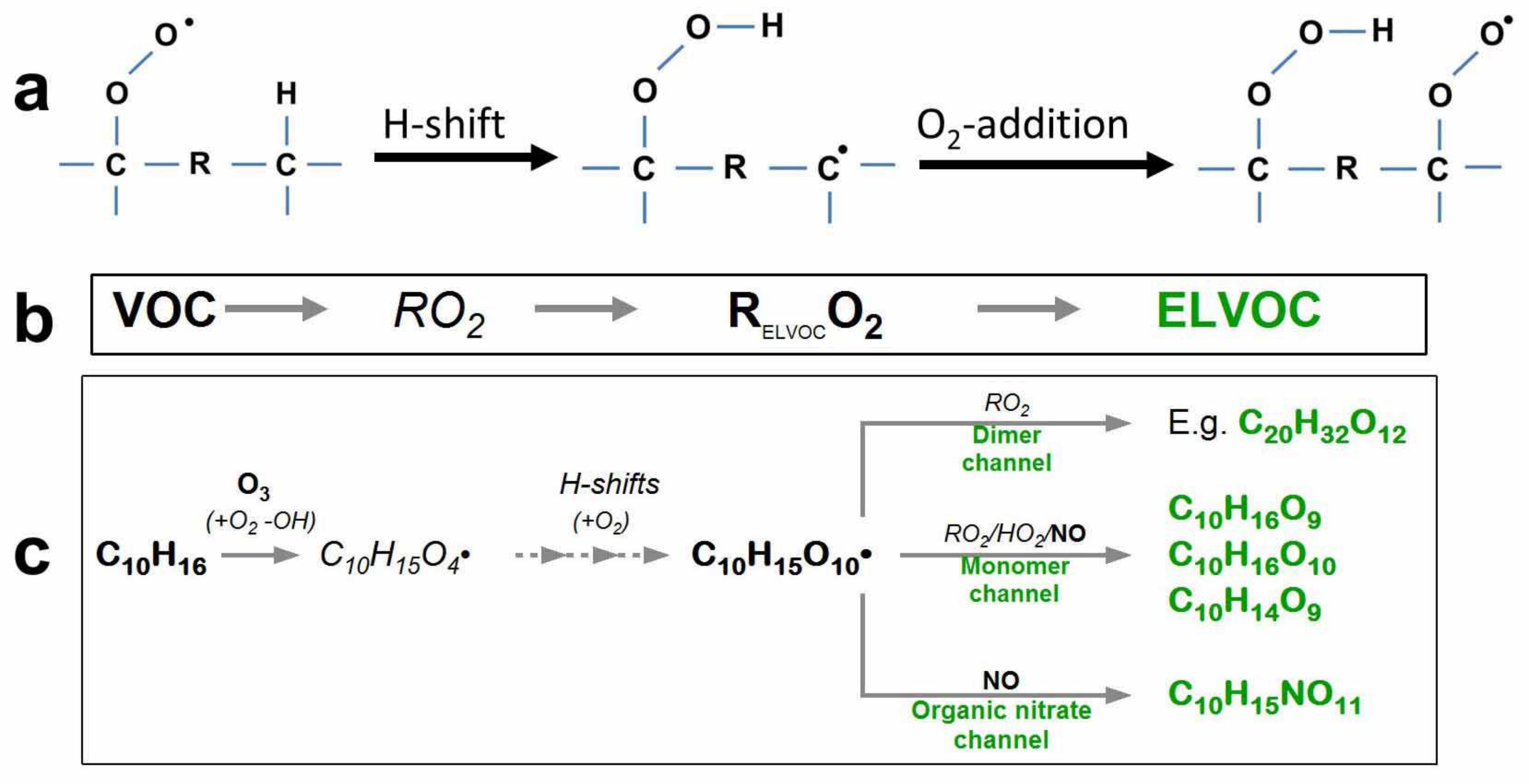
Photolysis to give OH

Hansen et al., *PCCP*, 2016

But most are only predictions from quantum theory. Need further experimental verification but difficult timescale to study (1-100s)

Fuchs et al., *Nat. Geosci.*, 2013

Repeated RO_2 isomerisation suggested to form extremely low volatility VOCs (ELVOC) which partition to form SOA



Ehn et al., *Nature*, **506**, 476, 2014

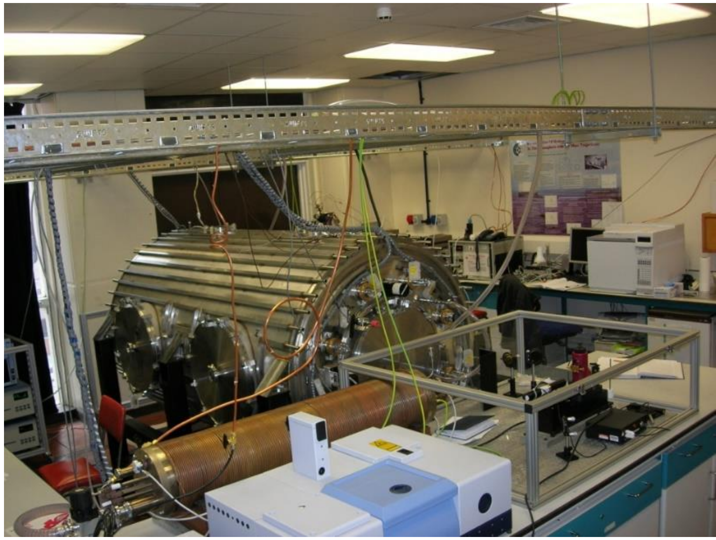
“Auto-oxidation”

Suggest biogenics as another theme

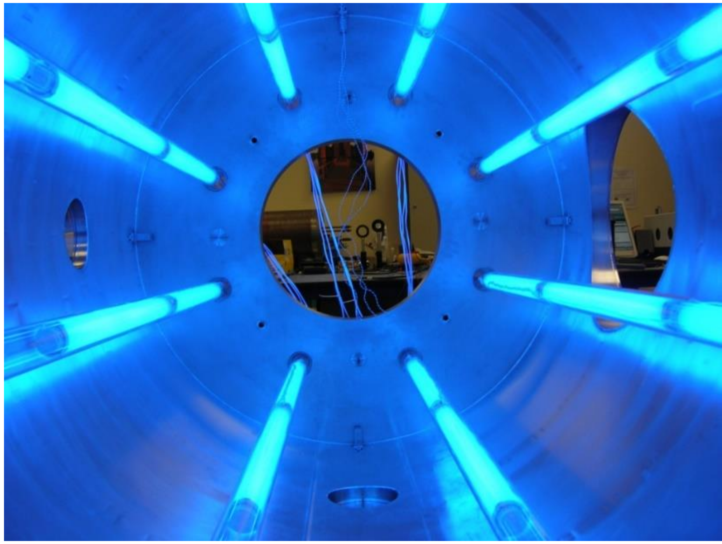
Approaches (2) HIRAC chamber

“Simple” reaction systems in a controlled environment

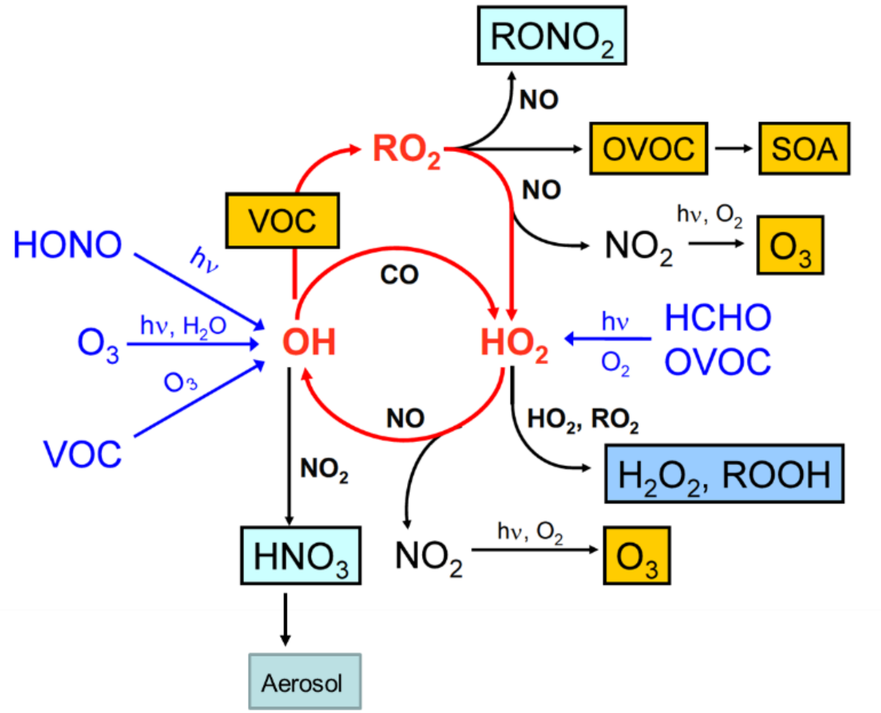
Part of EUROCHAMP2020

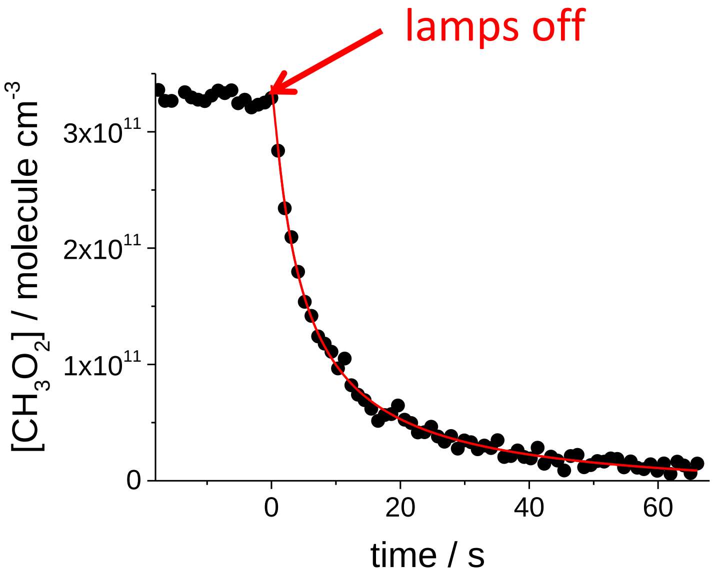


- HIRAC chamber, 2 m^3, stainless steel
- Introduce individual VOCs or simple mixes
- Can vary T, P, RH, O_3, NOx
- Equipped with FTIR, GCs, FTIR, commercial analysers for NOx, O3, CO, H2O
- Radical detection using FAGE (OH, HO_2, RO_2)
- Fit data using a simple mechanism (e.g. Facsimile, Kineticus, AtChem)
- Extract k(T,P), ϕ (λ, P, T), sometimes need model and best fit to extract values (not always)
- Currently just gas-phase
- Values then used as input to models to improve mechanisms
- Good place to test new instruments and new calibration methodologies



HIRAC





- Cl atom reactions with VOCs (e.g. acetates) k (T) using relative rate methods [lights on]
- O_3 + VOCs, k(T,P) and OH/HO_2 yields [lights off]
- Radical-radical reactions

  $CH_3C(O)O_2 + HO_2$, k(T) and product yields (e.g. OH, $CH_3C(O)OH$)

  $RO_2 + RO_2 \rightarrow$ k(T) and products (R=CH_3, C_2H_5)

  $CH_3O_2 + OH \rightarrow$
- Oxidation of biofuels and amines
- Development of new methods to measure HO_2 and CH_3O_2

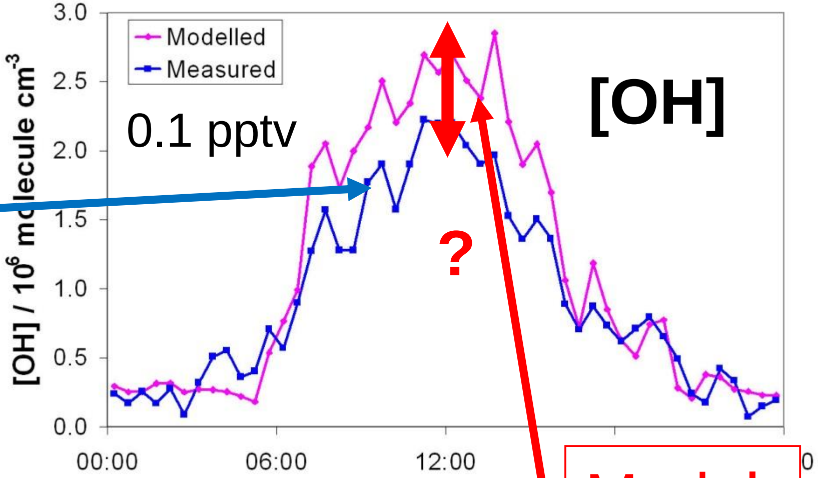
Approaches (3)

Model validation (using our new lab. and chamber data) in the real world via fieldwork

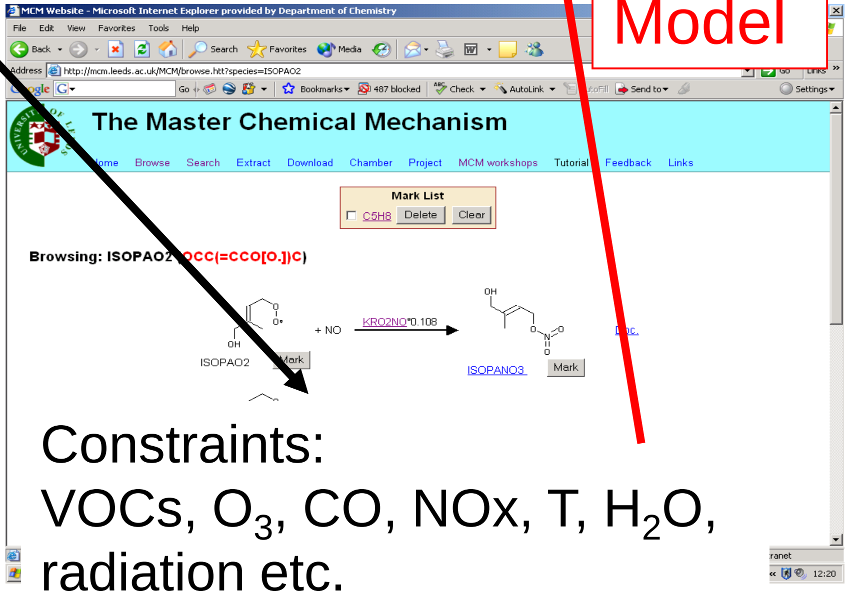
- OH, HO_2, RO_2 are ideal target species for the box model as short lifetimes and budgets not controlled by transport processes
- Models to predict climate or air quality need validation in a range of environments – hence field campaigns all around the world
- Over 30 field campaigns since 1996
- Constant improvements to instruments (improving sensitivity, accuracy, precision, reliability, size, weight)
- Detection of more species : RO_2 speciation, IO, HCHO, glyoxal
- OH reactivity allows check of whether model contains all OH sinks

Quite a few examples of collaborations with SEE where fundamental parameters or field measurements are exploited via modelling

A typical OH field experiment



Model



The Master Chemical Mechanism

Browsing: ISOPAO2 OCC(=CCO[O.])C

Constraints:
VOCs, O_3, CO, NOx, T, H_2O, radiation etc.

Then compare measurements and the model – do they agree?

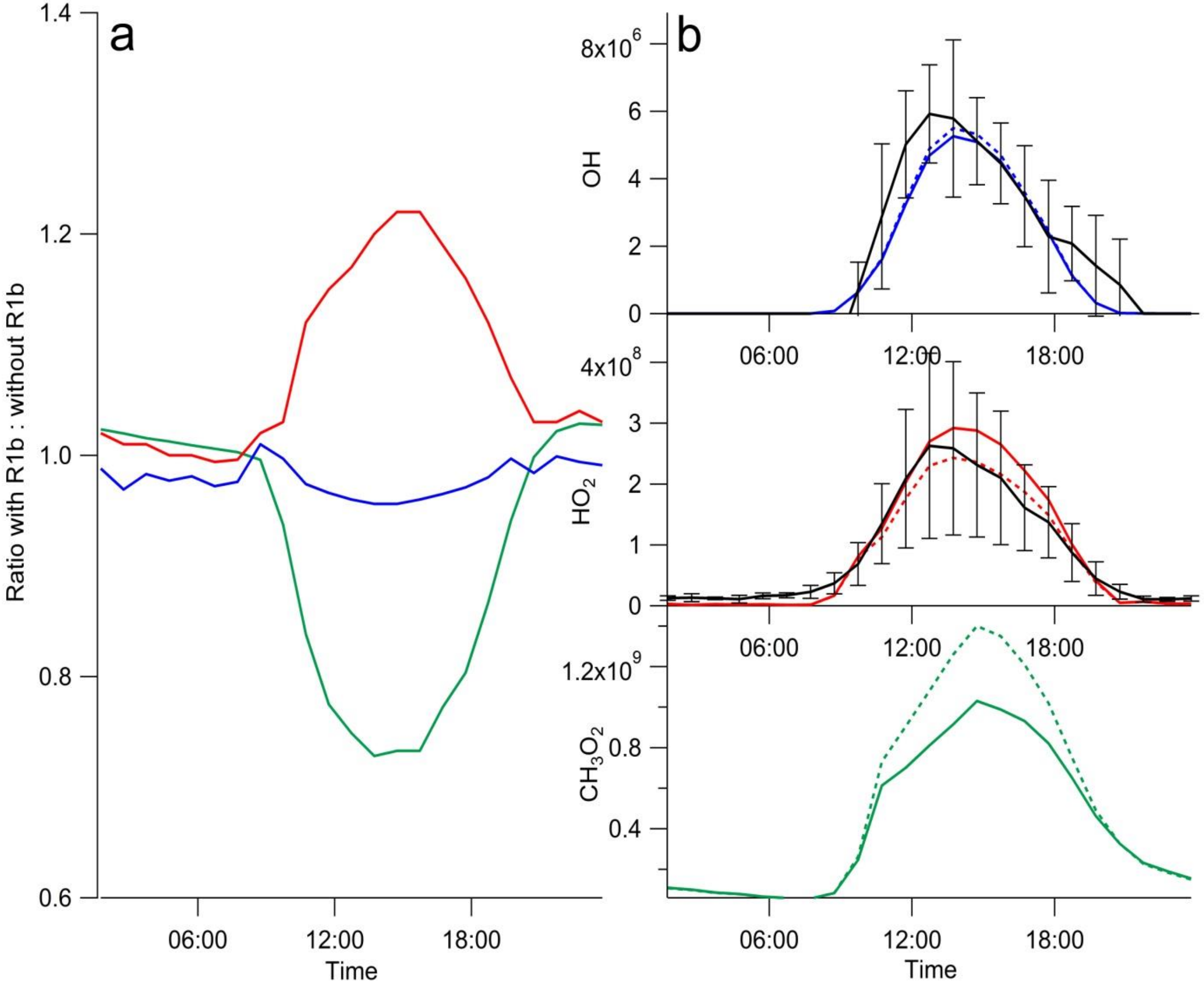
Master Chemical Mechanism

mcm.leeds.ac.uk/MCM/

- Oxidation of ~ 140 VOCs by OH, O_3 and NO_3
- 17,000 reactions and 6,700 species

National Centre for Atmospheric Science
NATURAL ENVIRONMENT RESEARCH COUNCIL

Including the CH_3O_2 + OH reaction (100% HO_2 product)
Cape Verde, Tropical Atlantic Ocean



OH

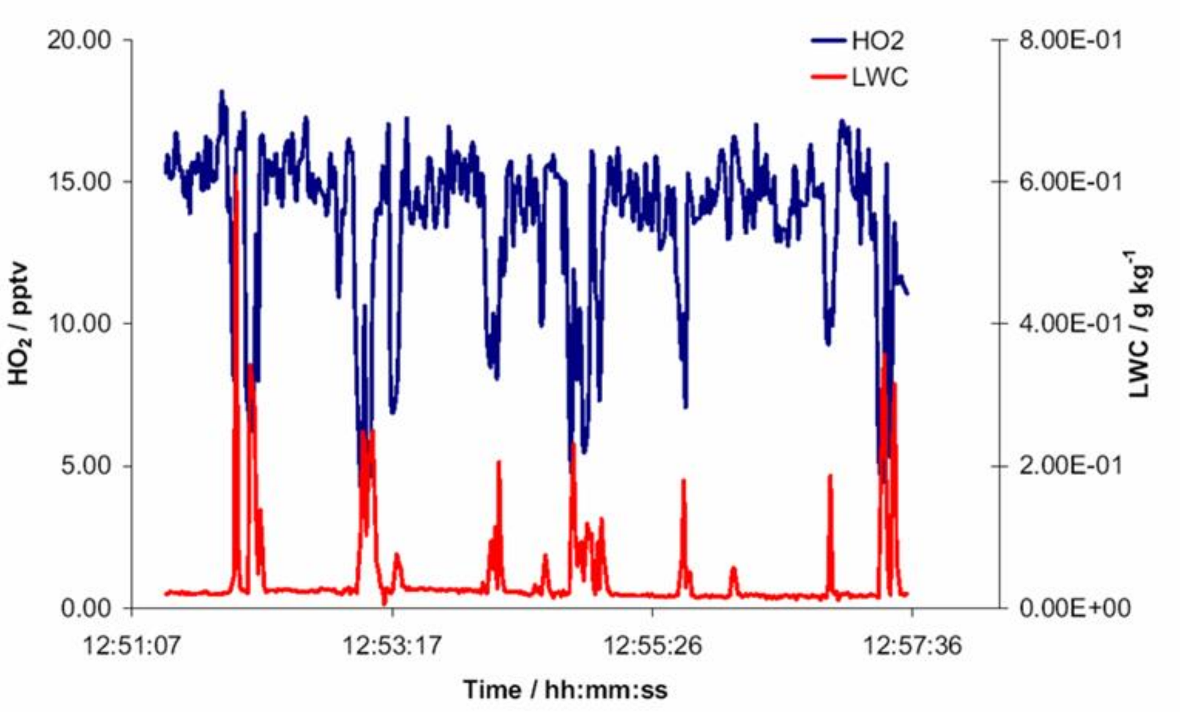
HO_2

CH_3O_2 (peak ~ 10^9 cm^{-3})

MCM modelling by Lisa Whalley

ES&T submitted (2016)

Uptake of radicals in clouds?



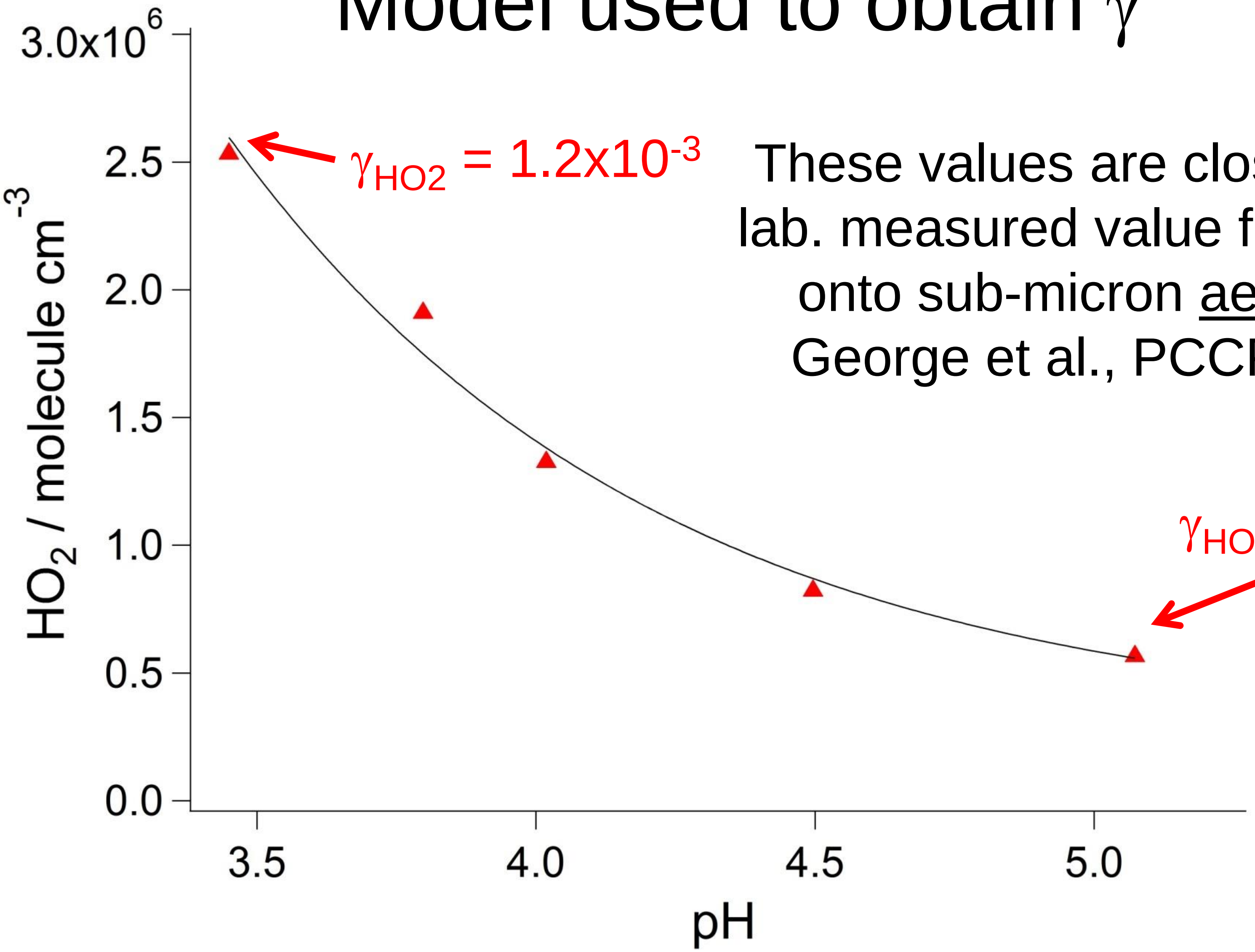
AMMA, West Africa (2006). Skimming in and out of clouds at constant altitude

Commane et al., *Atmos. Chem. Phys*., **10**, 8783-8801, 2010

Also older work from Fred Eisele on [OH] in and around clouds

Uptake of HO_2 onto clouds

HO_2 as a function of pH during cloud events
Model used to obtain γ



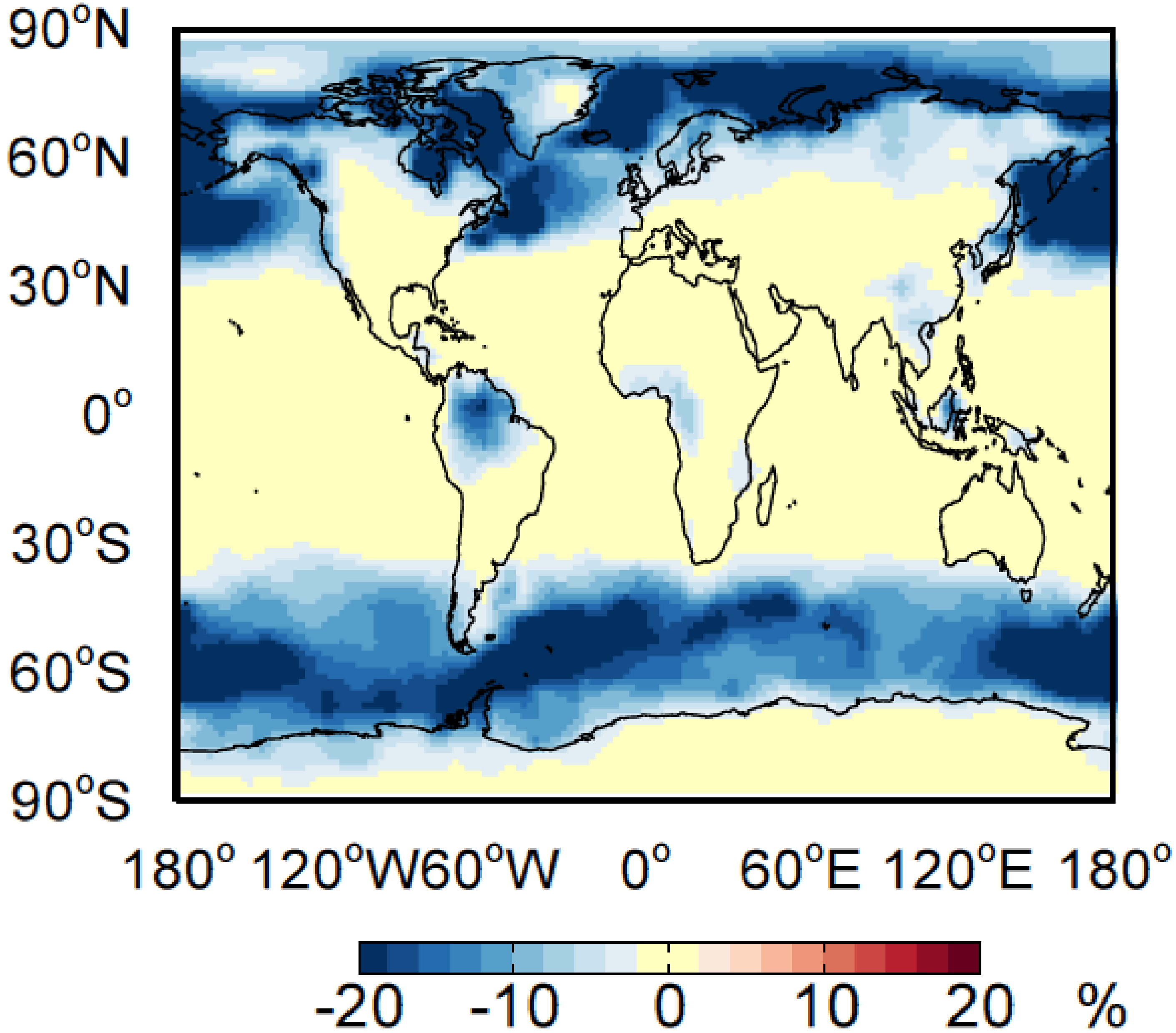
$\gamma_{HO2} = 1.2x10^{-3}$

$\gamma_{HO2} = 3.1x10^{-2}$

These values are close to our lab. measured value for uptake onto sub-micron aerosols, George et al., PCCP, 2013

$$\mathbf{HO_2(aq) \Leftrightarrow H^+(aq) + O_2^-(aq)}$$

GEOSChem simulations including loss of HO_2 to clouds

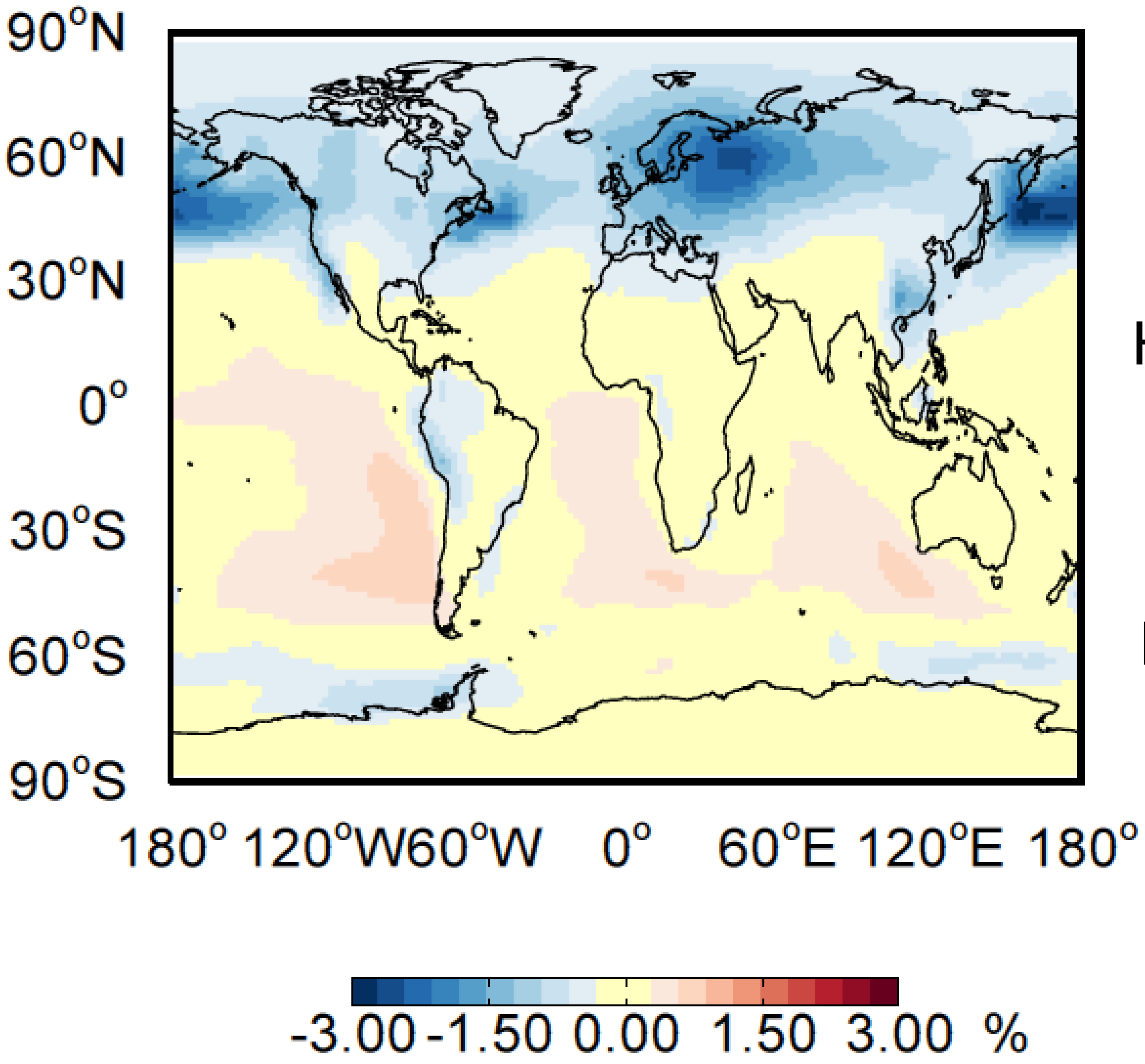


Surface HO2

Impact ?

Whalley et al.,
ACP, 2015

GEOSChem. Impact of cloud uptake on HO_2 on surface O_3 (climate gas, damaging to humans and plants)



Can go up or down !!

High NOx:

$HO_2+NO \rightarrow OH + NO_2$

Leads to less ozone

Low NOx:

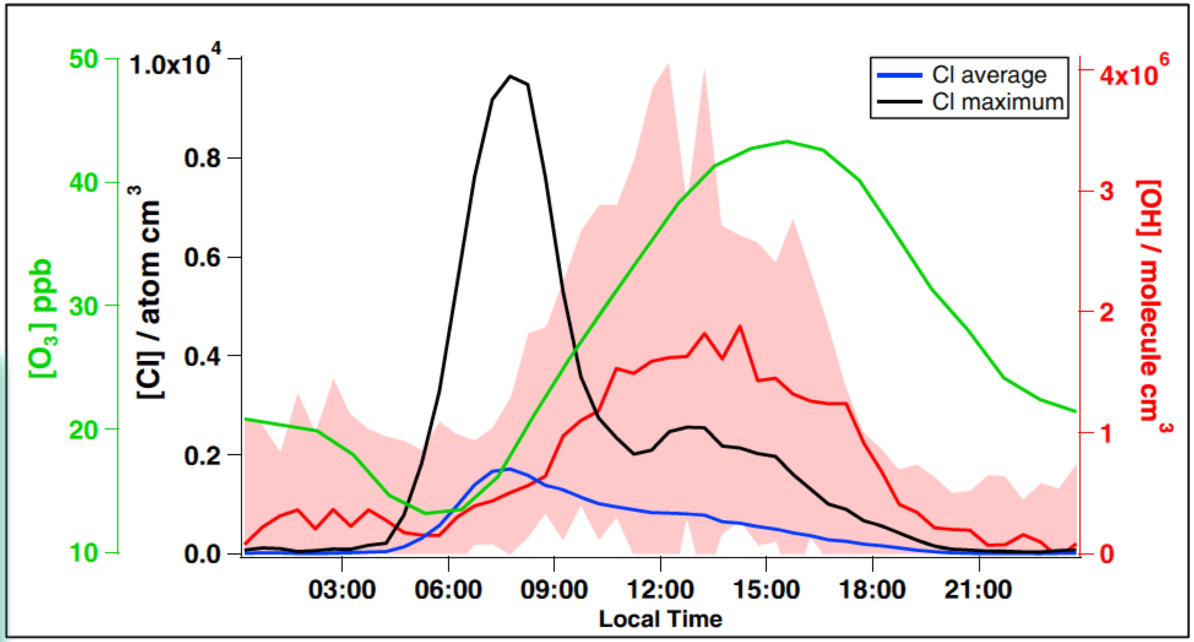
$HO_2+O_3 \rightarrow OH + 2\ O_2$

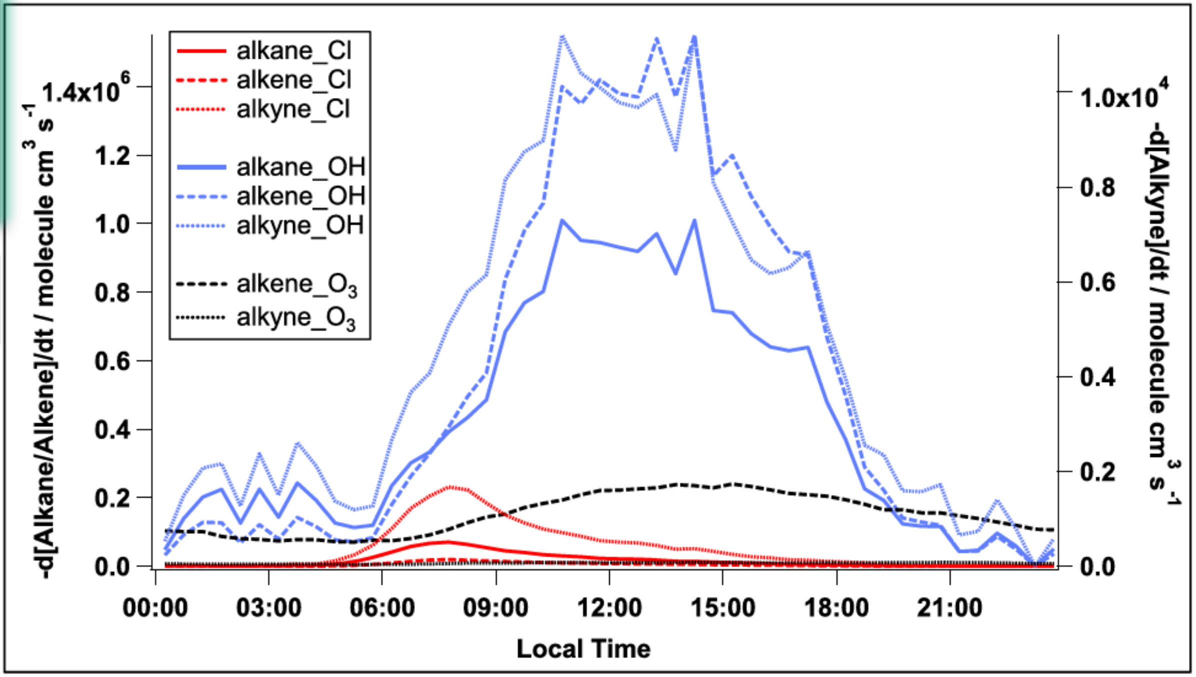
Leads to more ozone

Whalley et al., ACP, 2015

What is the main oxidant? London as an example

OH, O_3 or Cl atoms? (NO too high for significant NO_3 to survive)





$ClNO_2 + h\nu \rightarrow Cl + NO_2$

$$-\mathrm{d[alkanes]/d}t = [\mathrm{X}]\sum_i k_{\mathrm{X+alkane},i}[\mathrm{alkane}, i]$$

$$-\mathrm{d[alkenes]/d}t = [\mathrm{X}]\sum_i k_{\mathrm{X+alkene},i}[\mathrm{alkene}, i]$$

$$-\mathrm{d[alkynes]/d}t = [\mathrm{X}]\sum_i k_{\mathrm{X+alkyne},i}[\mathrm{alkyne}, i]$$

Bannan et al., JGR, 2015