

Topic 7

Atmospheric processes

Atmospheric chemistry

Air quality

Climate change

Synopsis

- Physical processes in the atmosphere - T , p , transport
- Emissions of organic compounds and nitrogen oxides.
- Atmospheric chemistry: oxidation of organic compounds. Influence of NO_x
- Air quality: ozone, particulate matter, nitrogen dioxide. Local, regional and hemispheric scales.
- Climate change: radiative forcing: carbon dioxide, methane, nitrous oxide, ozone, CFCs. Aerosols and clouds. Changes in albedo.
- How well do we understand atmospheric chemistry and the oxidation of organic compounds?

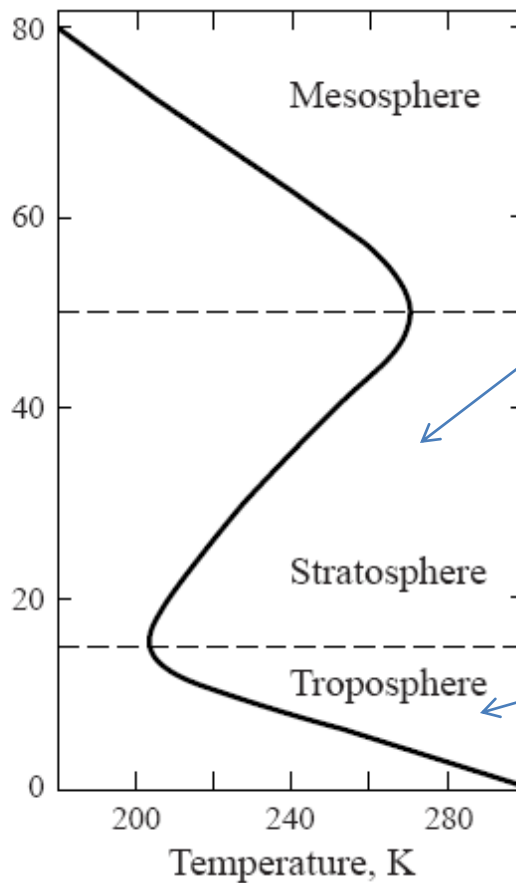
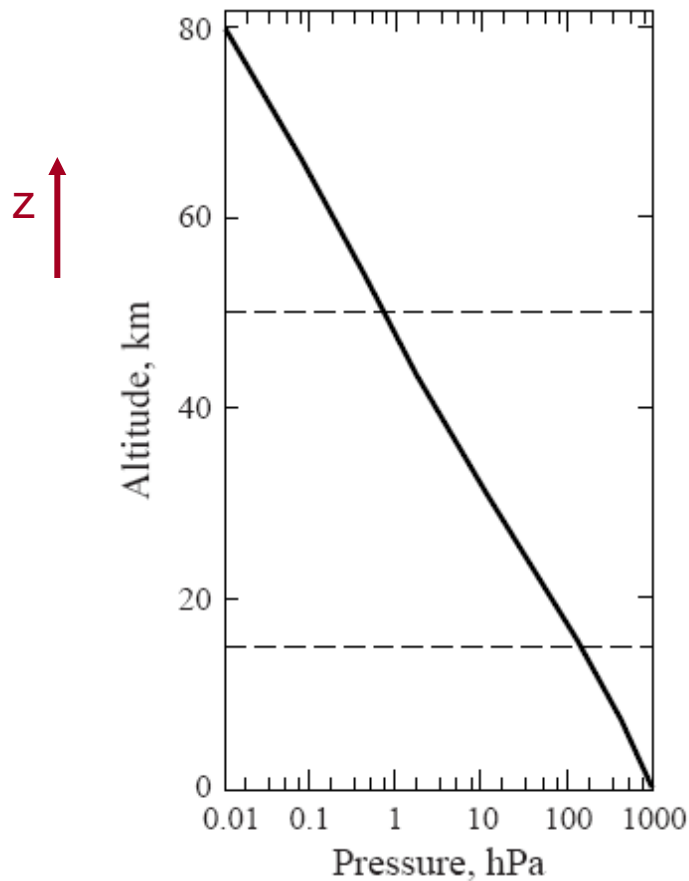
Structure of the atmosphere atmospheric transport

Temperature and pressure variations in the atmosphere

Barometric equation

$$p = p_0 \exp(-z/H_s)$$

$$H_s = k_b T / mg$$



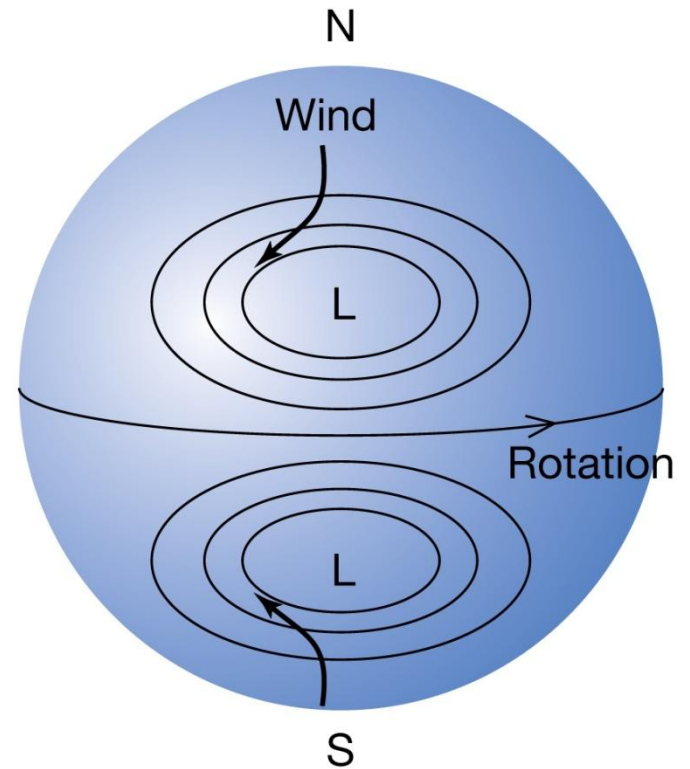
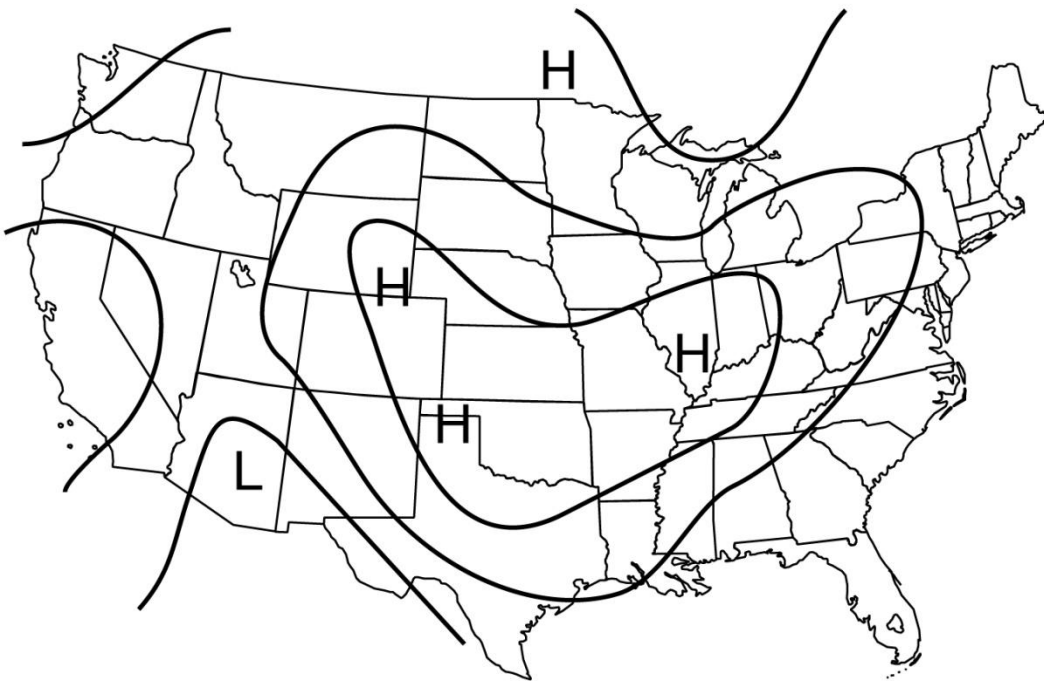
Heating by
exothermic
photochemical
reactions

Convective
heating from
surface.
Absorption of ir
(and some vis-uv)
radiation

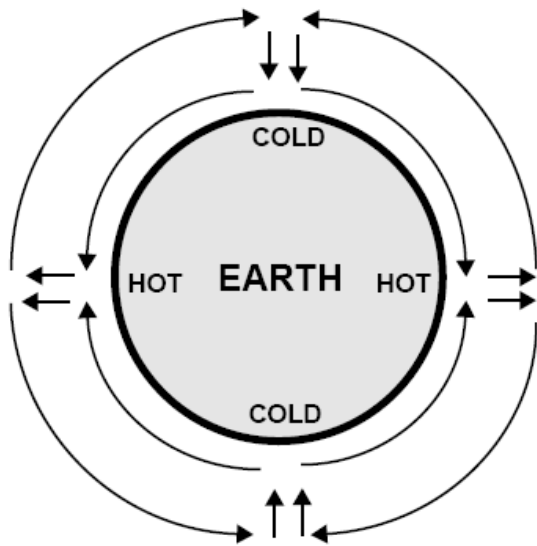
Atmospheric transport

- Random motion - mixing
 - Molecular diffusion is slow in the troposphere, diffusion coefficient $D \sim 2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
 - Average distance travelled in one dimension in time t is $\sim \sqrt{2Dt}$.
 - In the troposphere, eddy diffusion is more important:
 - $K_z \sim 20 \text{ m}^2 \text{ s}^{-1}$ Molecular diffusion more important at v high altitudes, low p. Takes \sim month for vertical mixing by eddy diffusion ($\sim 10 \text{ km}$). Implications for short and long-lived species.
- Directed motion
 - Advection - winds, e.g. plume from power station.
 - Occurs on
 - Local (e.g. offshore winds)
 - Regional (weather events)
 - Global (Hadley circulation)

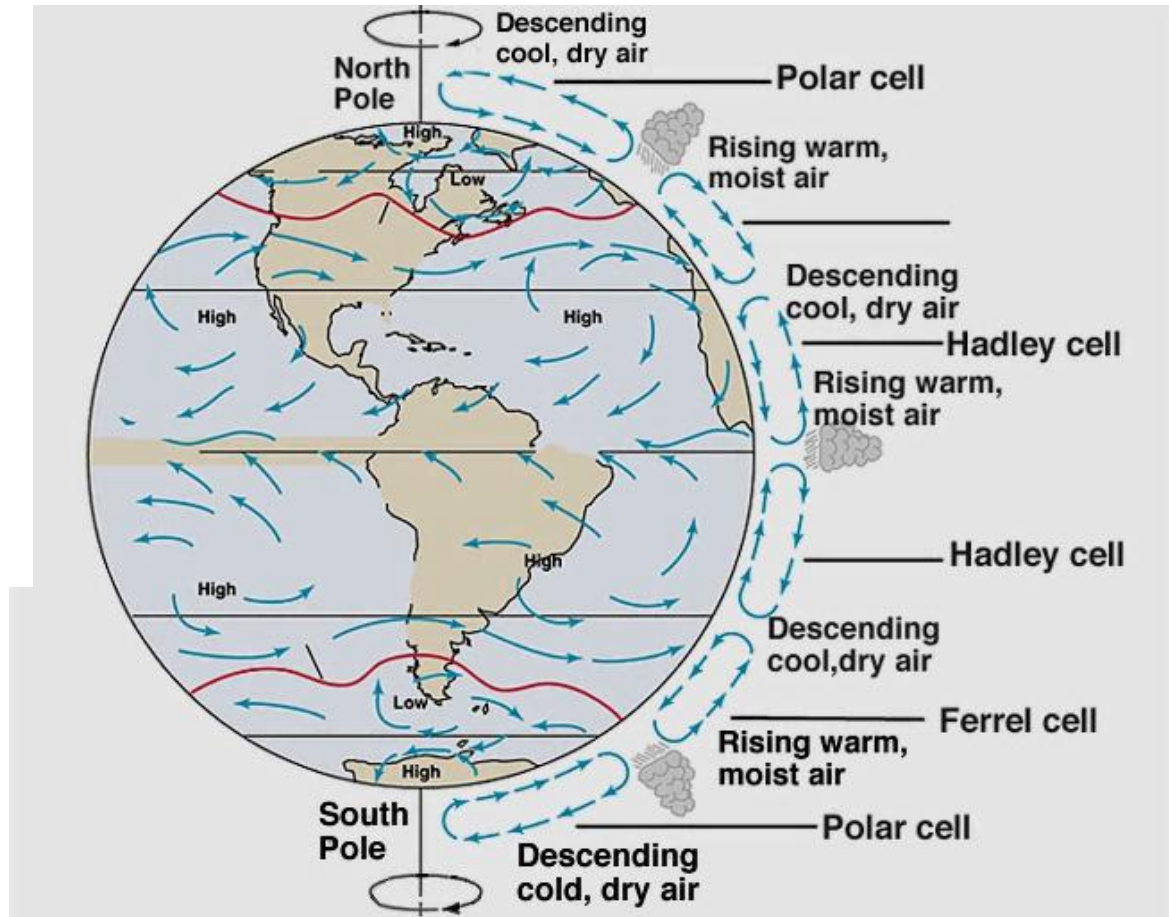
Winds due to weather patterns



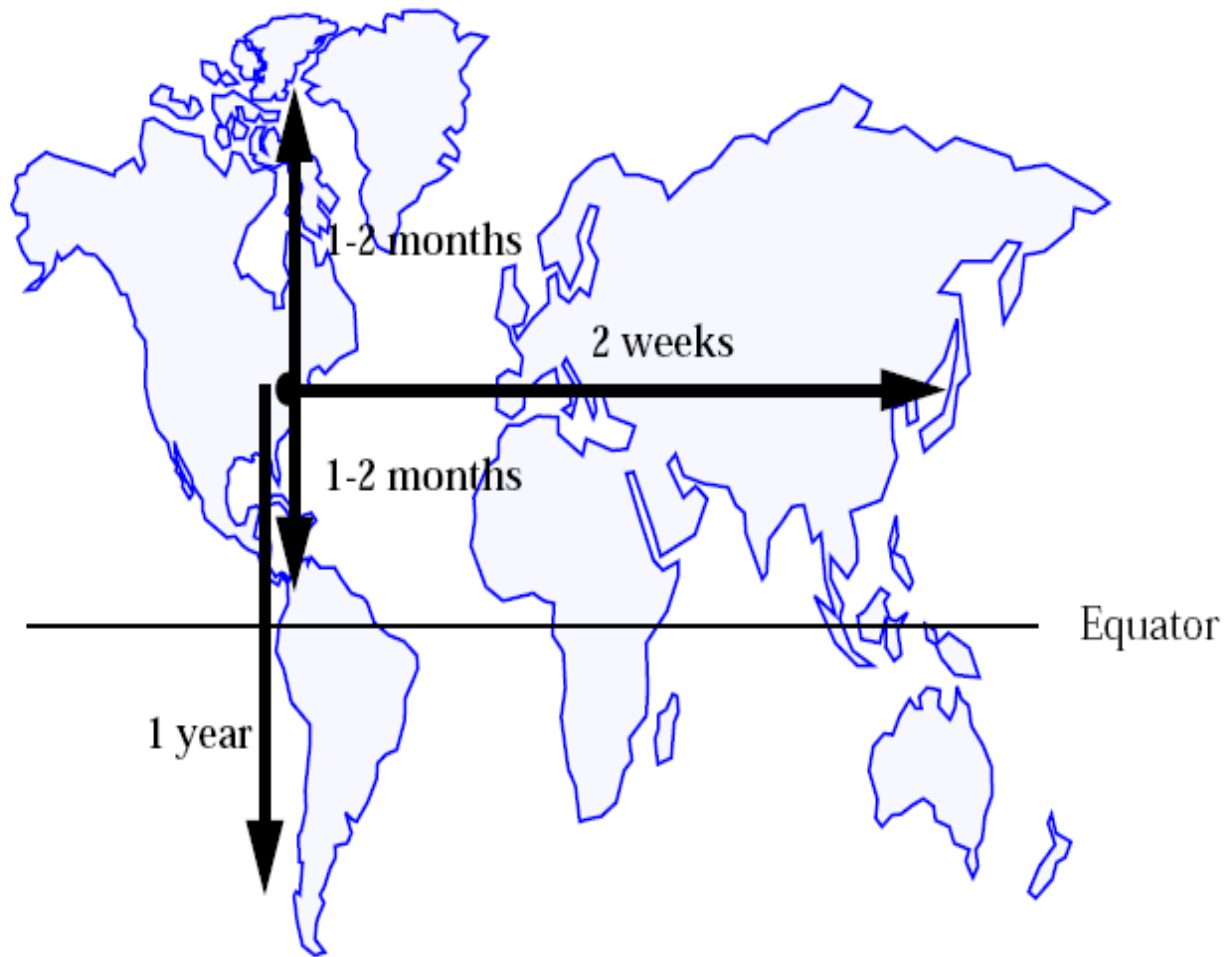
Global circulation - Hadley Cells



Intertropical convergence zone (ITCZ) - rapid vertical transport near the equator.



Horizontal transport timescales



Emissions of organic compounds and NO_x
Global budgets - sources and sinks

Global budget for methane ($\text{Tg CH}_4 \text{ yr}^{-1}$)

- *Sources:*

Natural	160
Anthropogenic	375
<u>Total</u>	<u>535</u>

Natural Sources:

wetlands, termites,
oceans...

Anthropogenic Sources:

natural gas, coal mines,
enteric fermentation,
rice paddies,

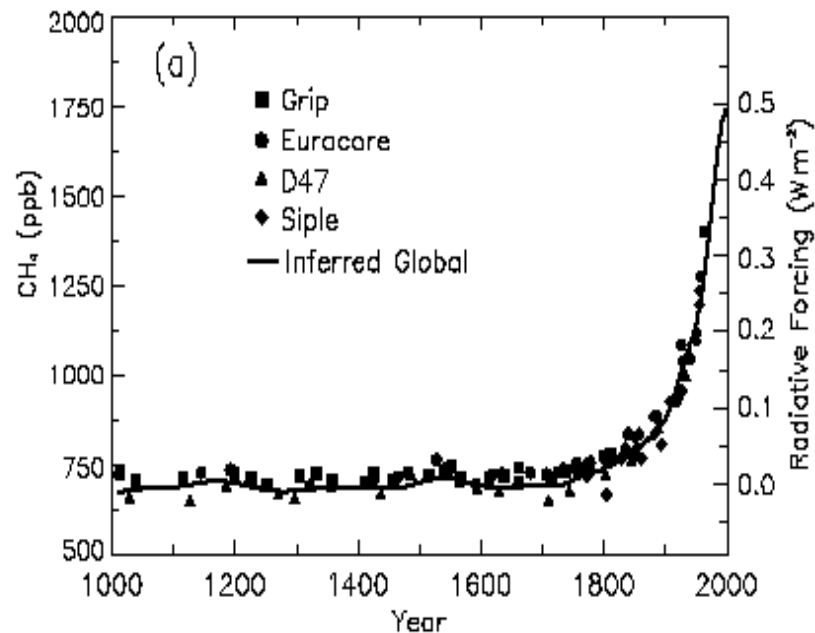
- *Sinks:*

– Trop. Oxidation by OH	445
– Transfer to stratosphere	40
– Uptake by soils	30
<u>Total</u>	<u>515</u>

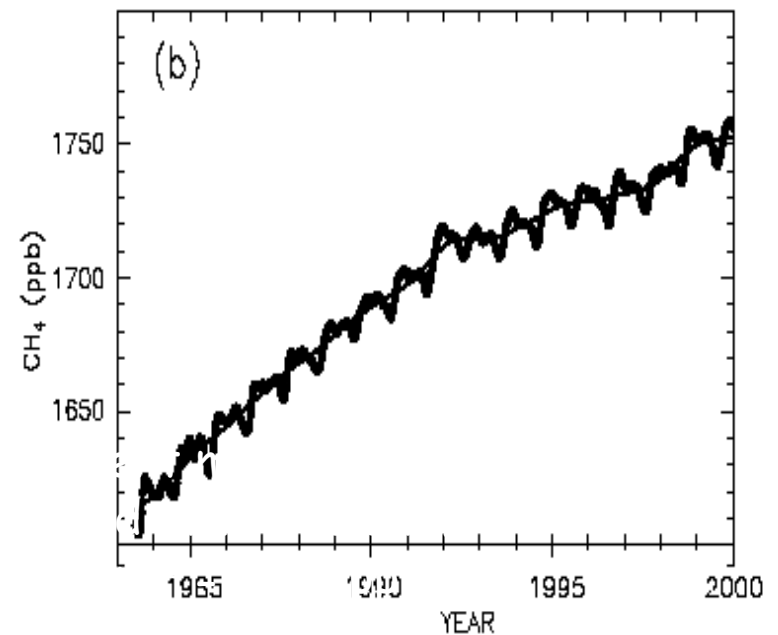
These rates are very
uncertain

HISTORICAL TRENDS IN METHANE

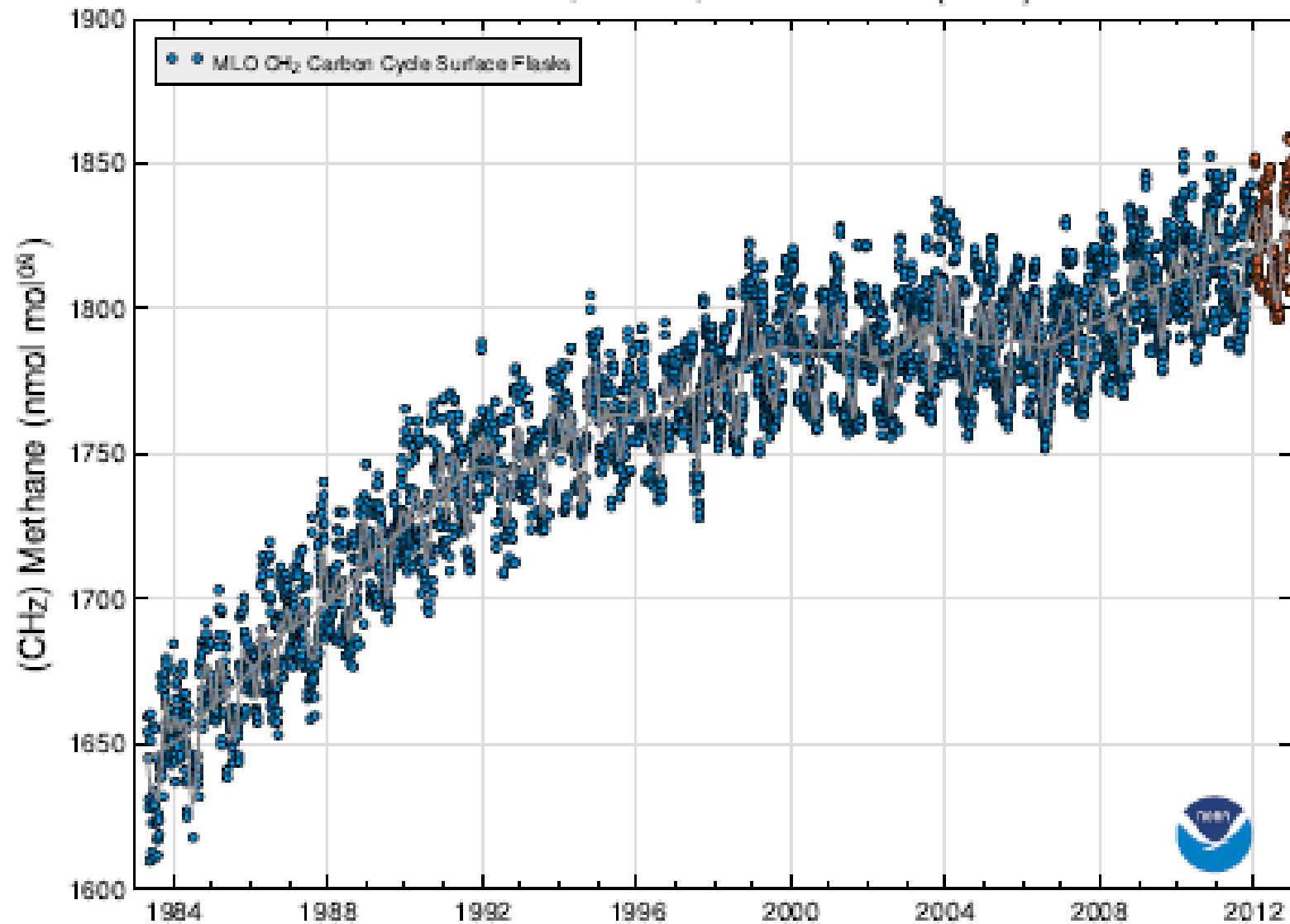
Historical methane trend



Recent methane trend



Mauna Loa, Hawaii, United States (MLO)



GLOBAL BUDGET OF CO

	<i>Range of estimates (Tg CO yr⁻¹)</i>
Sources	1800–2700
Fossil fuel combustion/industry	300–550
Biomass burning	300–700
Vegetation	60–160
Oceans	20–200
Oxidation of methane	400–1000
Oxidation of other hydrocarbons	200–600
Sinks	2100–3000
Tropospheric oxidation by OH	1400–2600
Stratosphere	~ 100
Soil uptake	250–640

Emissions of non methane volatile organic compounds (VOCs)

Anthropogenic:

fuel production and distribution 17; fuel consumption 49; road transport 36; chemical industry 2; solvents 20; waste burning 8, other 10. **Total 142 Tg yr⁻¹**

Biogenic:

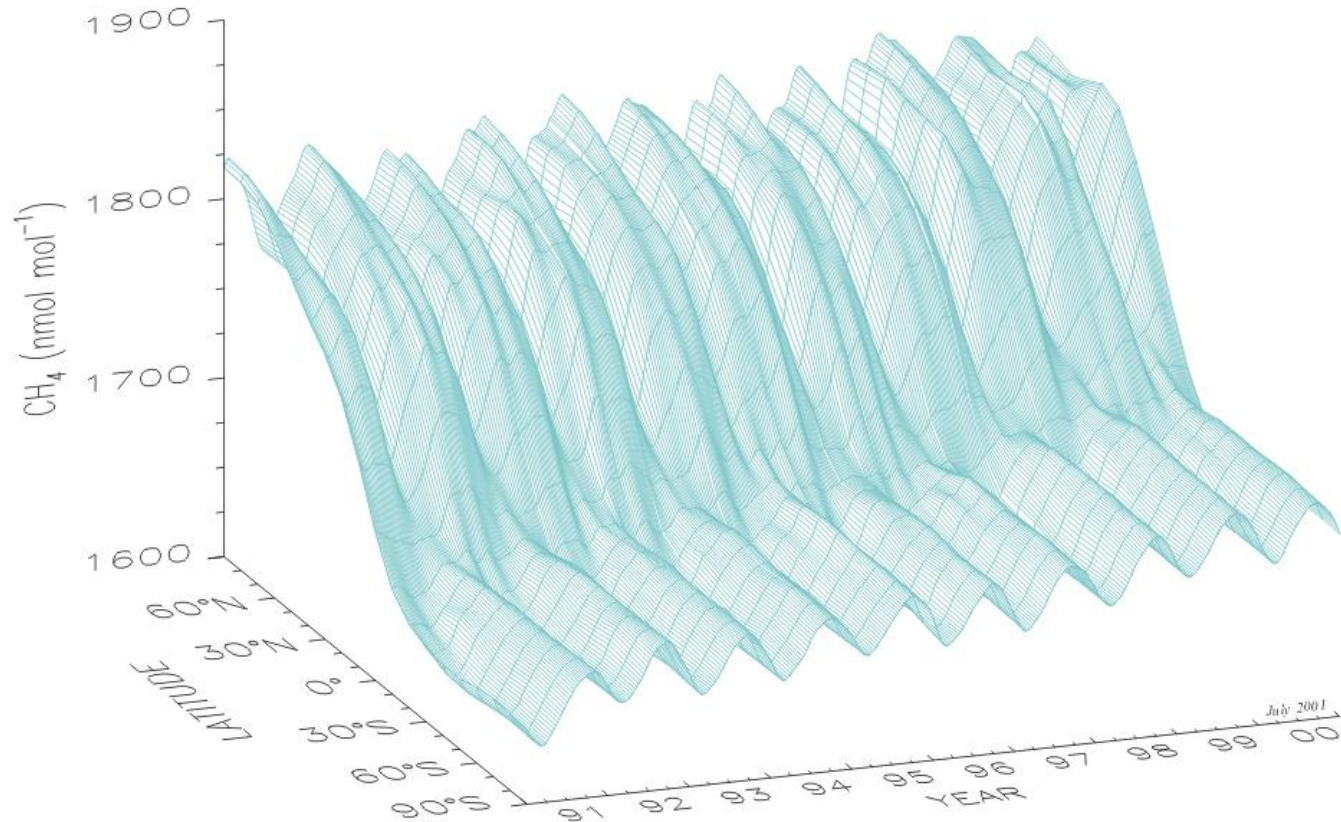
isoprene 503; monoterpenes 127; other reactive VOCs 260, unreactive VOCs 260;
Total 1150 Tg yr⁻¹

Removal of organic compounds from the atmosphere by reaction with OH

- Atmospheric lifetime = $1/\{k[\text{OH}]\} = 1/\{1 \times 10^6 k\}$ s. What does it mean?
- Rate coefficients at 298 K/ 10^{-12} cm³ molecule⁻¹ s⁻¹
CH₄: 7×10^{-3} ; CO: 0.24; isoprene: 110; ethane: 0.25
- Approximate lifetimes for OH = 1×10^6 molecule cm⁻³
CH₄: 5 yr; CO: 7 weeks; isoprene: 3 h; ethane: 7 weeks
- Atmospheric distribution depends on lifetime. NH is major source of anthropogenic pollutants. CH₄ is distributed globally with only a slight NH/SH difference. Isoprene is found only close to its (very extensive) sources.
- The *oxidising capacity* of the atmosphere refers to its capacity to remove VOCs and depends on [OH] (and the concentrations of other oxidants - O₃, NO₃)

GLOBAL DISTRIBUTION OF METHANE

NOAA/CMDL surface air measurements



- Seasonal dependence - higher in winter than summer (maximum in NH correlates with minimum in SH).
- NH concentrations > SH - main sources are in **NH**; slow transport across ITCZ.

Atmospheric oxidation of organic compounds

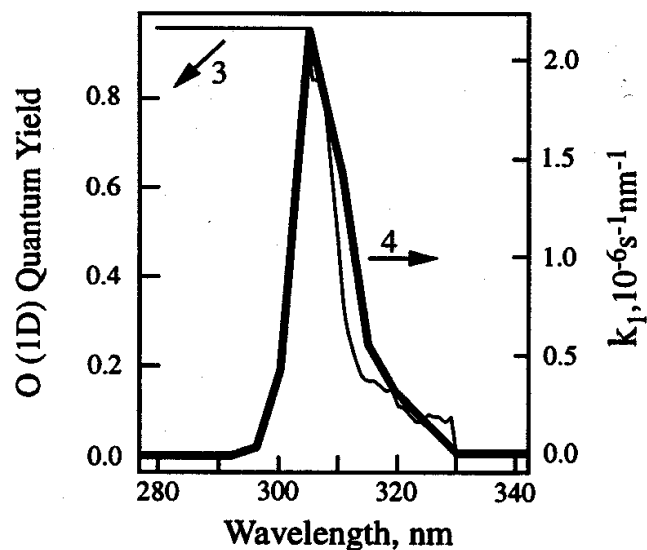
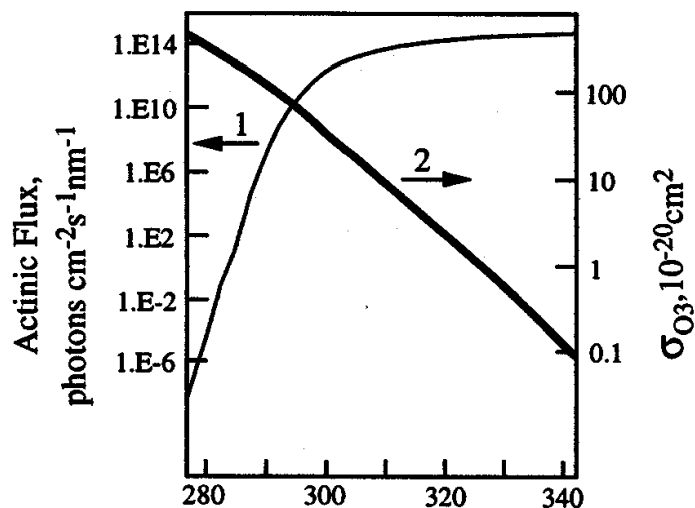
THE OH RADICAL: MAIN TROPOSPHERIC OXIDANT

What are its main global sources and sinks?

Primary source:



Sink: oxidation of reduced species



GLOBAL MEAN [OH] ~ 1.0x10⁶ molecules cm⁻³

Methane oxidation. (Effectively a very short radical chain)

Initiation by OH formation from ozone photolysis

Propagation:



Secondary radical formation



Termination



**** $k(\text{CH}_3 + \text{O}_2) \sim 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

General oxidation scheme for VOCs



Secondary chemistry from $\text{R}'\text{CHO}$ photolysis

Termination as before - NB the termination route depends on the NO_x : VOC ratio

OVERALL



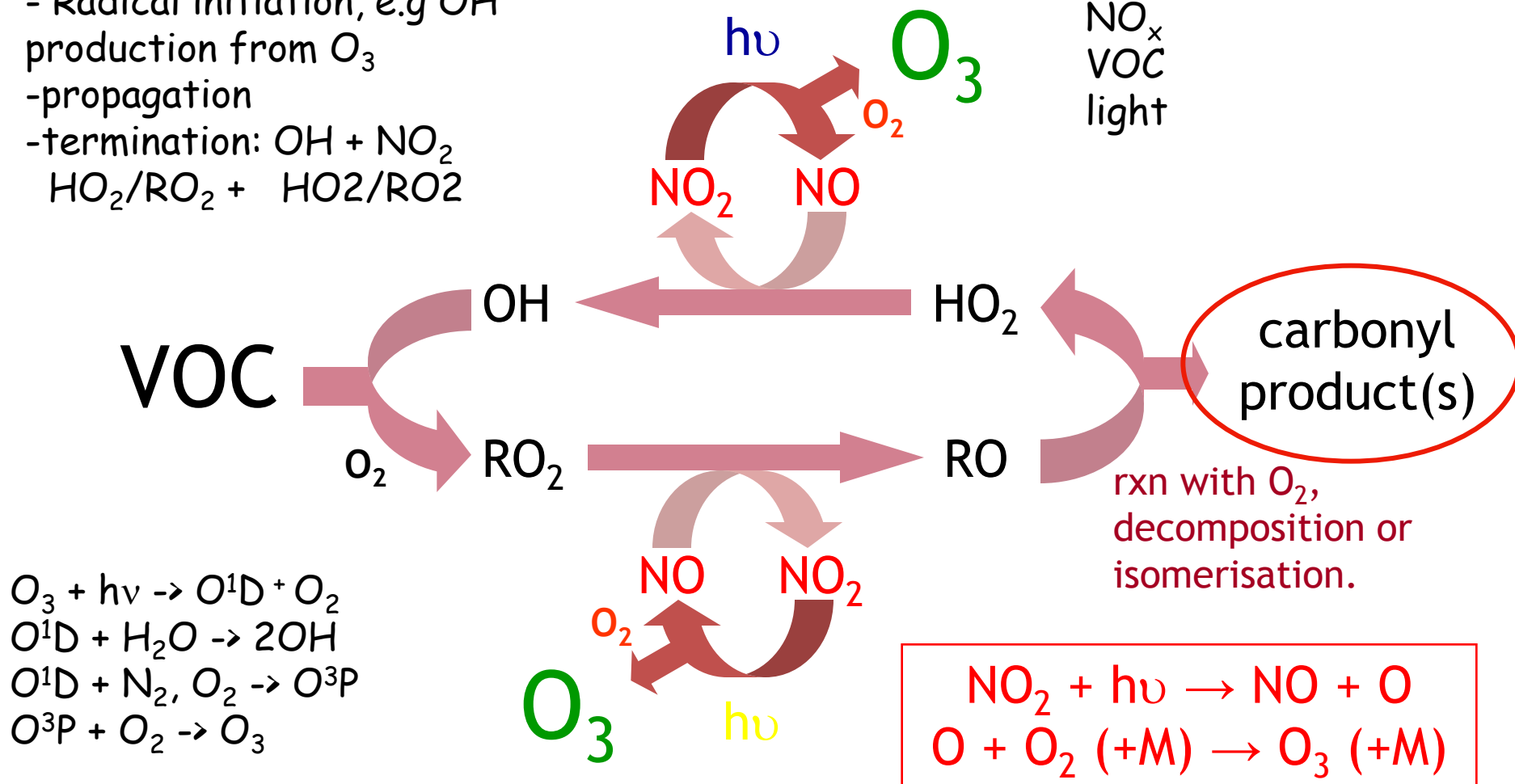
The same reactions can also lead to formation of secondary organic aerosol (SOA)

Free radical propagated oxidation cycle

Chain reaction:

- Radical initiation, e.g OH production from O_3
- propagation
- termination: $OH + NO_2$
 $HO_2/RO_2 + HO_2/RO_2$

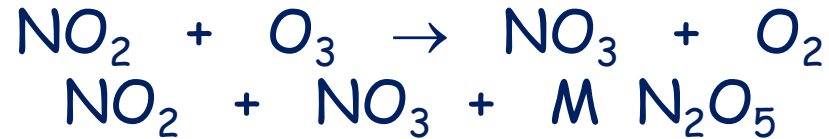
Dependence on:
 NO_x
VOC
light



Ozone formation from conversion of NO to NO_2

Other oxidising species /initiators of VOC oxidation

NO₃



NO₃ is rapidly lost in the day by photolysis and reaction with NO (\rightarrow NO₂), so that its daytime concentration is low. It is an important night time oxidant. It adds to alkenes to form nitroalkyl radicals which form peroxy radicals in the usual way and also abstracts H from the higher alkanes, aldehydes etc..

O₃

Ozone reacts with alkenes to form a carbonyl + an energised Criegee biradical. The latter can be stabilised or decompose. One important reaction product is OH: O₃ reactions with alkenes can act as a source of OH, even at night.

Photolysis

Why should we worry about ground level ozone?

- The human health impacts of ozone derive from its irritant properties and its induction of an inflammatory response in the lung.
- It is not clear whether or not it has a threshold for causing health effects.
- The WHO guideline is 50 ppb, measured as the daily maximum of a running 8-hour mean ozone concentration. The European Union (EU) - less stringent target of a daily maximum of a running 8-hour mean of 60 ppb, not to be exceeded more than 25 times a year, averaged over three years. from 31st December 2010. The US has just introduced an objective value of 75 ppb.
- Concentrations are highest during summer episodes, but exceedances of AQ objectives can occur throughout the year. (See discussion on NH background ozone)
- Ozone also has adverse effects on crop yields, on tree growth and on the composition of natural plant communities and on materials.

Global budget for tropospheric NO_x: Formation and coupling

- NO_x is central to tropospheric ozone formation.
What are its global sources and sinks?

- Global sources (Tg N yr⁻¹):

Fossil fuel combustion	21;	Biomass burning:	12
Soils	6	Lightning	3
Ammonia oxidation	3	Aircraft	0.5
Transport from stratosphere			0.1

- Coupling (rapid - ~ 1 minute in the day



Global budget for tropospheric NO_x: Loss and coupling

- Loss

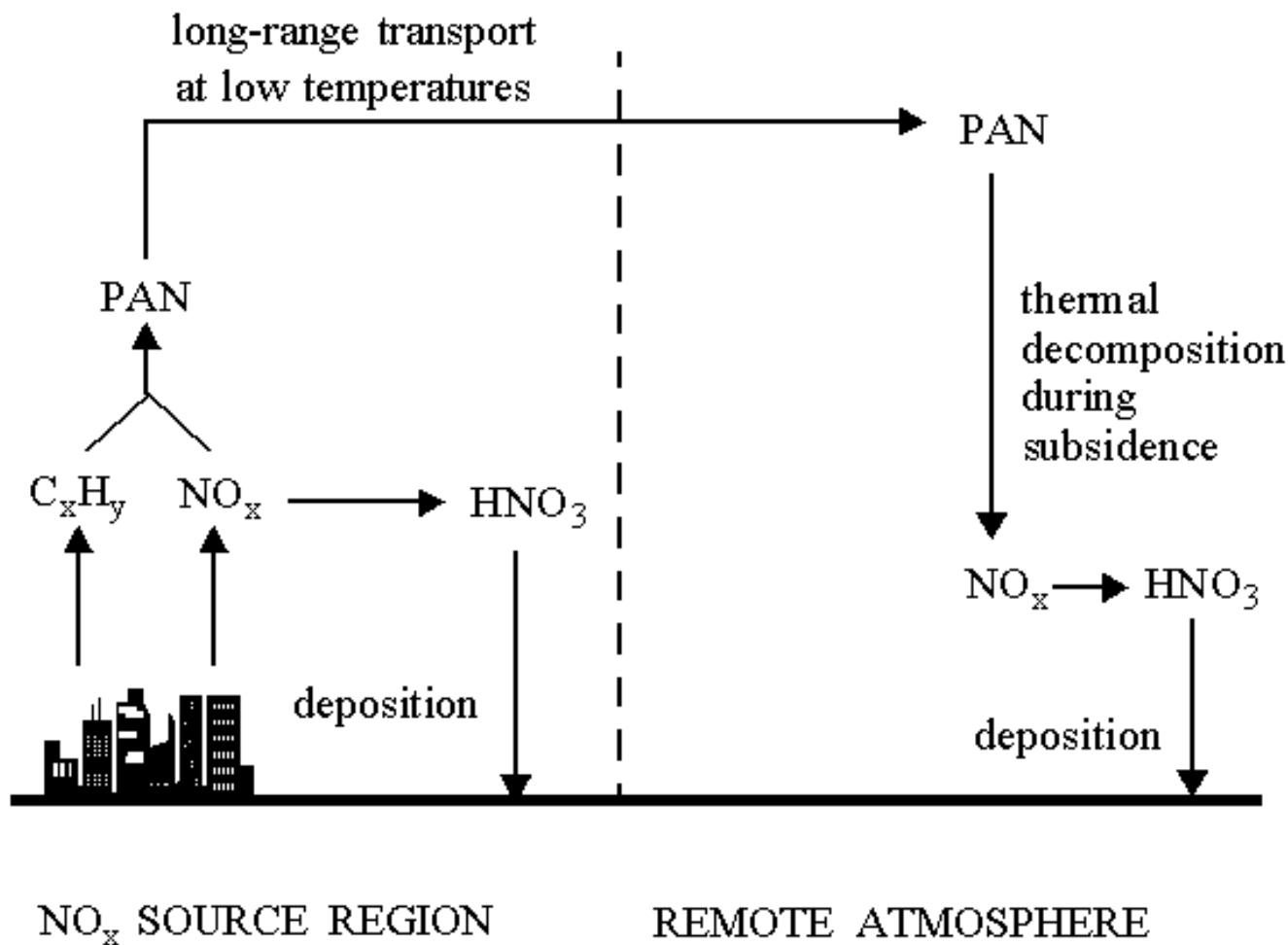


Rainout of HNO₃.

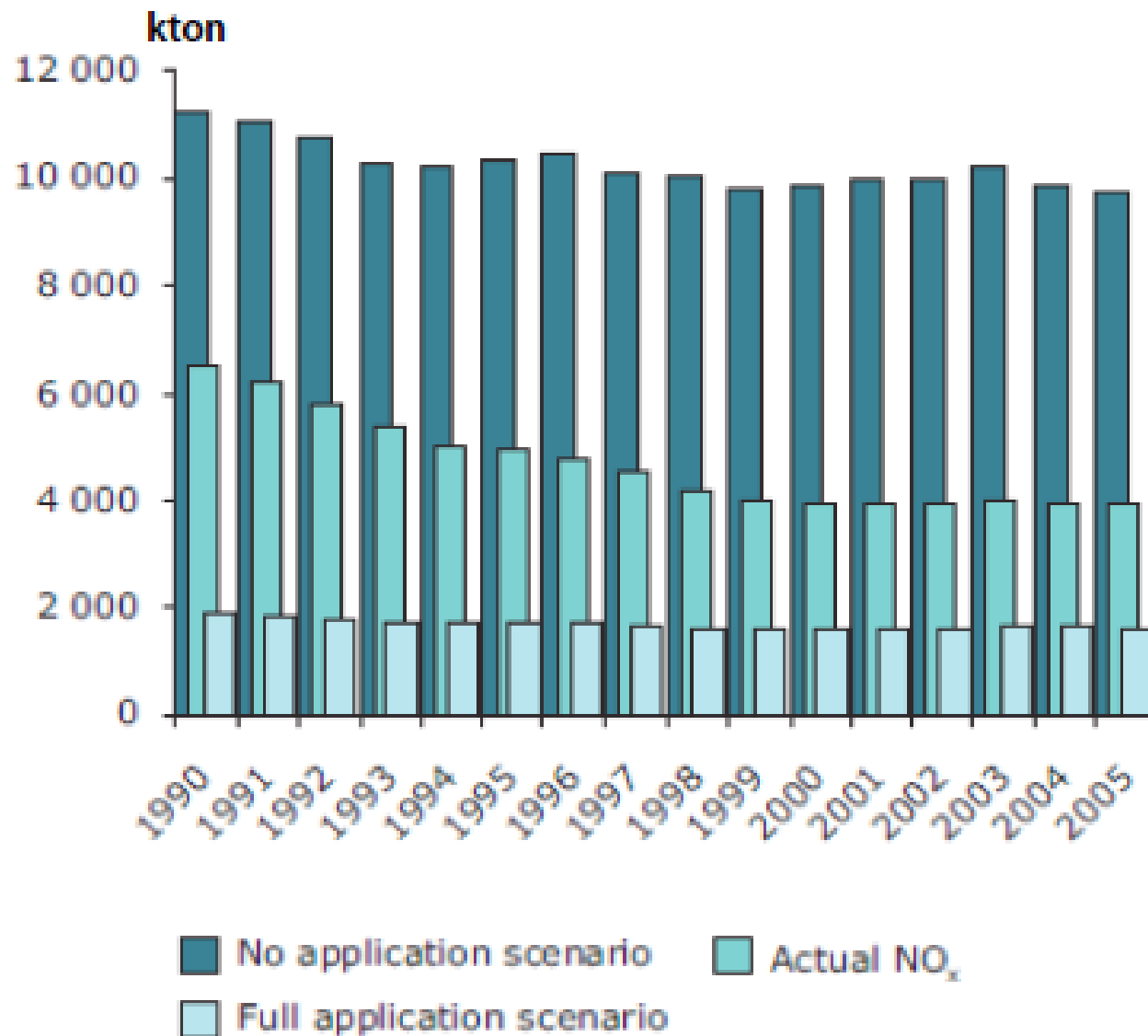
Conversion into other forms of oxidised nitrogen, e.g. organic nitrates

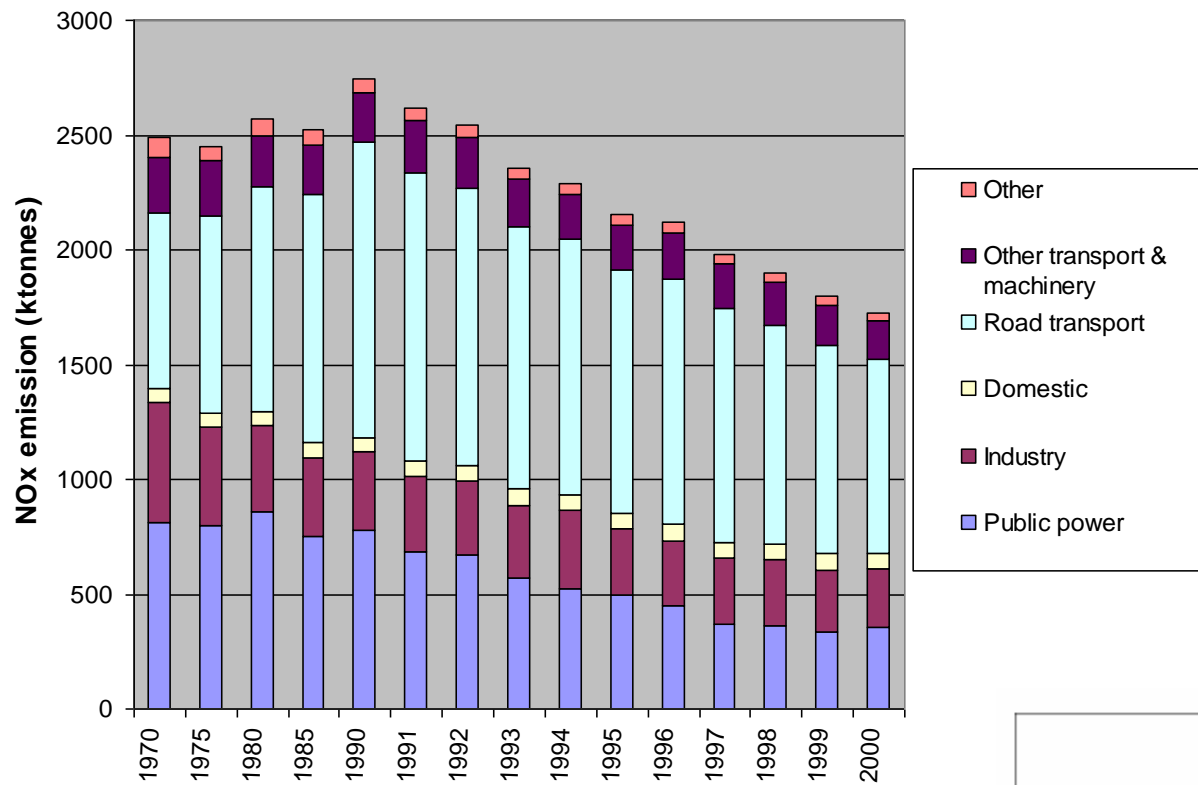
- Lifetime of NO_x is about 1 day. NO_x is a key component in ozone formation. It is emitted mainly from anthropogenic sources, in populated regions. Can it be transported to regions where it is not strongly emitted?

PEROXYACETYLNITRATE (PAN) AS RESERVOIR FOR
LONG-RANGE TRANSPORT OF NO_x
 $\text{PAN} = \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$

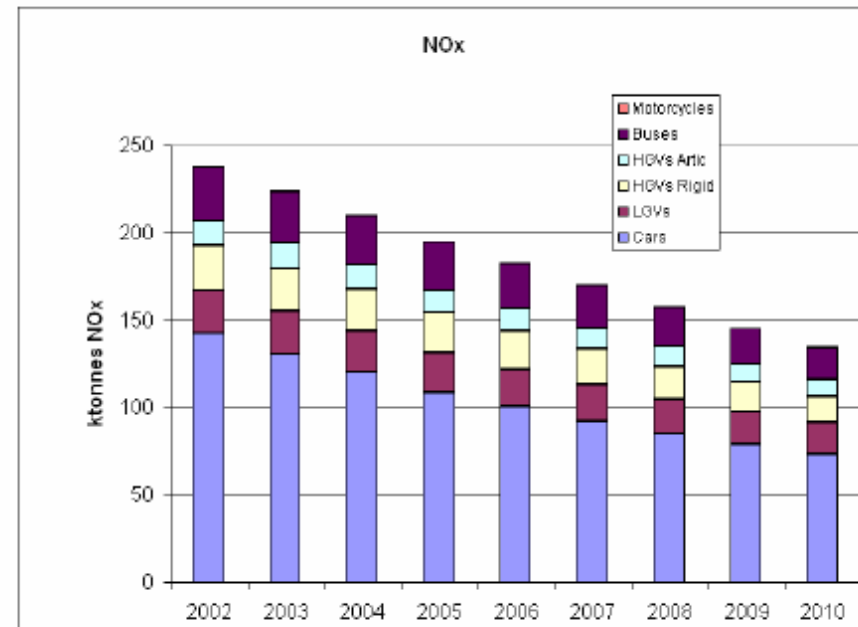


Reductions in NO_x emissions from industrial combustion plant in Europe





Sector sources of NOx and their reductions in the UK



Links between policy actions for O_3 reduction and chemical mechanisms

- Initiation: OH formed from ozone photolysis at a rate $P_{OH} (= 2k_3[H_2O]J_1[O_3]/\{k_2[M] + k_3[H_2O]\})$

- Propagation



- Termination



- Ozone formation

O_3 is formed by NO_2 photolysis with a rate equal to the sum of the rates of reactions 5 and 7 ($= v_5 + v_7$)

NO_x and VOC control of ozone formation

- Under polluted conditions, chain propagation is fast, so $v_4 = v_5 = v_6 = v_7$
- $P_{O_3} = v_5 + v_7 = 2v_7 = 2k_7[HO_2][NO]$ A
- Also $v_4 = v_7 \quad \therefore [OH] = k_7[HO_2][NO]/\{k_4[RH]\}$ B
- Steady state for radicals: rate of termination = rate of initiation, ie $P_{OH} = v_8 + v_9$

1. Low NO_x: $v_8 \gg v_9 \quad P_{OH} = 2k_8[HO_2]^2;$
 $[HO_2] = \sqrt{(P_{OH}/2k_8)}$

Sub in A: $P_{O_3} = 2k_7[NO] \sqrt{(P_{OH}/2k_8)}.$

$P_{O_3} \propto [NO], \text{ independent } [RH] \quad \text{NO}_x \text{ limited}$

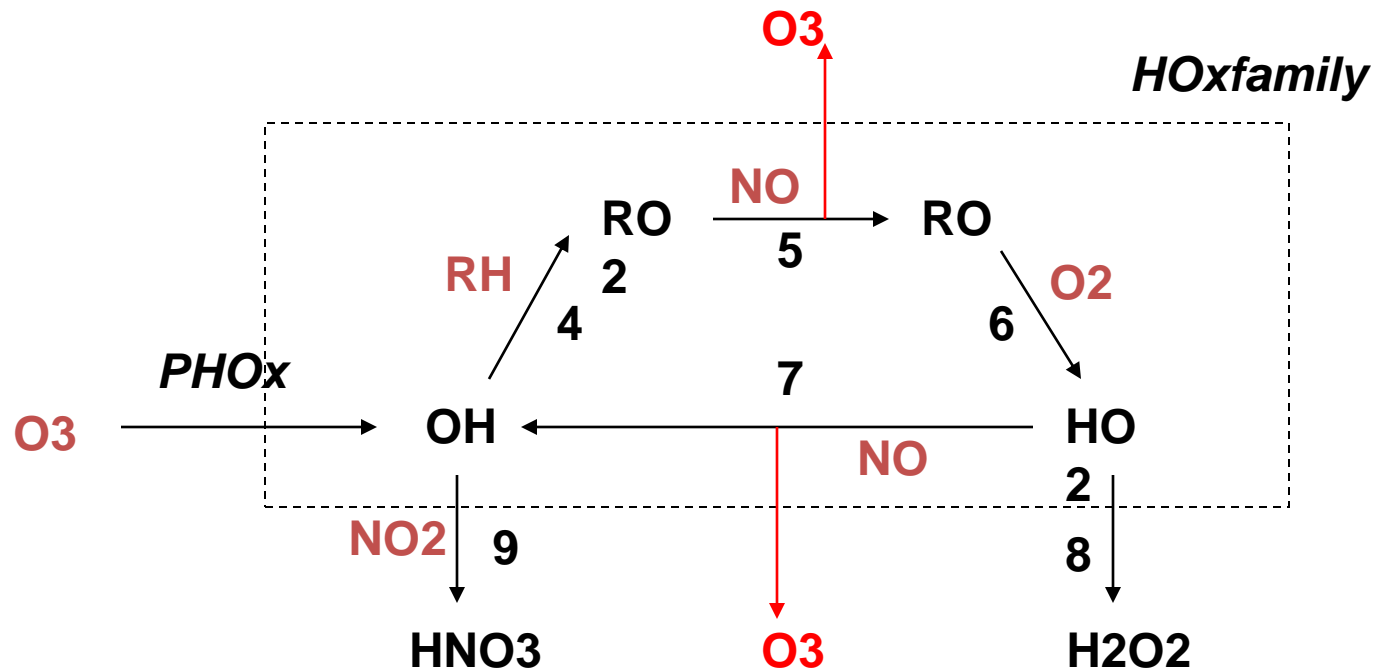
2. High NO_x: $v_8 \ll v_9 \quad [OH] = P_{OH}/(k_9[NO_2][M])$

Sub in B: $[HO_2] = P_{OH}k_4[RH]/\{k_7k_9\{NO\}[NO_2][M]\}$

Sub in A: $P_{O_3} = 2k_4[RH]/\{k_9[NO_2][M]\}$

$P_{O_3} \propto [NO_2]^{-1}; [RH] \quad \text{VOC limited}$

DEPENDENCE OF OZONE PRODUCTION ON NO_x AND HYDROCARBONS



$$P(\text{O}_3) = \frac{2k_4 P_{\text{HOx}} [\text{RH}]}{k_9 [\text{NO}_2] [\text{M}]}$$

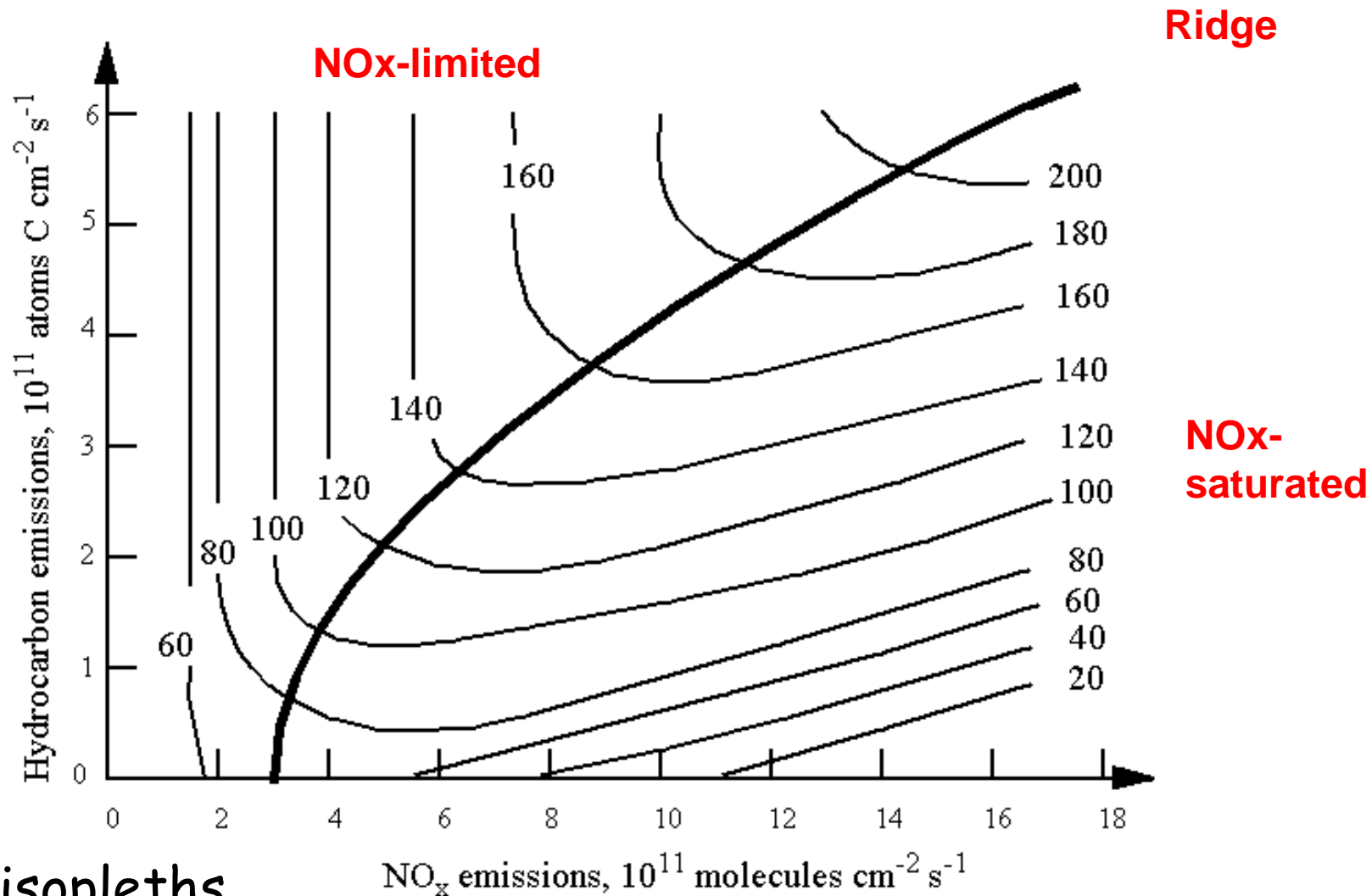
“NOx- saturated” or
“VOC-limited” regime

$$P(\text{O}_3) = 2k_7 \left(\frac{P_{\text{HOx}}}{k_8} \right)^{1/2} [\text{NO}]$$

“NOx-limited” regime

OZONE CONCENTRATIONS vs. NO_x AND VOC EMISSIONS

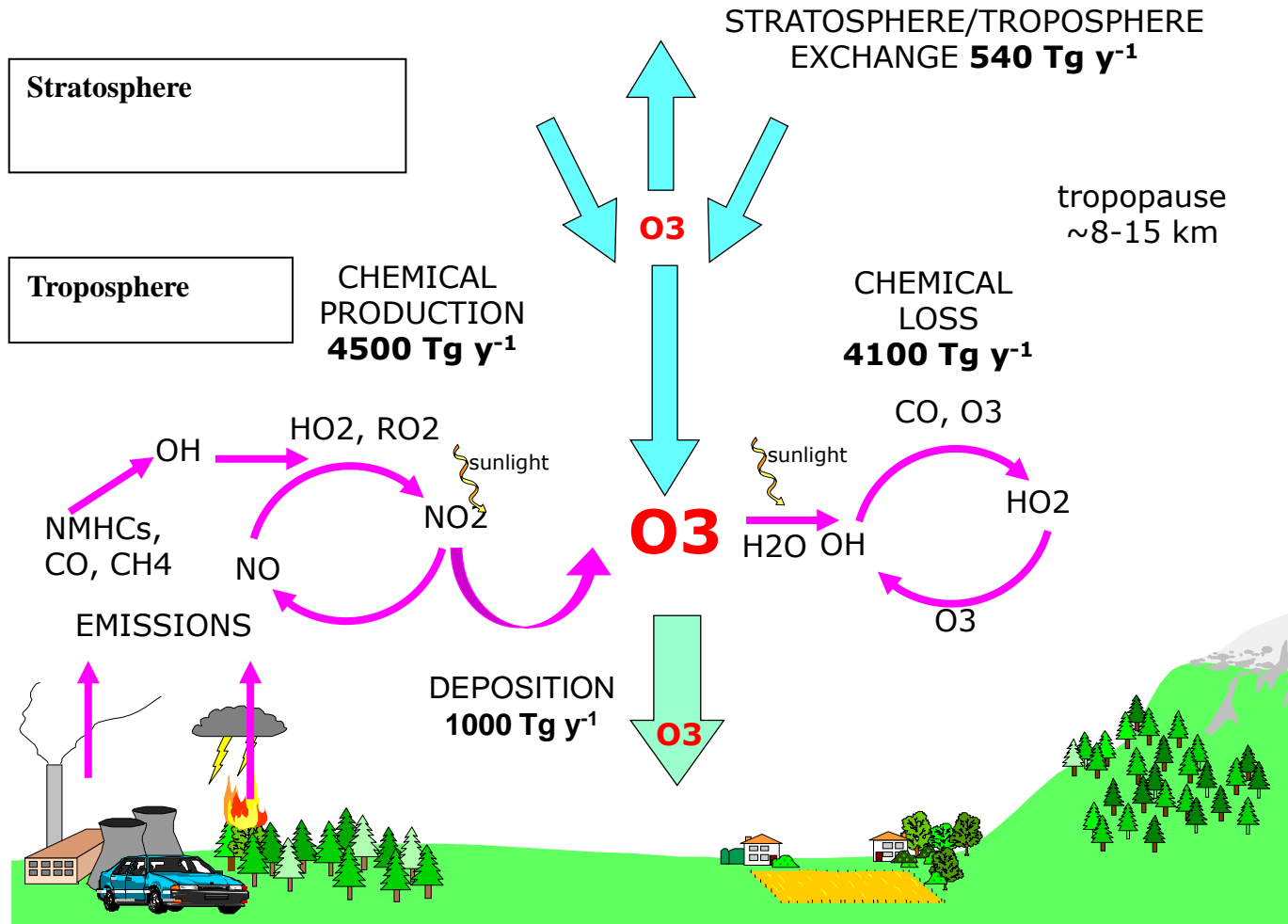
Air pollution model calculation for a typical urban airshed



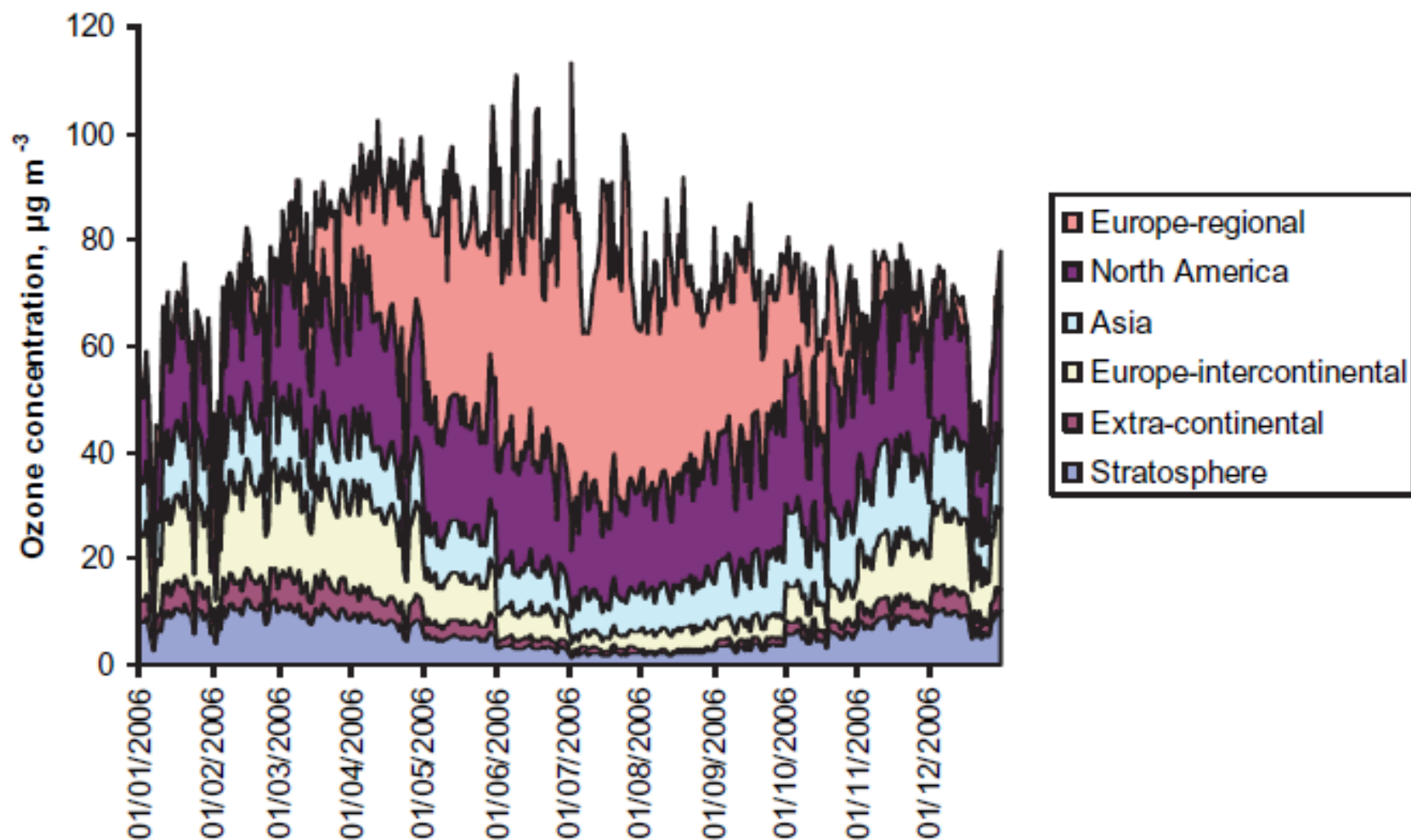
Global budget for ozone ($\text{Tg O}_3 \text{ yr}^{-1}$)

- *Chemical production* *3000 - 4600*
 - $\text{HO}_2 + \text{NO}$ 70%
 - $\text{CH}_3\text{O}_2 + \text{NO}$ 20%
 - $\text{RO}_2 + \text{NO}$ 10%
- *Transport from stratosphere* *400 - 1100*
- *Chemical loss* *3000 - 4200*
 - $\text{O}^1\text{D} + \text{H}_2\text{O}$ 40%
 - $\text{HO}_2 + \text{O}_3$ 40%
 - $\text{OH} + \text{O}_3$ 10%
 - others 10%
- *Dry deposition* *500 - 1500*

Global budget of ozone



Geographical determinants of ozone in W. Europe



What is happening to background ozone - a selection of results

- Ozone in range 5 - 16 ppb, Montsouris Observatory in Paris 1876 - 1910
- O₃ at Arosa, Switzerland, during the 1950s give mixing ratios of ~18 ppb with doubling over next 30 years.
- Ozone sondes (26 - 59 N). Increase in 1970s; no clear trend 1980 to 1996
- Ozone sonde at Hohenpeissenberg (alpine location in southern Germany; 1966 -present day). mid-troposphere layer - large increases 1960s - 1980s; with smaller increases and even declines thereafter
- Surface ozone, 17 background stations up to mid-1990s - no clear and consistent trend even in northern latitudes
- Background ozone has increased by up to 5 ppb per decade over the last 20 to 30 years, according to measurements at sea level and on mountain tops that are less influenced by European sources

Annual mean ozone at Mace Head, Western Ireland (screened)

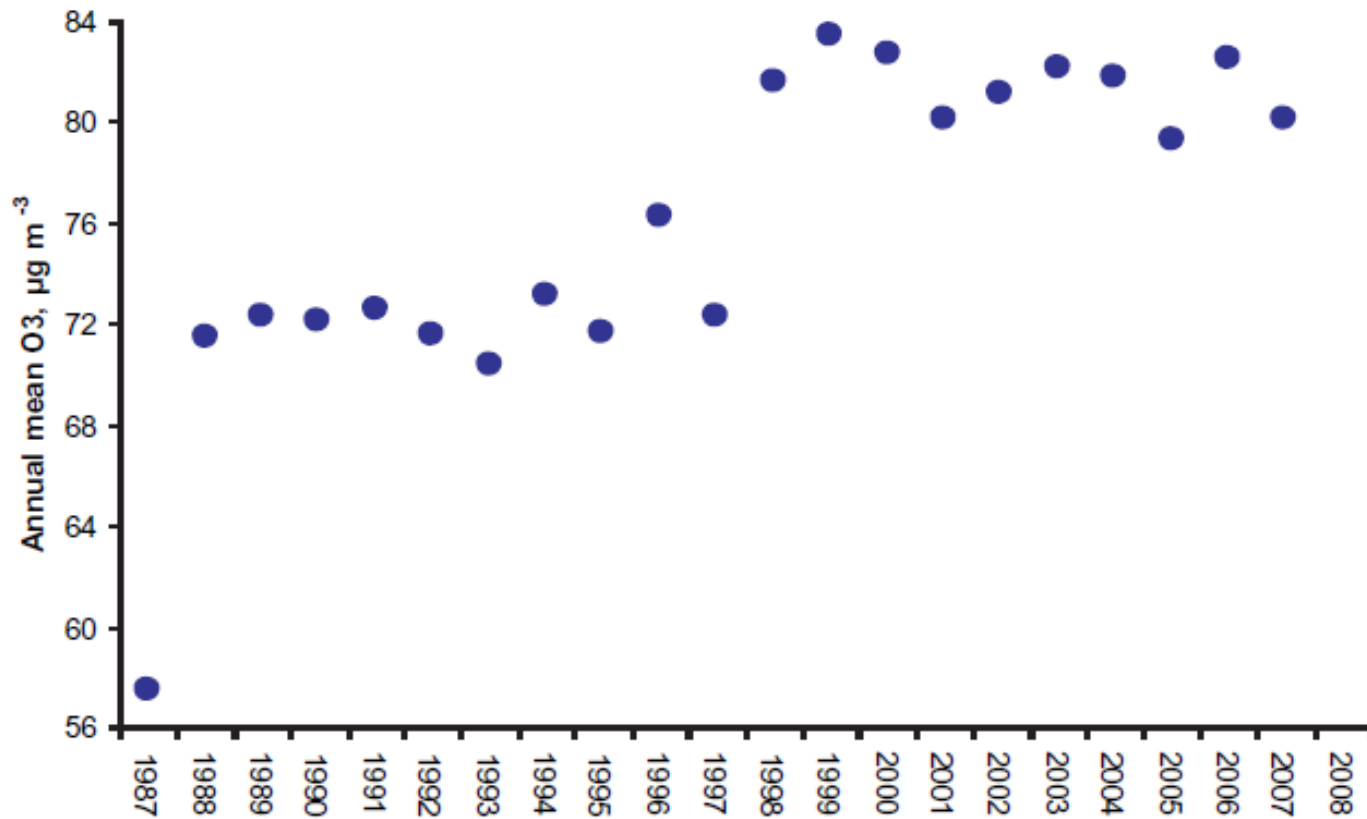
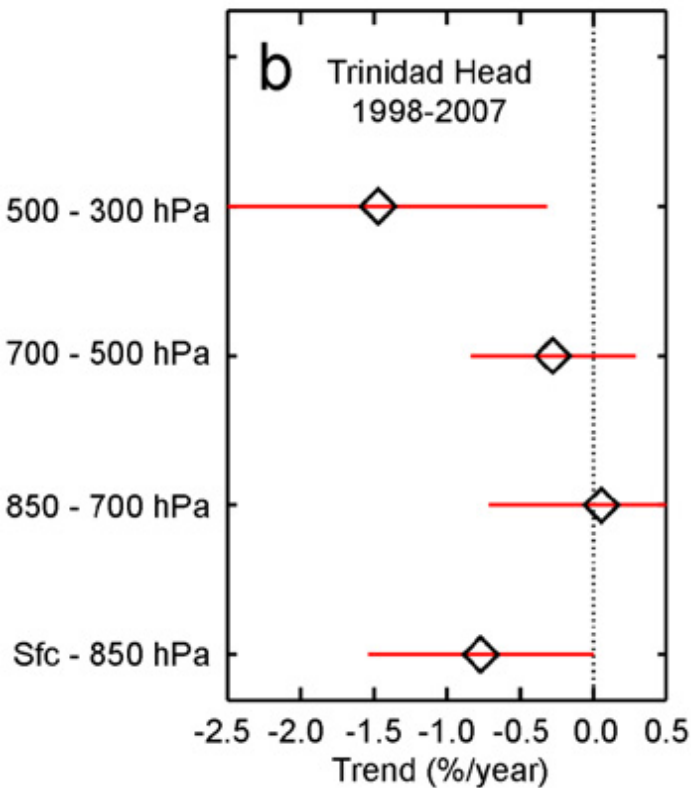


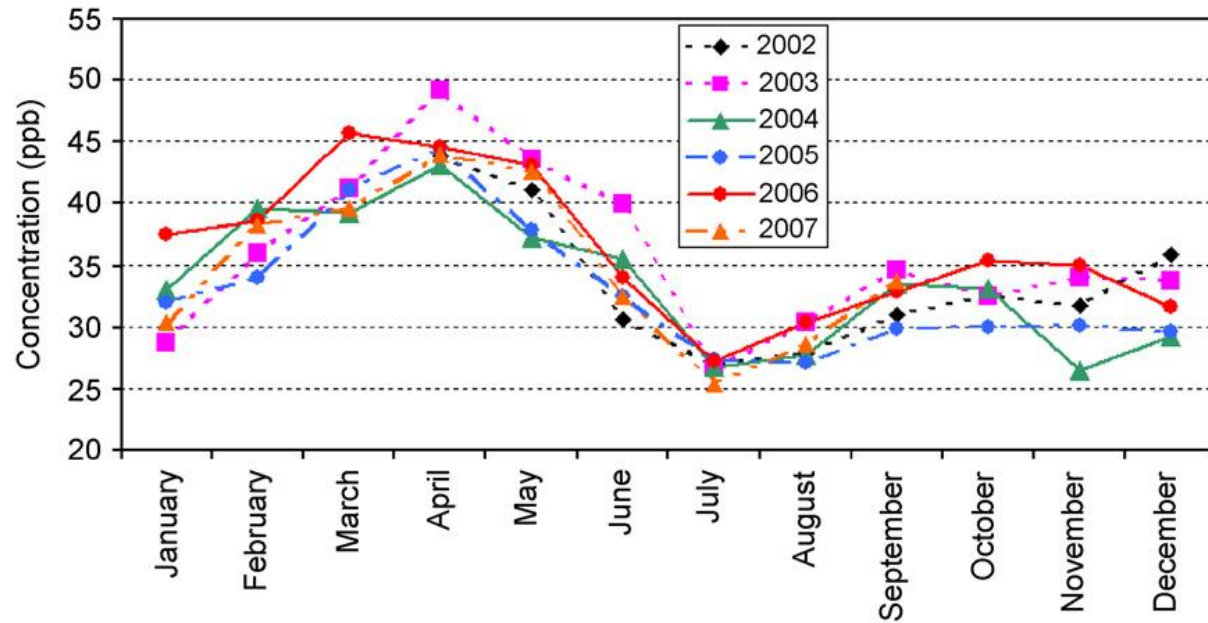
Figure 3.3 Annual mean background ozone concentrations for filtered air masses at Mace Head, Ireland, as determined by Derwent *et al.* (2007a).



What is happening in the US?

(i) Trends in ozone at Trinidad Head vs altitude 1998-2007

(ii) Monthly average daytime ozone mixing ratios, Trinidad Head, 2002 - 2007 vs earlier analyses which suggest increasing background ozone



Background ozone is primarily determined by NO_x, CH₄ and CO concentrations, which provide the best policy opportunity for control.

Next slide:

IIASA: Planned global legislation for road vehicles

Country	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14	
European Union	E1	Euro 2					Euro 3				Euro 4				Euro 5					E6	
Bangladesh ^a											Euro 2										
Bangladesh ^b											Euro 1										
Hong Kong, China	Euro 1		Euro 2				Euro 3				Euro 4										
India ^c							Euro 1				Euro 2				Euro 3						
India ^d					E1	Euro 2				Euro 3				Euro 4							
Indonesia											Euro 2										
Malaysia				Euro 1		Euro 2										Euro 4					
Nepal						Euro 1															
Pakistan																					
Philippines									Euro 1				Euro 2		Euro 4						
PRC ^a							Euro 1		Euro 2			Euro 3		Euro 4							
PRC ^e							Euro 1		Euro 2			Euro 3		Euro 4 Beijing only							
Singapore ^a	Euro 1						Euro 2														
Singapore ^b	Euro 1						Euro 2				Euro 4										
Sri Lanka									Euro 1												
Taipei, China					US Tier 1										US Tier 2 for diesel ^g						
Thailand	Euro 1						Euro 2			Euro 3										Euro 4	
Viet Nam													Euro 2		Euro 4						

Notes:

Italics – under discussion

a – gasoline

b – diesel

c – Entire country

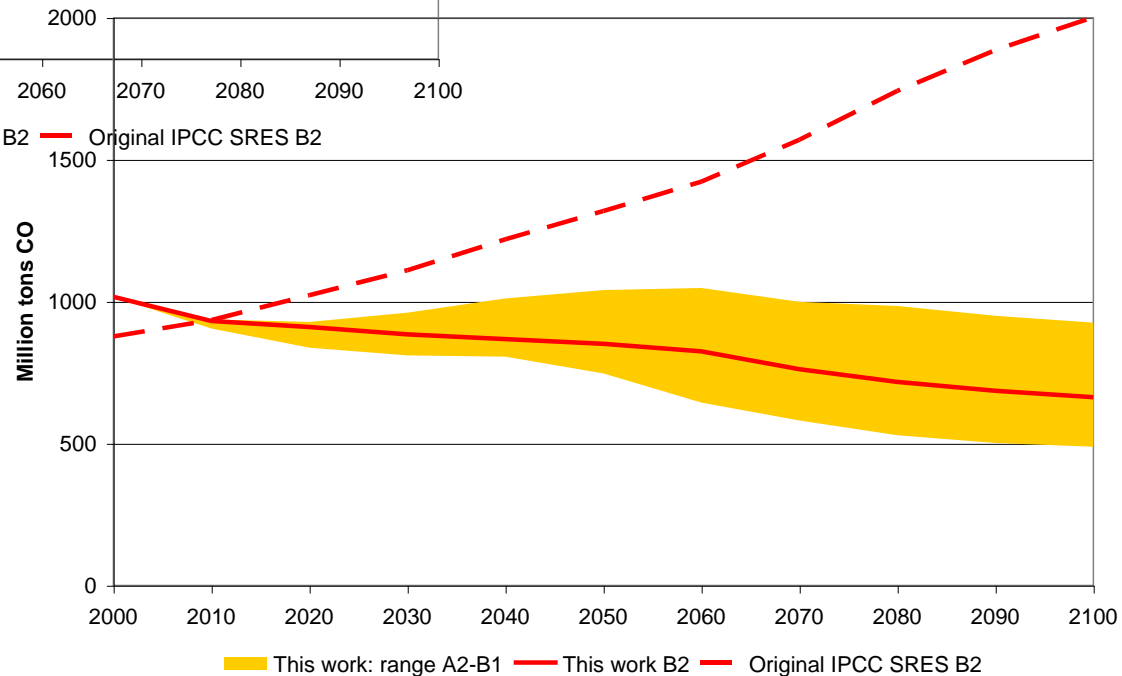
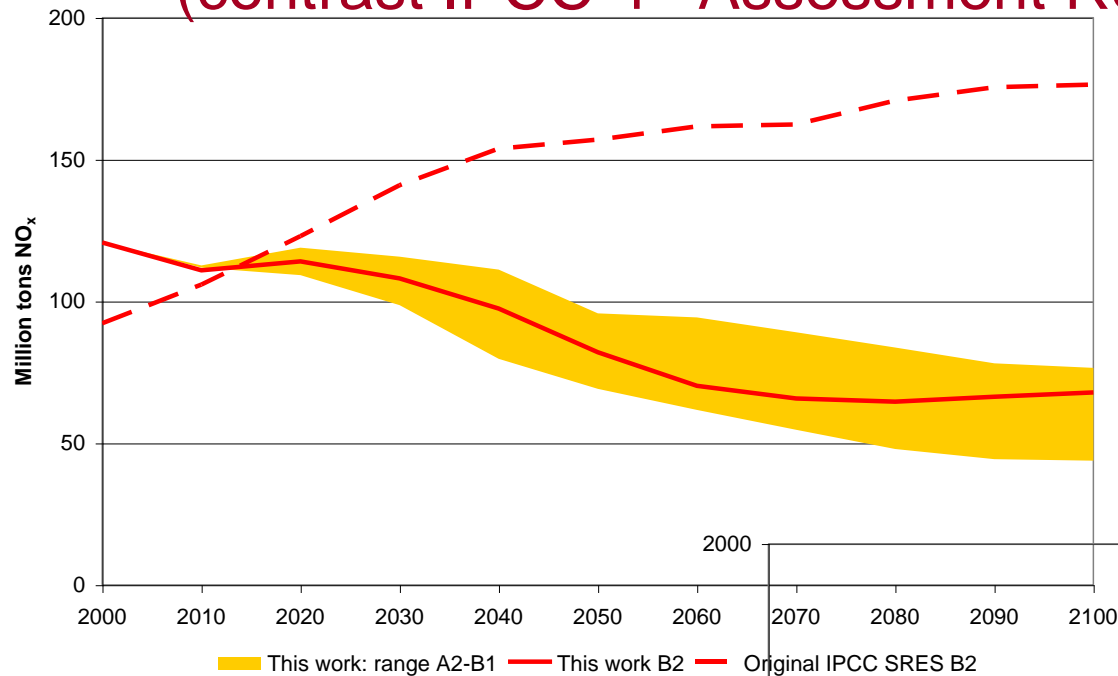
d – Delhi, Chennai, Mumbai, Kolkata, Bangalore, Hyderabad, Agra, Surat, Pune, Kanpur, Ahmedabad, Sholapur, Lucknow; Other cities in India are in Euro 2

e – Beijing and Guangzhou (as of 01 September 2006) have adopted Euro 3 standards; Shanghai has requested the approval of the State Council for implementation of Euro 3

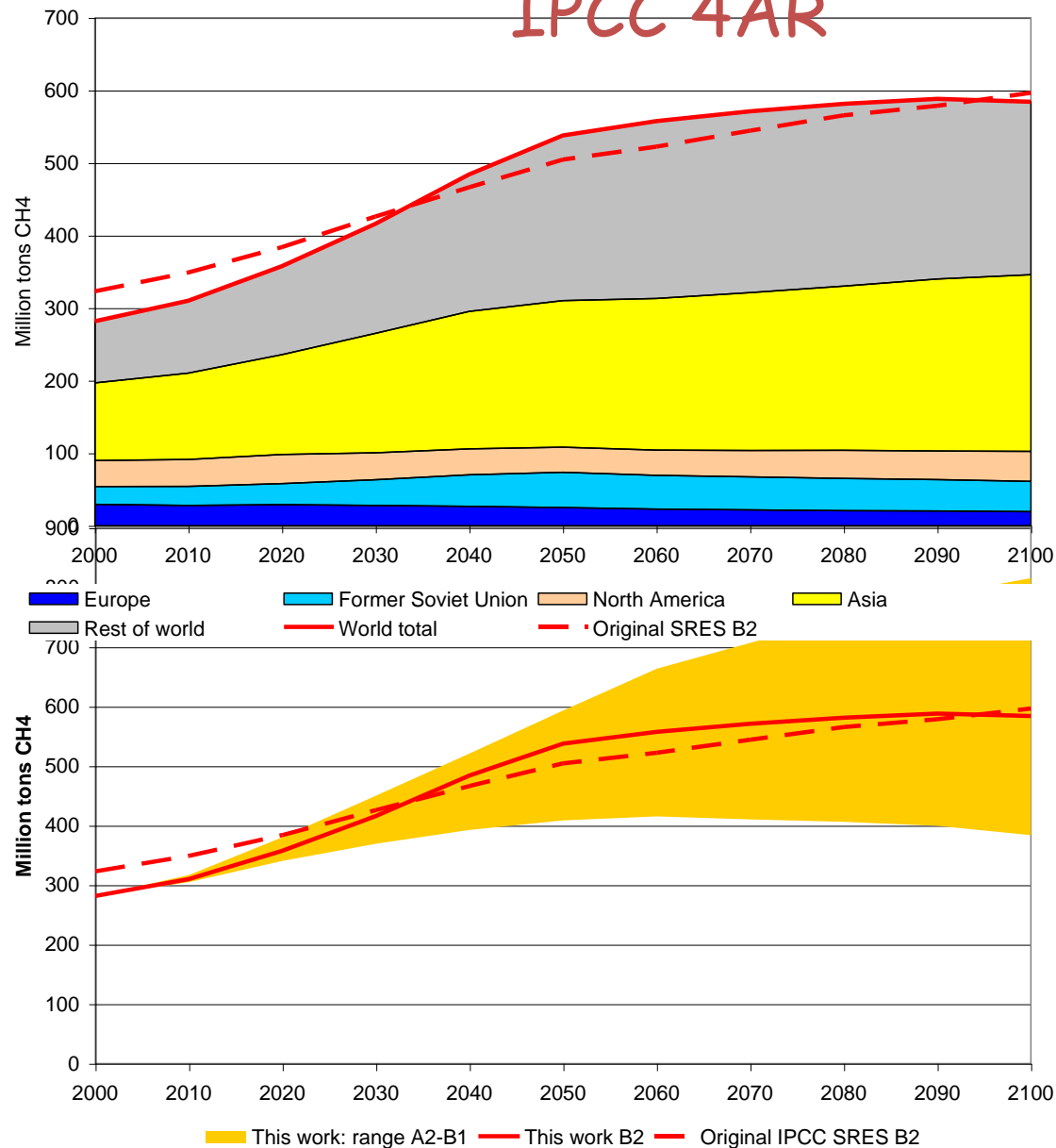
f – Euro 4 for gasoline vehicles and California ULEV standards for diesel vehicles

g – Gasoline vehicles under consideration

Revised NO_x and CO emissions projections (contrast IPCC 4th Assessment Report)



CH₄ emissions projections - little change from IPCC 4AR



Regional Air Quality

World Health Organisation, Air Quality Guidelines, 2005 (apply world-wide)

Ozone (O_3):	100 $\mu\text{g}/\text{m}^3$ 8-hour mean
$PM_{2.5}$	10 $\mu\text{g}/\text{m}^3$ annual mean; 25 $\mu\text{g}/\text{m}^3$ 24-hour mean
PM_{10}	20 $\mu\text{g}/\text{m}^3$ annual mean; 50 $\mu\text{g}/\text{m}^3$ 24-hour mean
NO_2	40 $\mu\text{g}/\text{m}^3$ annual mean 200 $\mu\text{g}/\text{m}^3$ 1-hour mean
SO_2	20 $\mu\text{g}/\text{m}^3$ 24-hour mean 500 $\mu\text{g}/\text{m}^3$ 10-minute mean

- The *WHO Air quality guidelines* represent the most widely agreed and up-to-date assessment of health effects of air pollution, recommending targets for air quality at which the health risks are significantly reduced. The Guidelines indicate that by reducing particulate matter (PM_{10}) pollution from 70 to 20 micrograms per cubic metre, we can cut air quality related deaths by around 15%.

Air Quality Standards in the US

<http://www.epa.gov/air/criteria.html>

National Ambient Air Quality Standards (NAAQS) | Air and Radiation | US EPA - Mozilla Firefox

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US EPA National Ambient Air Quality Standards ...

www.epa.gov/air/criteria.html

epa ozone standard

National Ambient Air Quality Standards (NAAQS)

The [Clean Air Act](#), which was last amended in 1990, requires EPA to set [National Ambient Air Quality Standards](#) (40 CFR part 50) for pollutants considered harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards. **Primary standards** provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. **Secondary standards** provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.

EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" pollutants. They are listed below. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air ($\mu\text{g}/\text{m}^3$).

Pollutant [final rule cite]	Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide [76 FR 54294, Aug 31, 2011]	primary	8-hour	9 ppm	Not to be exceeded more than once per year
		1-hour	35 ppm	
Lead [73 FR 66964, Nov 12, 2008]	primary and secondary	Rolling 3 month average	0.15 $\mu\text{g}/\text{m}^3$ ⁽¹⁾	Not to be exceeded
Nitrogen Dioxide [75 FR 6474, Feb 9, 2010] [61 FR 52852, Oct 8, 1996]	primary	1-hour	100 ppb	98th percentile, averaged over 3 years
	primary and secondary	Annual	53 ppb ⁽²⁾	Annual Mean
Ozone [73 FR 16436, Mar 27, 2008]	primary and secondary	8-hour	0.075 ppm ⁽³⁾	Annual fourth-highest daily maximum 8-hr concentration, averaged over 3 years
Particle Pollution Dec 14, 2012	PM _{2.5}	primary	Annual	12 $\mu\text{g}/\text{m}^3$
		secondary	Annual	15 $\mu\text{g}/\text{m}^3$
	PM ₁₀	primary and secondary	24-hour	35 $\mu\text{g}/\text{m}^3$
		primary and secondary	24-hour	150 $\mu\text{g}/\text{m}^3$
Sulfur Dioxide [75 FR 35520, Jun 22, 2010] [38 FR 25678, Sept 14, 1973]	primary	1-hour	75 ppb ⁽⁴⁾	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
	secondary	3-hour	0.5 ppm	Not to be exceeded more than once per year

as of October 2011

(1) Final rule signed October 15, 2008. The 1978 lead standard (1.5 $\mu\text{g}/\text{m}^3$ as a quarterly average) remains in effect until one year after an area is designated for the 2008 standard, except that in areas designated nonattainment for the 1978, the 1978 standard remains in effect until implementation plans to attain or maintain the 2008 standard are approved.

(2) The official level of the annual NO₂ standard is 0.053 ppm, equal to 53 ppb, which is shown here for the purpose of clearer comparison to the 1-hour standard.

(3) Final rule signed March 12, 2008. The 1997 ozone standard (0.08 ppm, annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years) and related implementation rules remain in place. In 1997, EPA revoked the 1-hour ozone standard (0.12 ppm, not to be exceeded more than once per year) in all areas, although some areas have continued obligations under that standard ("anti-backsliding"). The 1-hour ozone standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is less than or equal to 1.

(4) Final rule signed June 2, 2010. The 1971 annual and 24-hour SO₂ standards were revoked in that same rulemaking. However, these standards remain in effect until one year after an area is designated for the 2010 standard, except in areas designated nonattainment for the 1971 standards, where the 1971 standards remain in effect until implementation plans to attain or maintain the 2010 standard are approved.

See historical tables of NAAQS standards

- [Carbon Monoxide](#)
- [Lead](#)
- [Nitrogen Dioxide](#)

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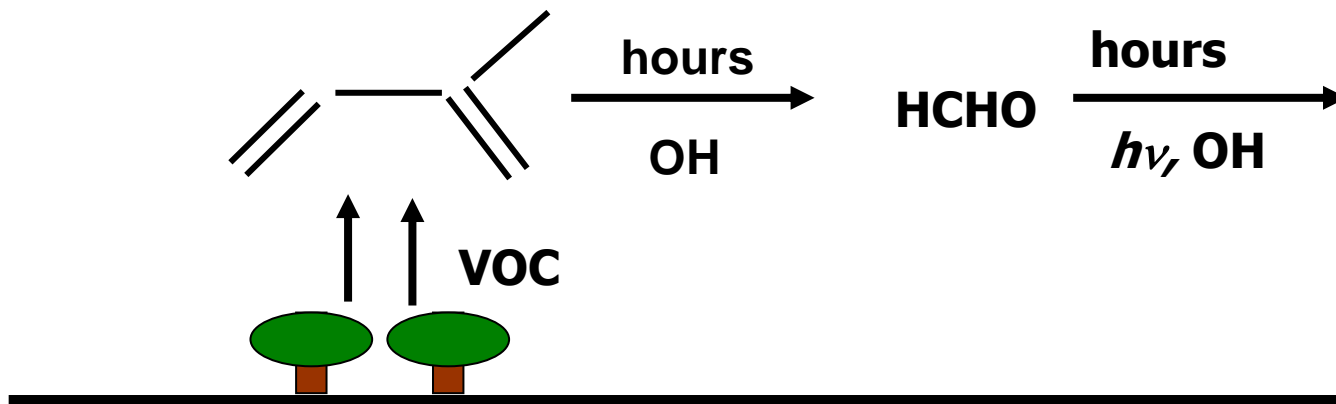
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12:32

Use of satellite measurements of HCHO columns to infer emissions and sources of non-methane VOCs (NMVOCs) in China and to assess the impact on ozone formation.

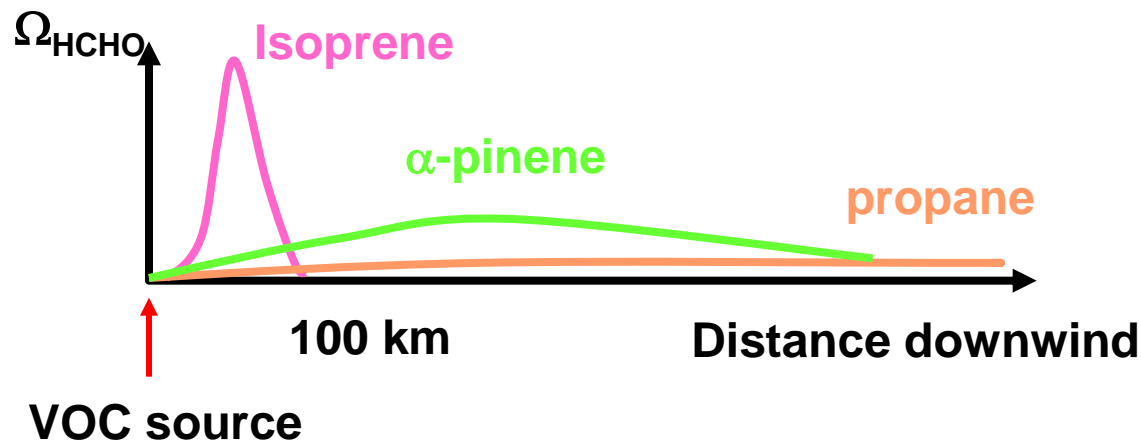
Fu et al, J Geophys Res 2007, 112, D06312

Relating HCHO Columns to VOC Emissions (Palmer)



$$E_{\text{ISOP}} = \frac{k_{\text{HCHO}} \Omega_{\text{HCHO}}}{k_{\text{ISOP}} \text{Yield}_{\text{ISOP} \rightarrow \text{HCHO}}}$$

Master Chemical
Mechanism

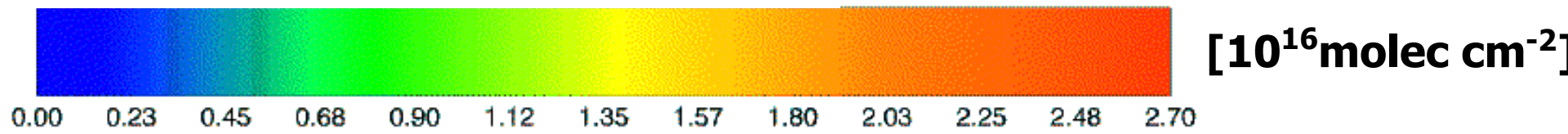
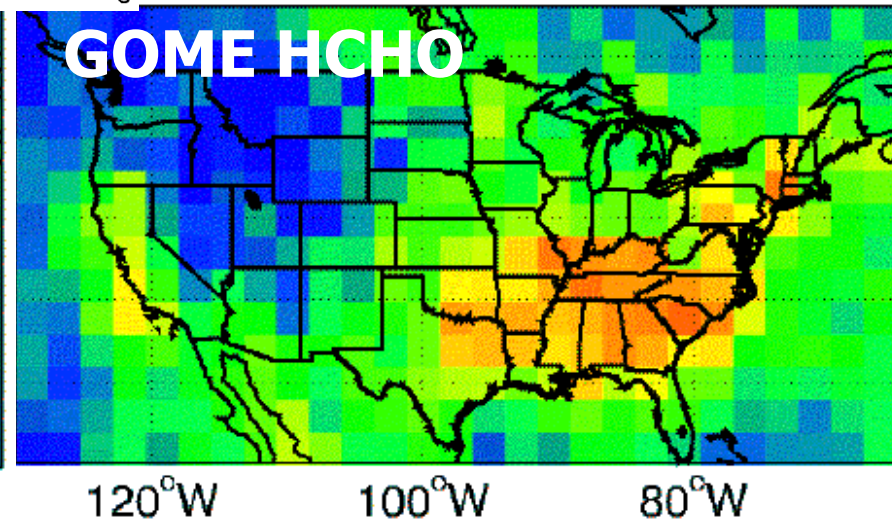
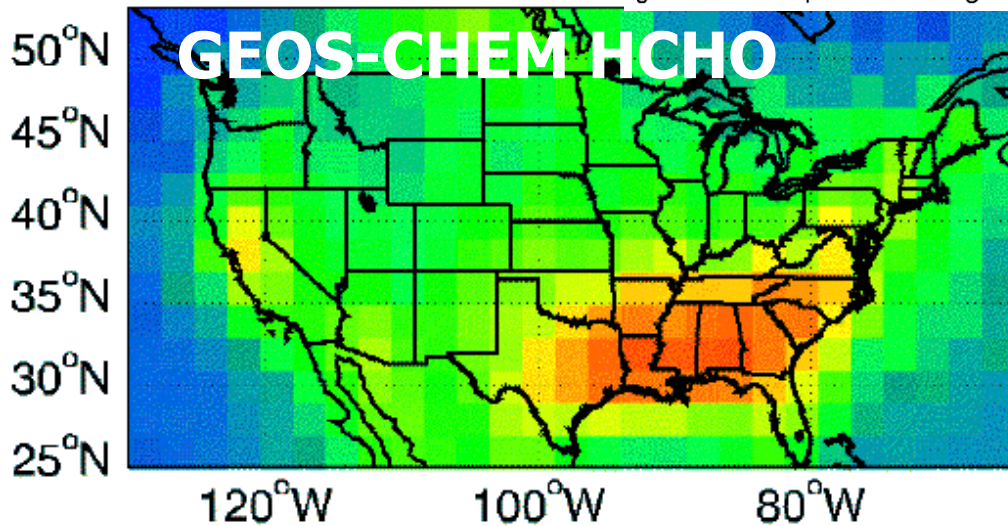
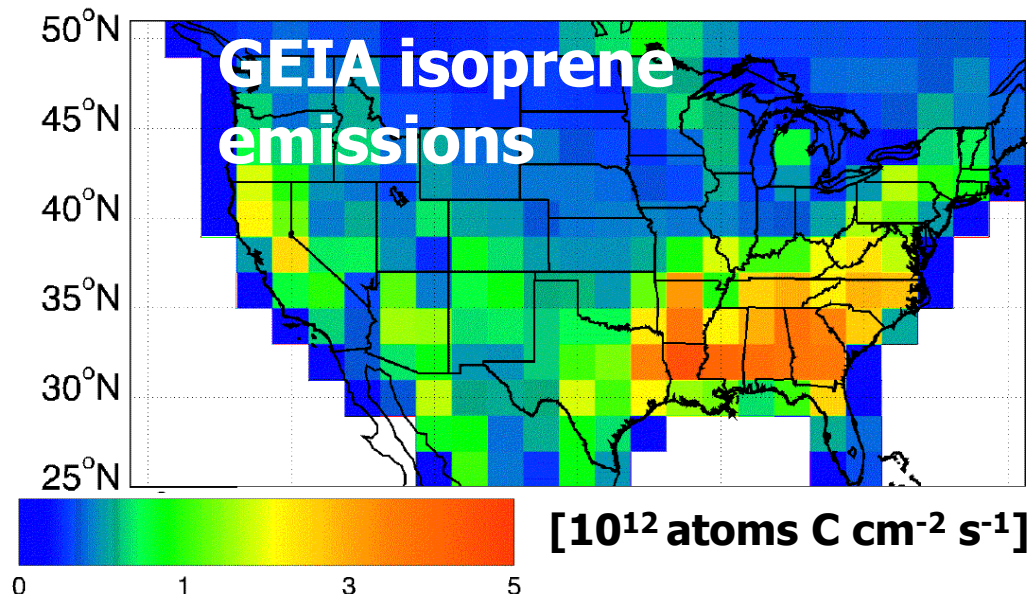


	Ultimate Yield Y (per C)	Approx. Time to Y
isoprene	~0.5	2-3 hrs
α pinene	~0.3	3-4 days
β pinene	~0.25	3-4 days
MBO	~0.4	3-4 days

HCHO columns – July 1996

BIOGENIC ISOPRENE IS THE MAIN SOURCE OF HCHO IN U.S. IN SUMMER

GOME footprint
320X40 km²

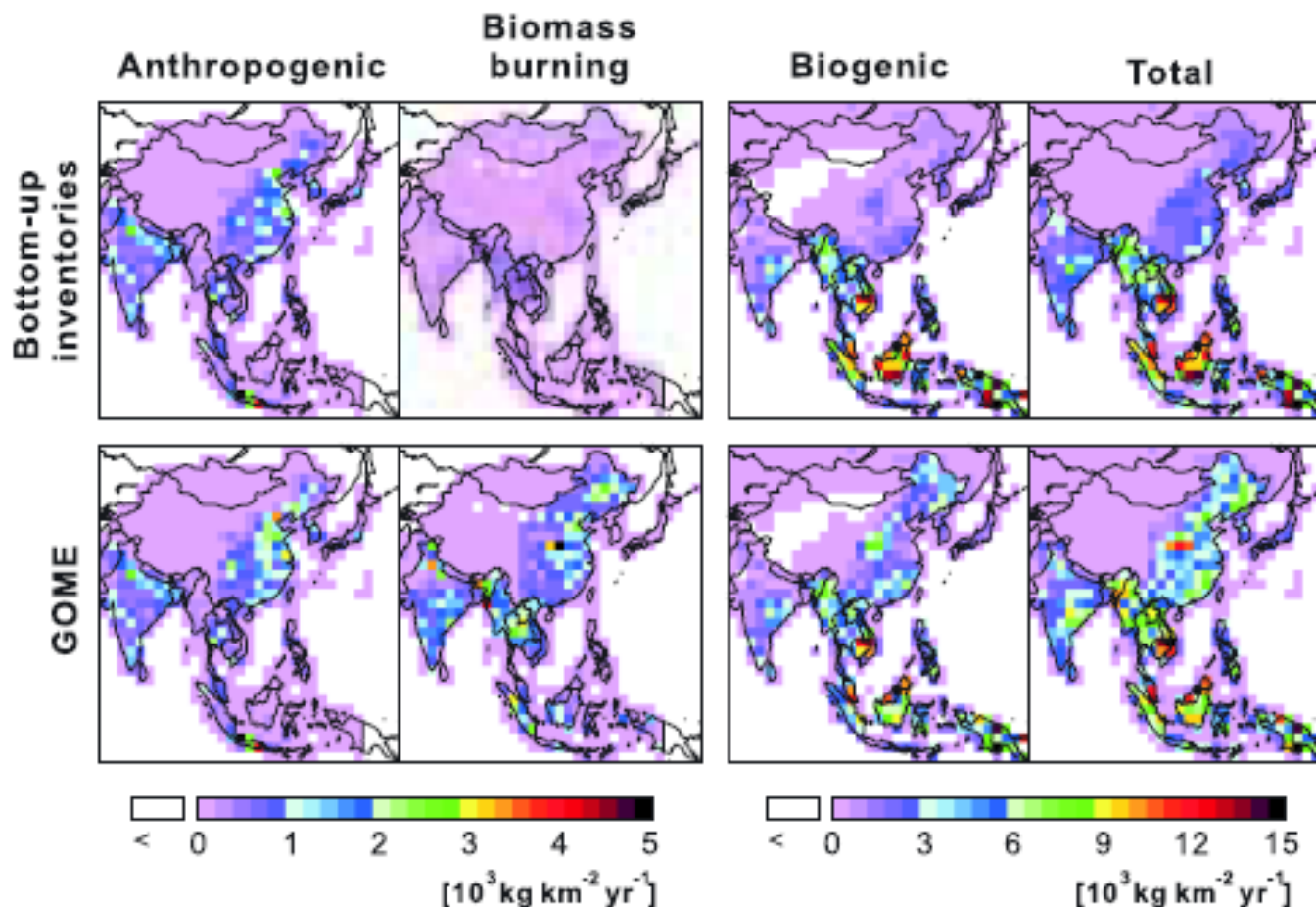


Annual mean reactive NMVOC emissions from east and south Asia.

(top) Bottom-up inventories

(bottom) Emissions inferred from GOME HCHO on the basis of the regression analysis

Colour scale at the left indicates anthropogenic and biomass burning, and the color scale on the right indicates biogenic and total sources.

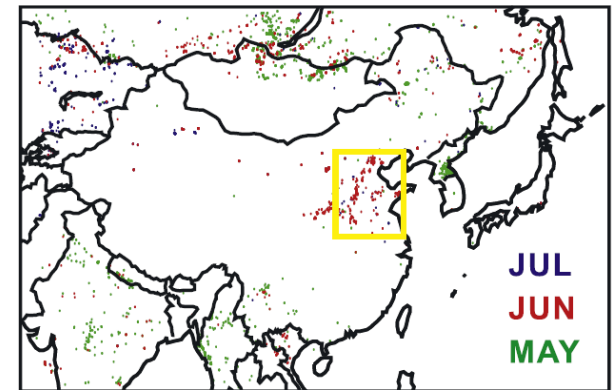


Satellite hot spot counts (ATSR = Along track scanning radiometer)

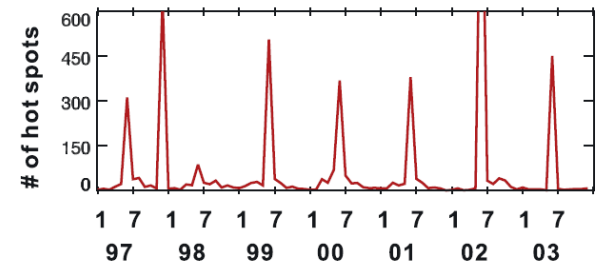
Evidence for large agricultural
biomass burning in the North
China Plain in June.

- (a) ATSR hot spots over China
for May-July 1997;
- (b) ATSR monthly hot spot
counts time series over the
North China Plain (yellow box)
for 1997-2003;
- (c) spatial extent and timing of
winter wheat harvest in China,
based on data from Ministry of
Agriculture of China [2007].

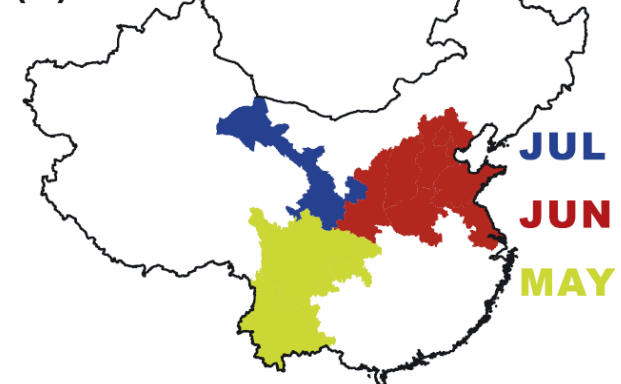
(a) Summer 1997 ATSR hot spots



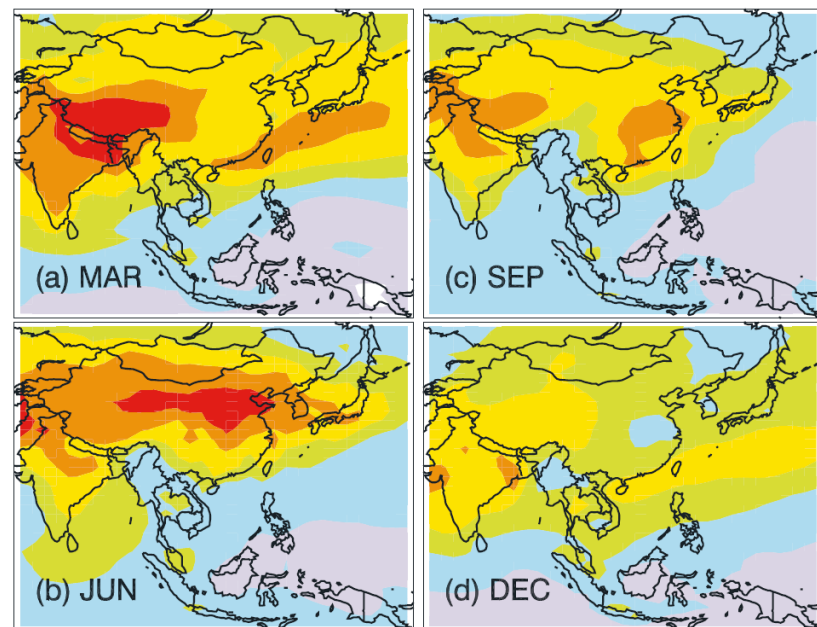
(b) ATSR hot spots 1997 - 2003
North China Plain



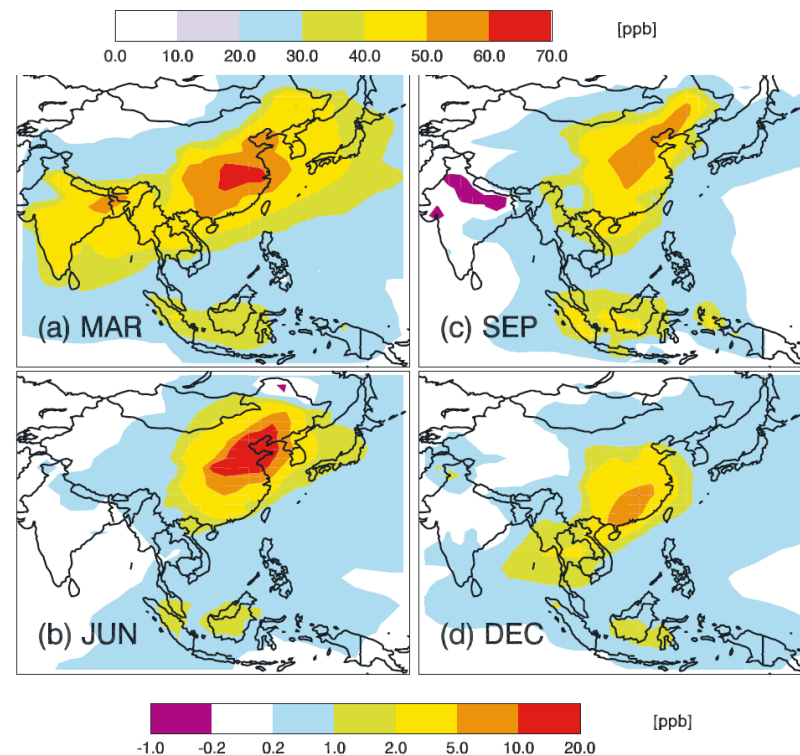
(c) Winter Wheat Harvest



Monthly mean afternoon (1300 to 1700 LT) surface ozone concentrations simulated by a global model (GEOS-Chem) using bottom-up inventories for NMVOCs in (a) March, (b) June, (c) September, and (d) December 2001.



Difference in modeled monthly mean afternoon (1300 to 1700 LT) surface ozone concentrations using GOME-inferred reactive NMVOC emission versus the bottom-up inventories for (a) March, (b) June, (c) September, and (d) December 2001.



Particulate matter

PM10 and PM2.5

World Bank data: most polluted cities as measured by particulate matter concentration

Most Polluted World Cities by PM^[33]

Particulate matter, $\mu\text{g}/\text{m}^3$ (2004 and 2011)	City
508	Skopje, Macedonia
279	Korfu, Greece
169	Cairo, Egypt
150	Delhi, India
128	Kolkata, India (Calcutta)
125	Tianjin, China
123	Chongqing, China
109	Kanpur, India
109	Lucknow, India
104	Jakarta, Indonesia
101	Shenyang, China

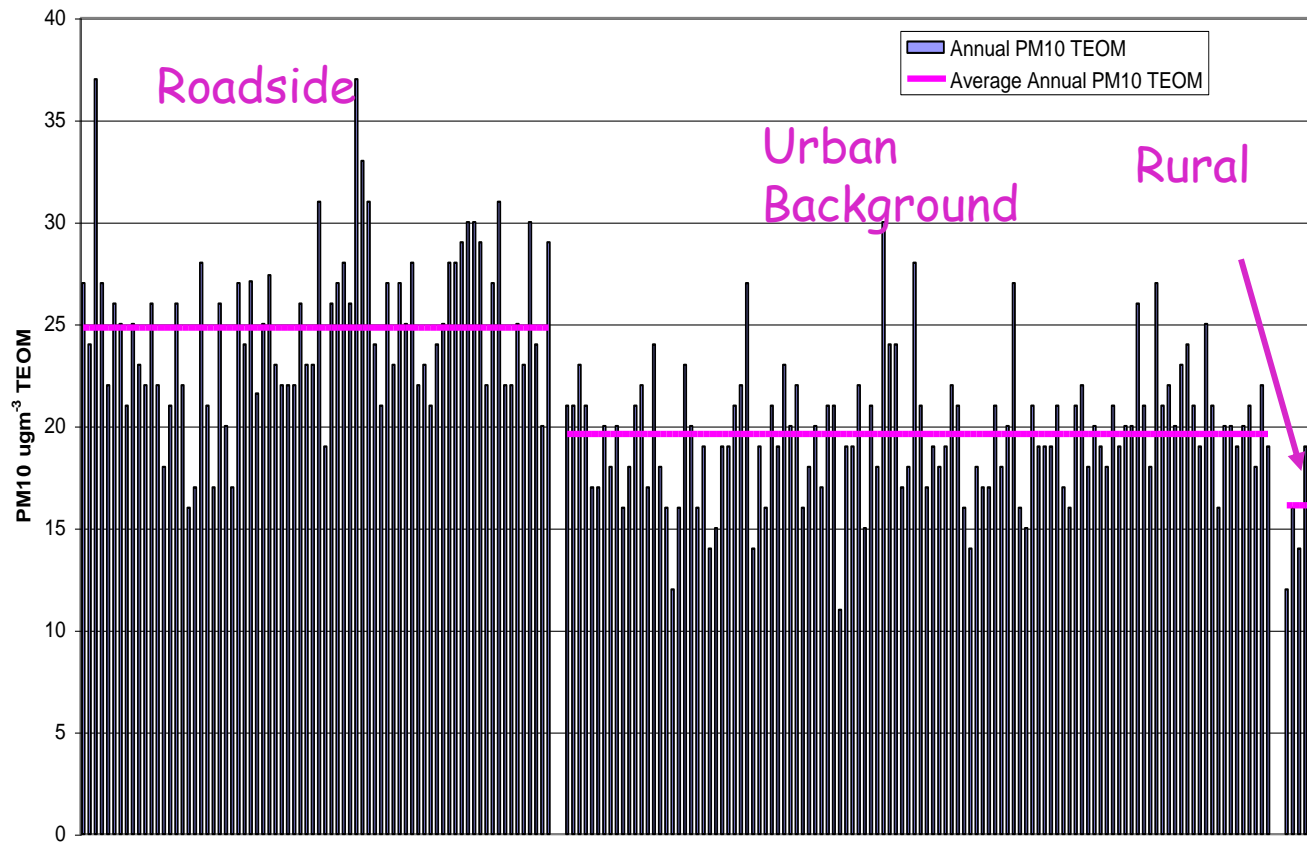
- http://siteresources.worldbank.org/DATASTATISTICS/Resources/table3_13.pdf

Reminder: WHO AQ guidelines $\text{PM}_{2.5}$ 10 $\mu\text{g}/\text{m}^3$ annual mean; 25 $\mu\text{g}/\text{m}^3$ 24-hour mean

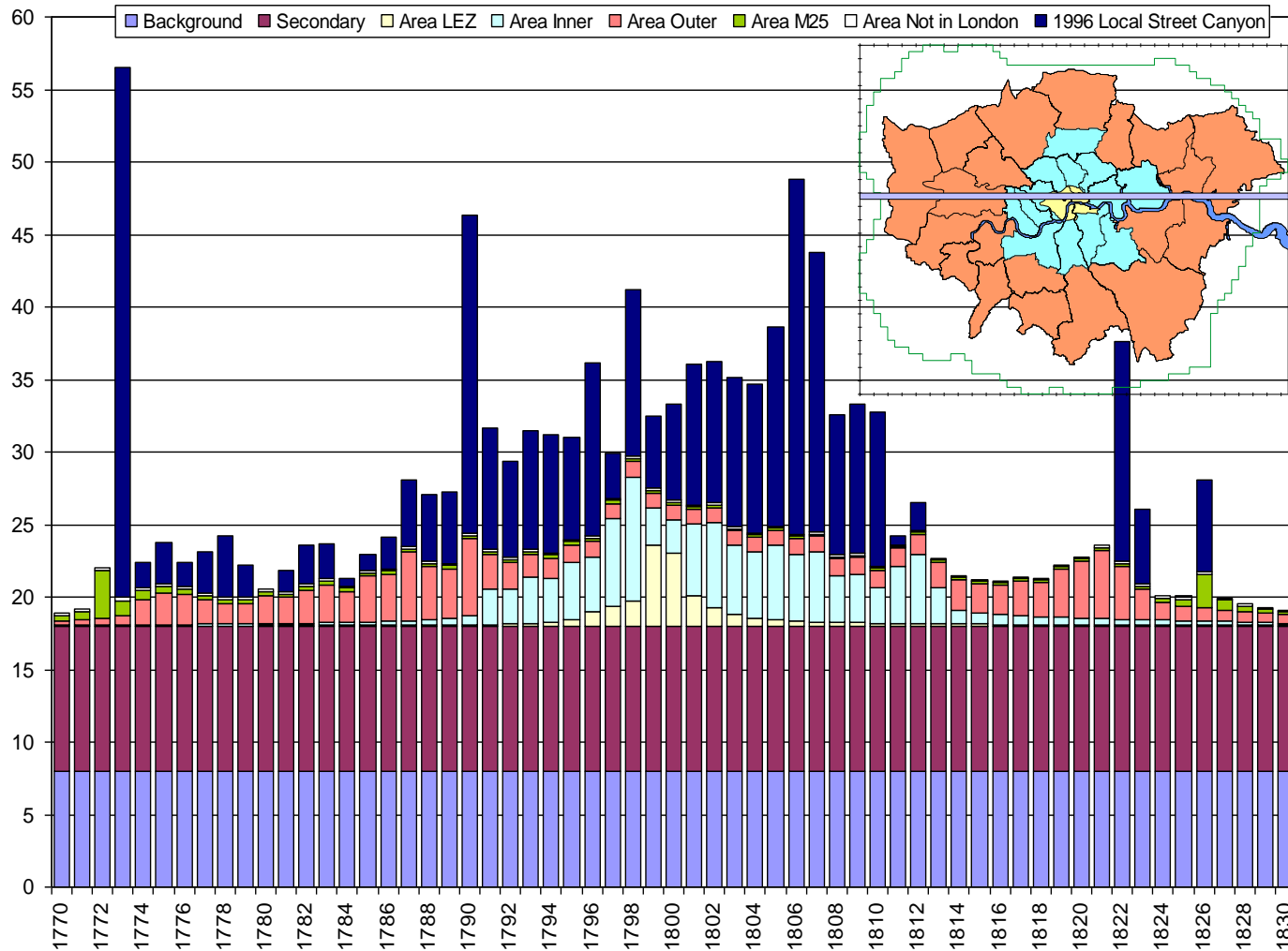
PM_{10} 20 $\mu\text{g}/\text{m}^3$ annual mean; 50 $\mu\text{g}/\text{m}^3$ 24-hour mean

Analysis of PM₁₀ from 196 sites in UK in 2003

AQEG report on Particulate Matter:

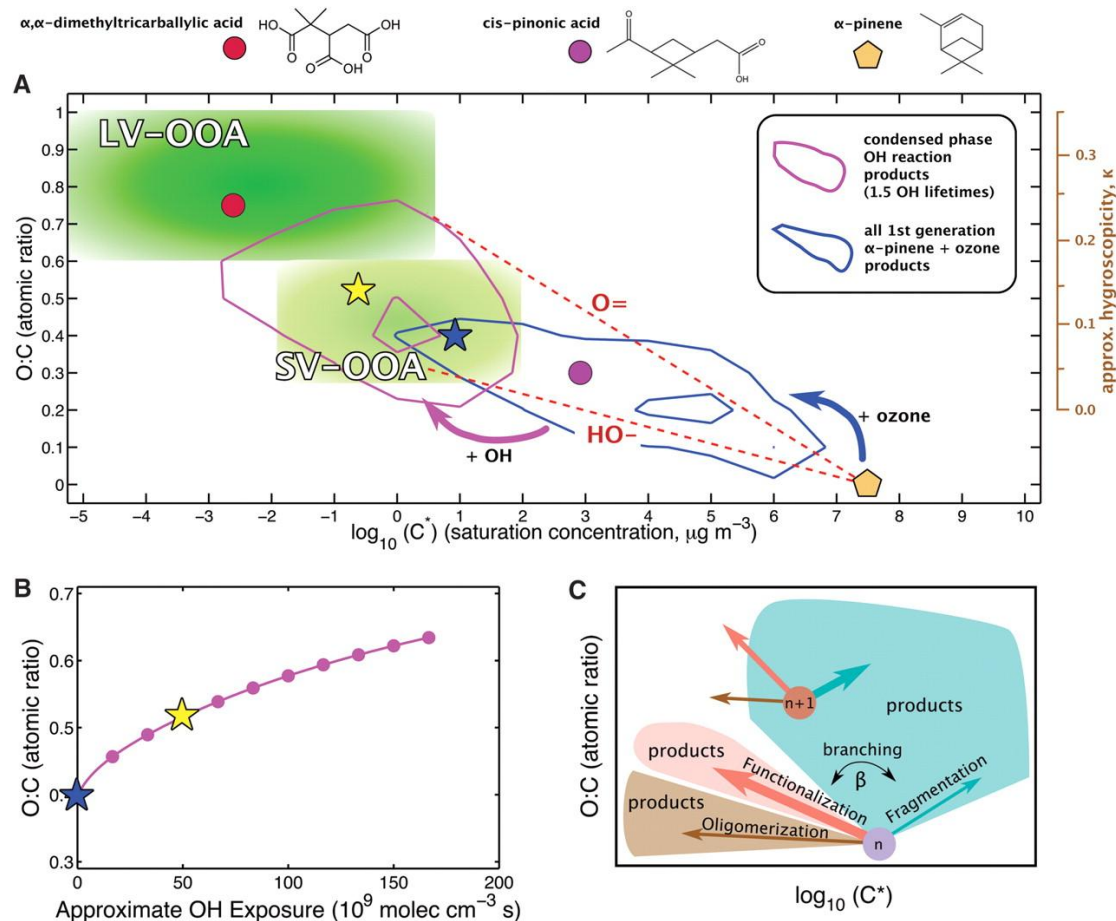


Schematic illustration of relative contributions to PM concentrations in $\mu\text{g m}^{-3}$ for road side sites in an east-west row of grid squares (right to left) across London (based on estimates for 1996).



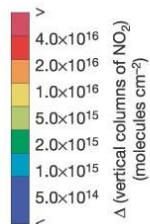
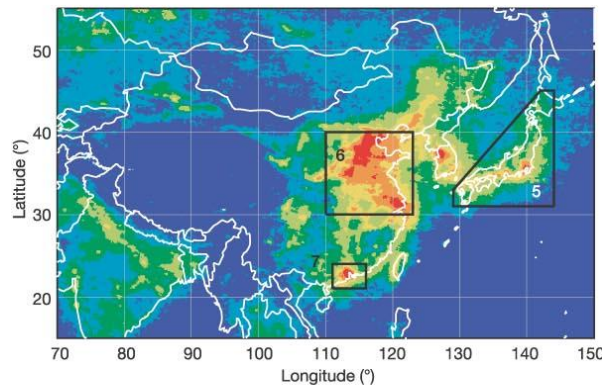
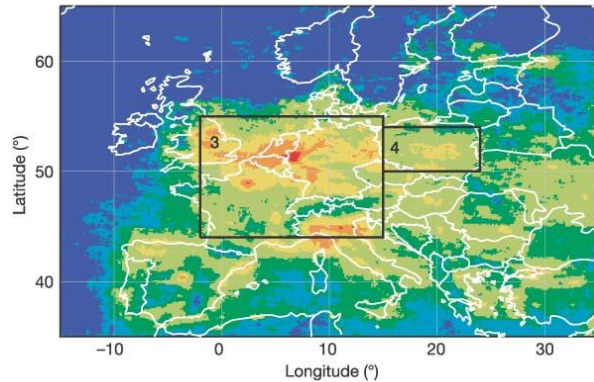
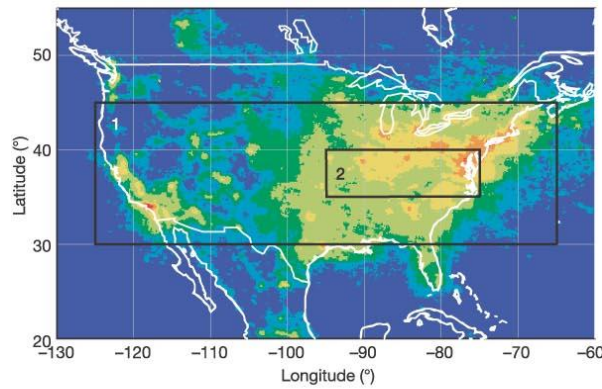
SOA formation,

Jimenez et al. *Science* 326, 1525 December 2009



Functionalization reduces volatility, fragmentation can generate more-volatile species - less likely to partition to the OA.
Branching ratio (β) between these pathways is critical

NO₂ over China observed by satellite



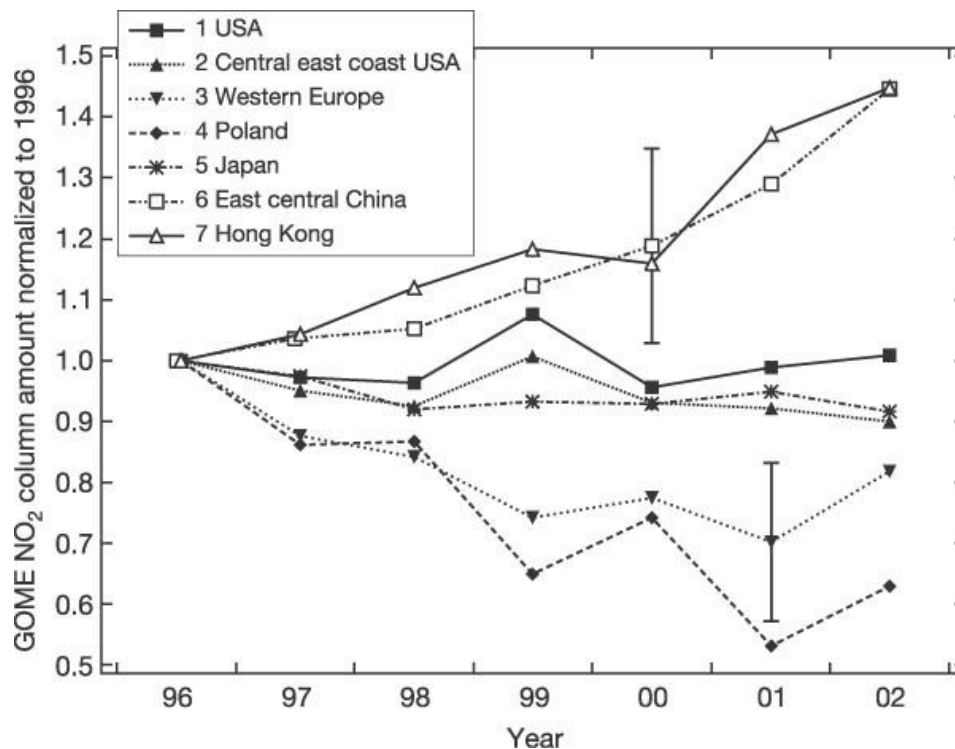
SCIAMACHY tropospheric NO₂ vertical columns averaged between December 2003 and November 2004 for selected industrial regions

Richter et al., Nature, 2005, 437, 129

Region 6 is that referred to as 'East Central China'

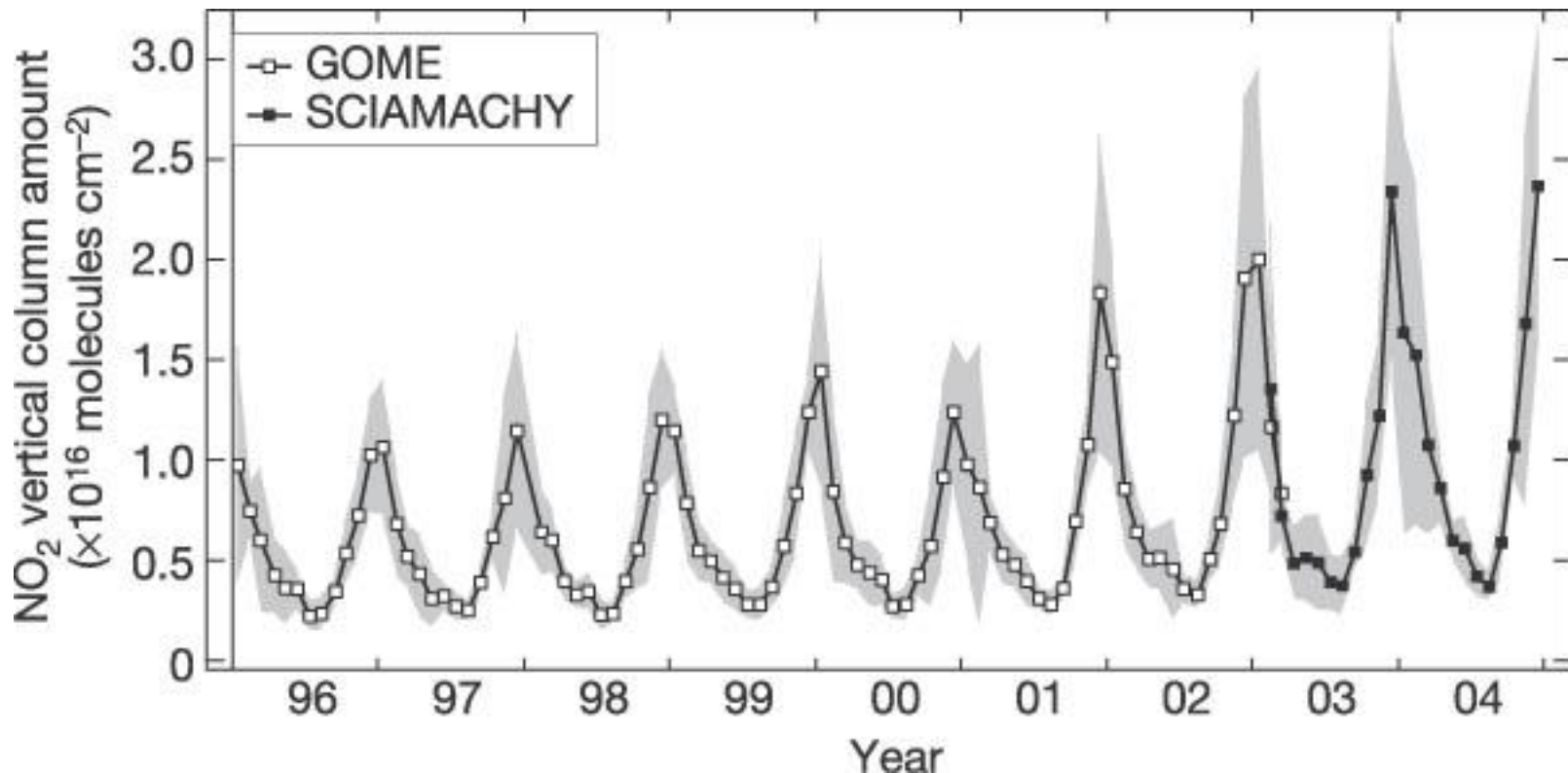
NO₂ columns 1996 - 2002

The mean annual NO₂ column amount normalized to that in 1996 for the geographical regions USA, Central East Coast USA, Western Europe, Poland, Japan, East Central China, and Hong Kong, which are defined in Fig. 2. The error bars represent the estimated uncertainty (s.d.) for an individual year, the values over China being larger as a result of the poorer knowledge and therefore larger uncertainty of the aerosol loading and its changes.



Satellite measurements of NO₂ over East Central China

A plot of the monthly mean of the three-day composite of the tropospheric NO₂ vertical column versus time is presented for the area defined by latitudes 30° N to 40° N and longitudes 110° E to 123° E. Both GOME data (open symbols) and SCIAMACHY measurements (filled symbols) are shown. SCIAMACHY nadir measurements started in August 2002, but limited data are available prior to 2003. Shaded areas represent the standard deviation estimated for the monthly mean three-day composite, and take into account the variability of the measurements resulting from changes in NO₂ and data gaps arising from cloud cover and any missing observations.

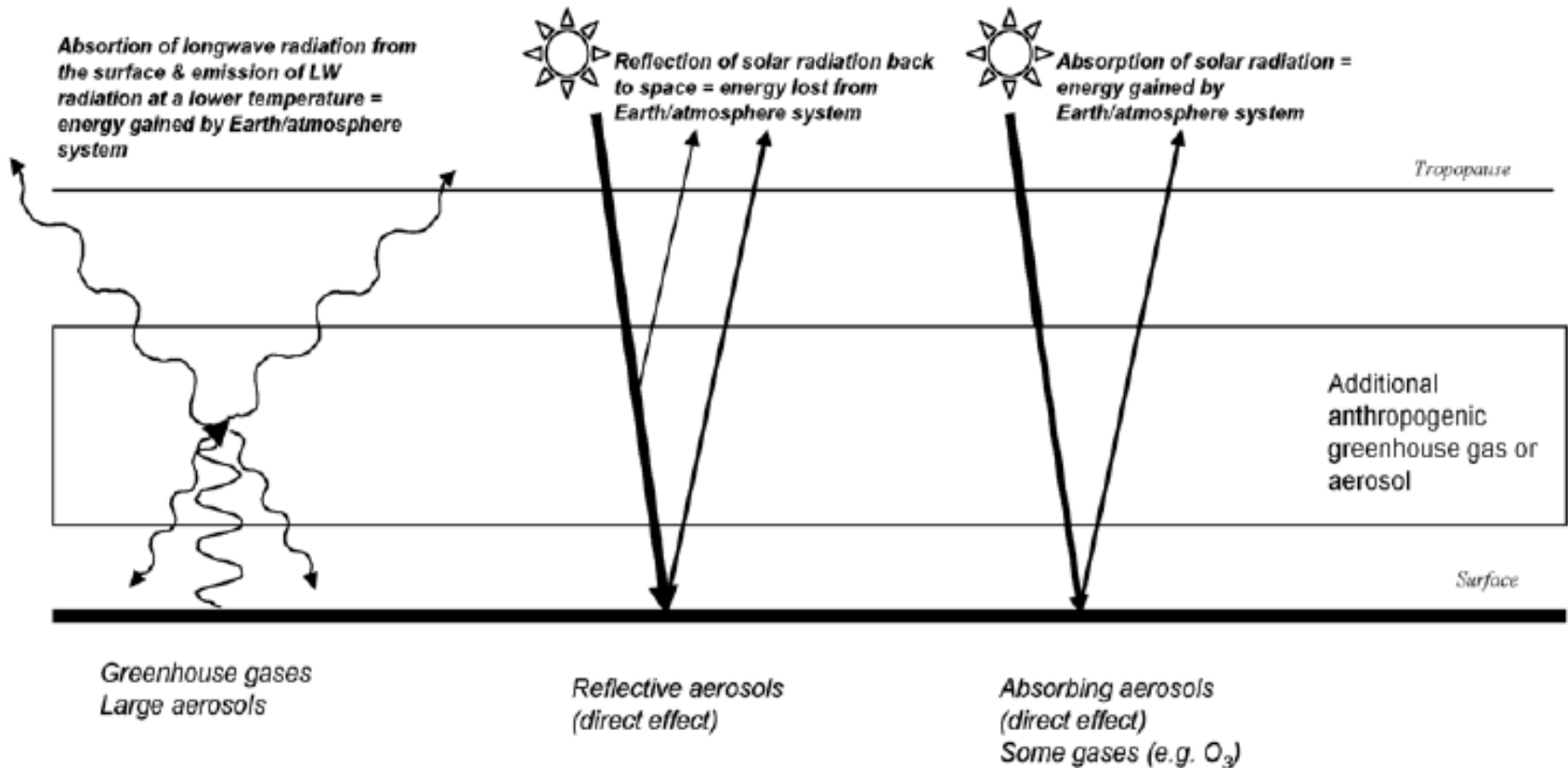


Climate change and chemistry

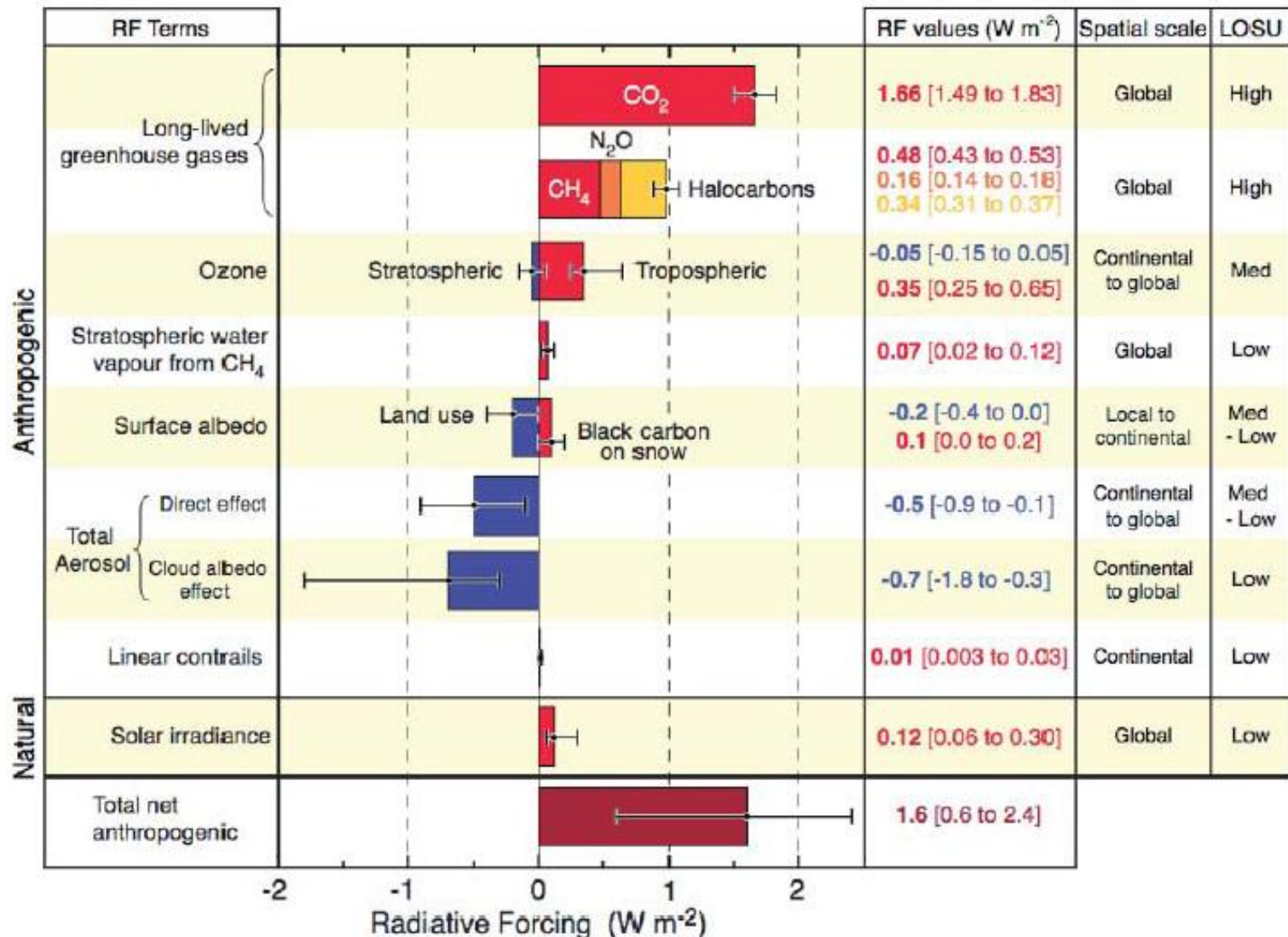
Radiative Forcing

- **Radiative forcing:** the change in the net radiation balance at the tropopause caused by a particular external factor in the absence of any climate feedbacks.
- These forcing mechanisms can be caused by:
 - change in the atmospheric constituents such as the increase in greenhouse gases (GHGs)
 - aerosols due to anthropogenic activity,
 - changes in other components of the Earth/atmosphere system such as changes in the surface albedo (the fraction of incoming radiation that is reflected). Albedo changes are caused, e.g., by changes in vegetation (e.g. burn scars or agriculture).

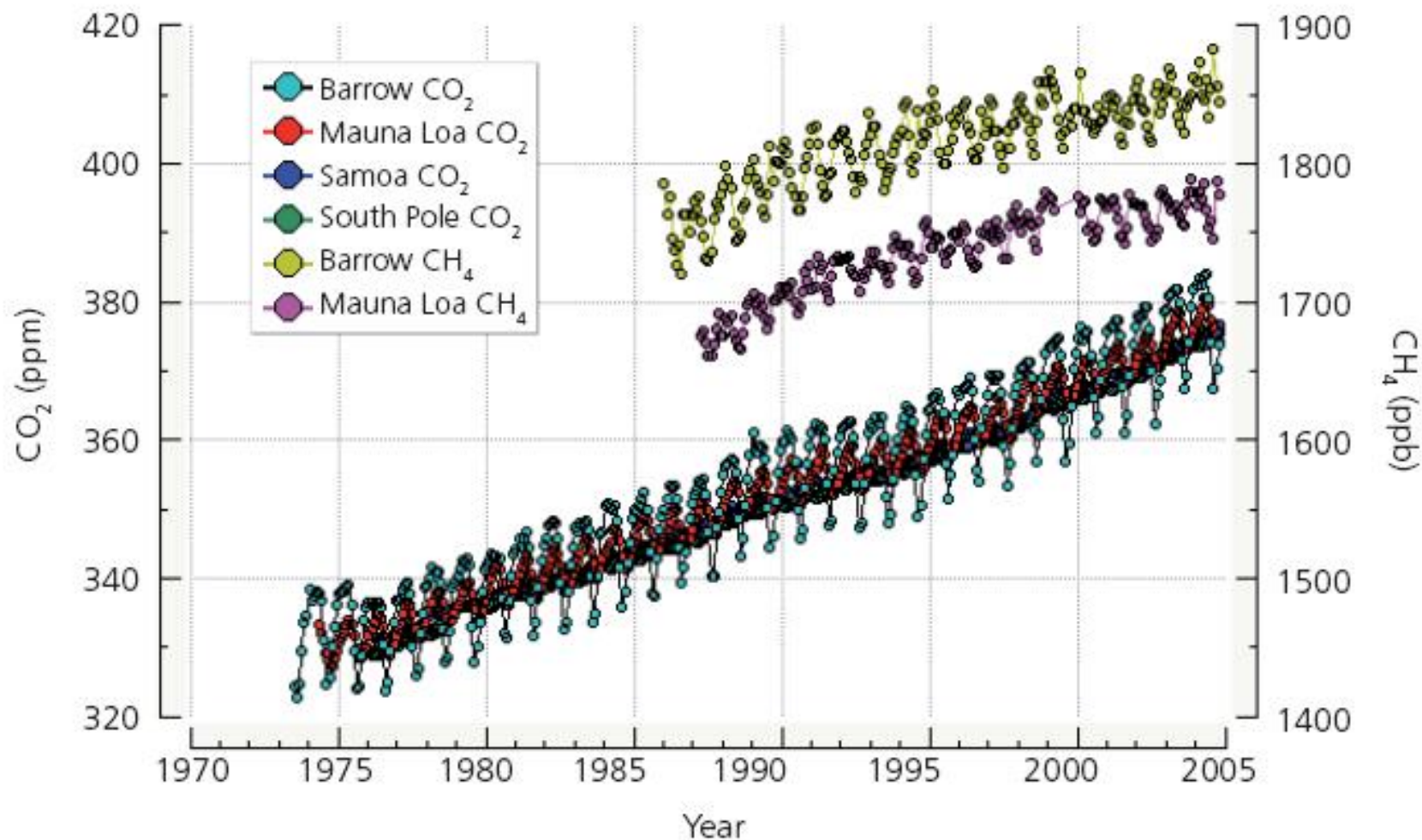
Mechanisms of the radiative forcing due to greenhouse gases and of the direct radiative forcings due to aerosols



Global-average radiative forcing (RF) estimates and ranges in 2005 (relative to 1750) for anthropogenic GHGs and other important agents and mechanisms



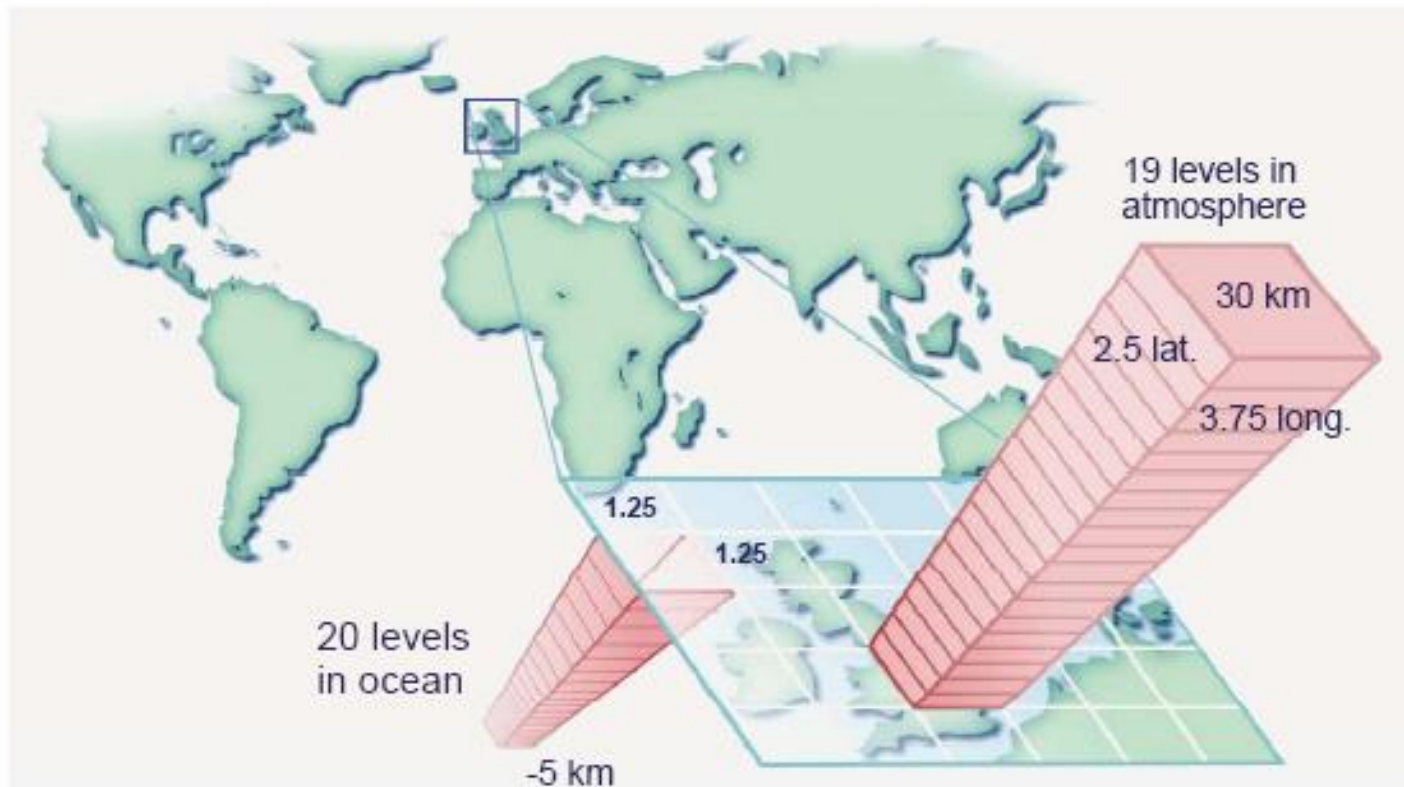
Carbon dioxide and methane mixing ratios versus time (NOAA Climate Monitoring and Diagnostics Laboratory <http://www.cmdl.noaa.gov/ccgg/insitu.html>)



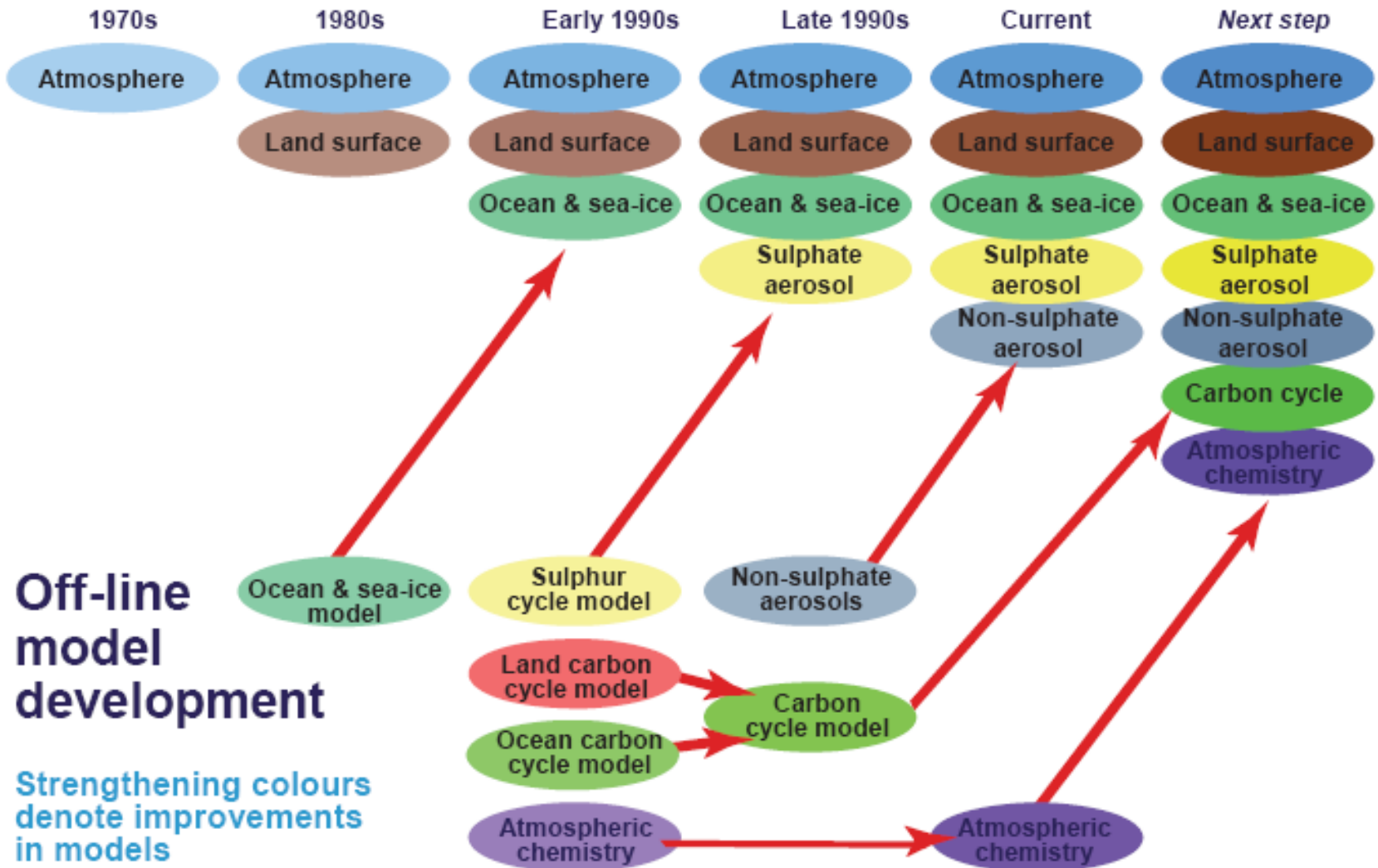
Other GHGs

- N_2O mixing ratios show an increase from a pre-industrial value of around 270 ppb (Prather *et al.*, 2001) to 318 - 319 ppb in early 2004
- CFC-11, CFC-12, CFC-13, HCFC-22, and CCl_4 concentrations increased from a pre-industrial value of zero to 268 ppt, 533 ppt, 4 ppt, 132 ppt, and 102 ppt respectively (1998 concentrations) - leads to radiative forcings of 0.07 W m^{-2} , 0.17 W m^{-2} , 0.03 W m^{-2} , 0.03 W m^{-2} and 0.01 W m^{-2}
- Ozone: approximate doubling of concentrations between the pre-industrial and present day.

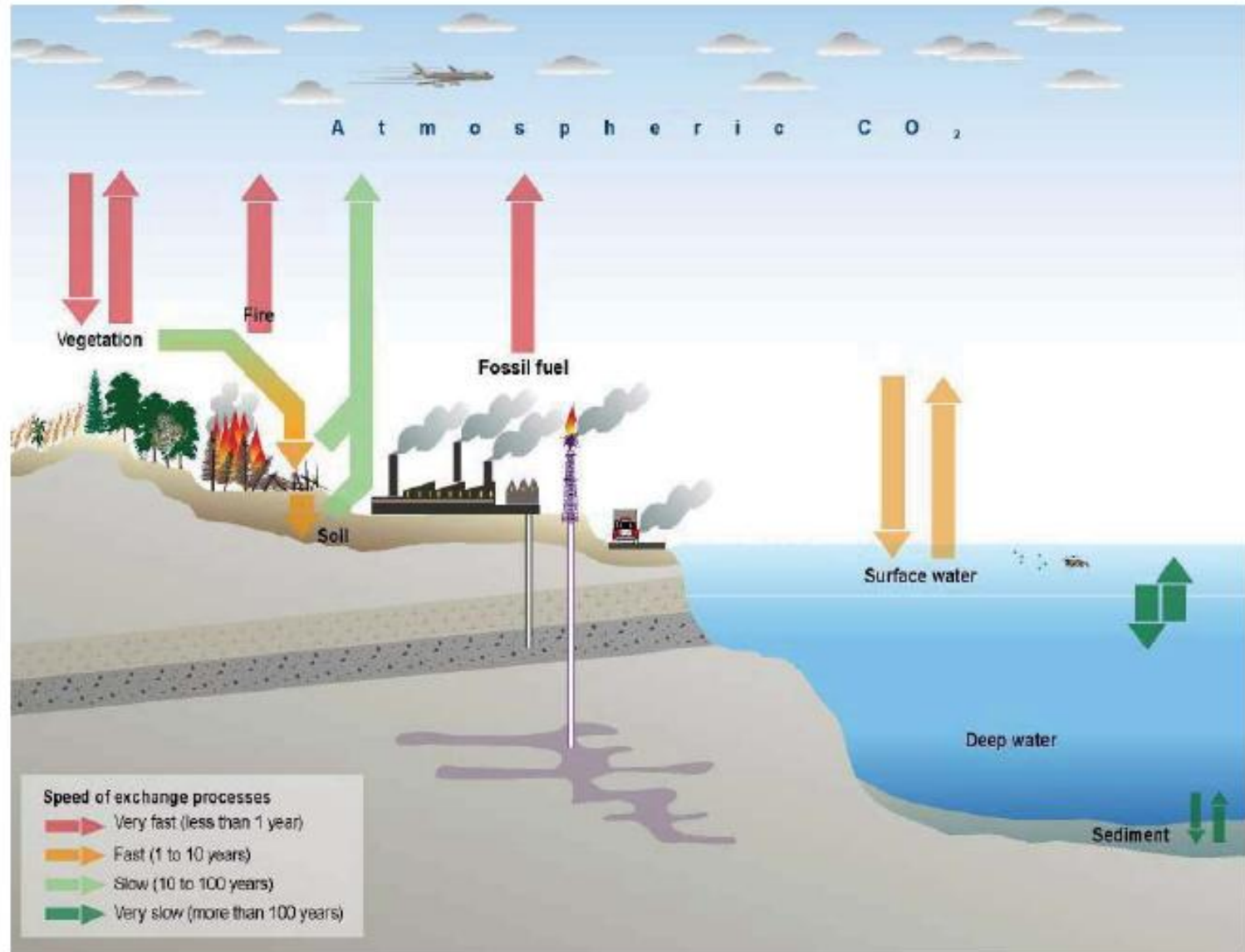
Schematic description of an ocean atmosphere general circulation model



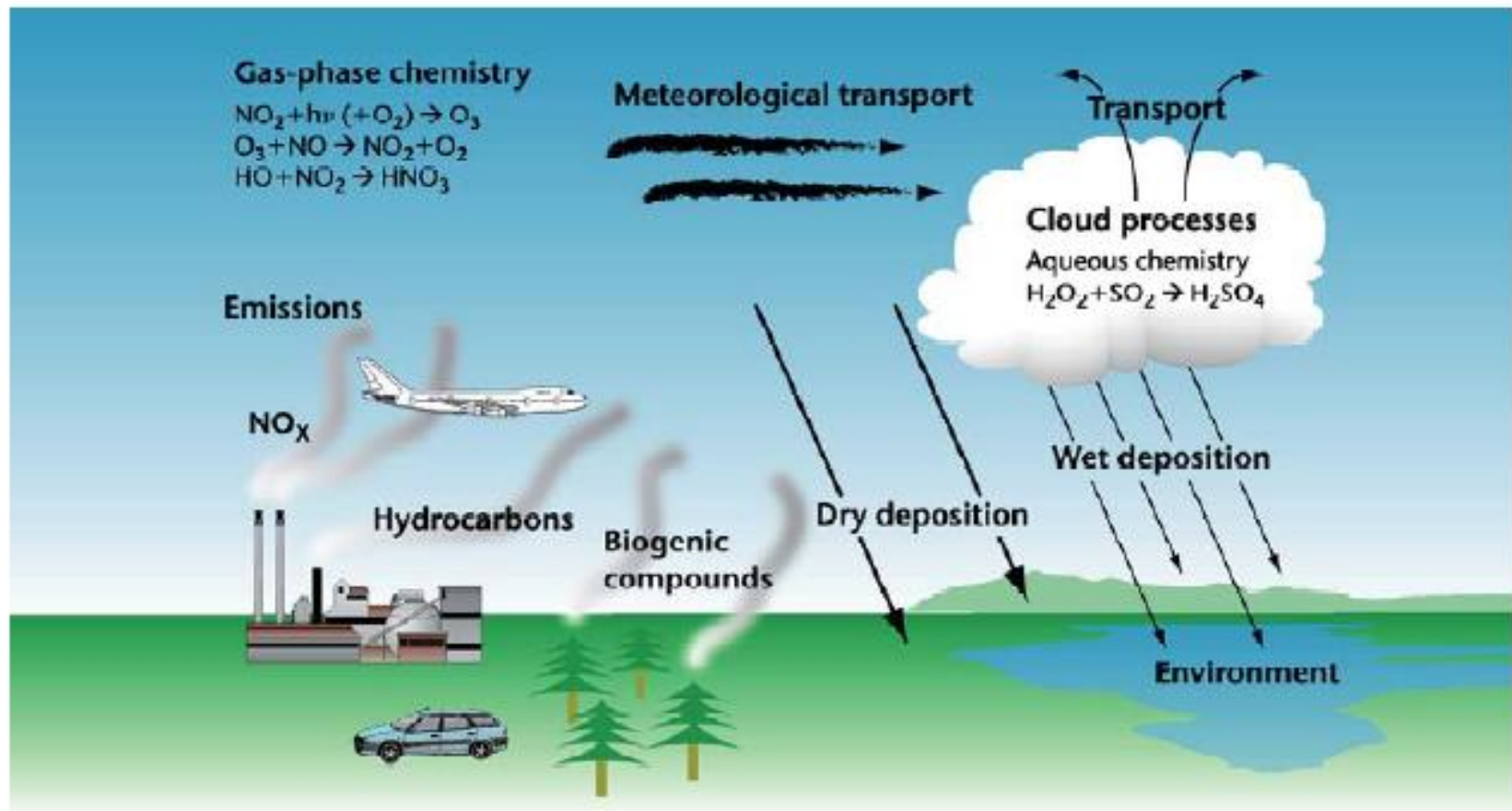
Evolution of models



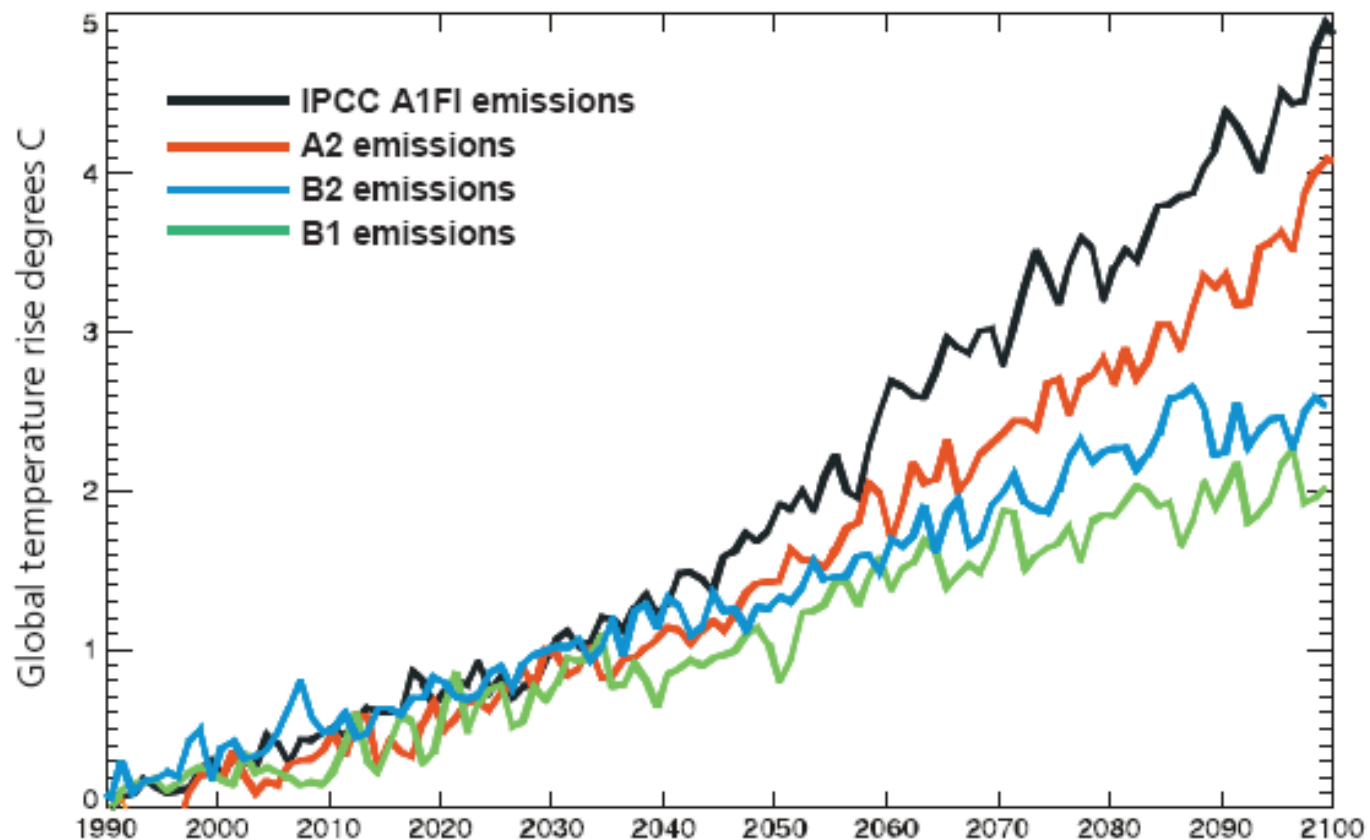
Carbon cycle



Processes in an atmospheric chemistry model

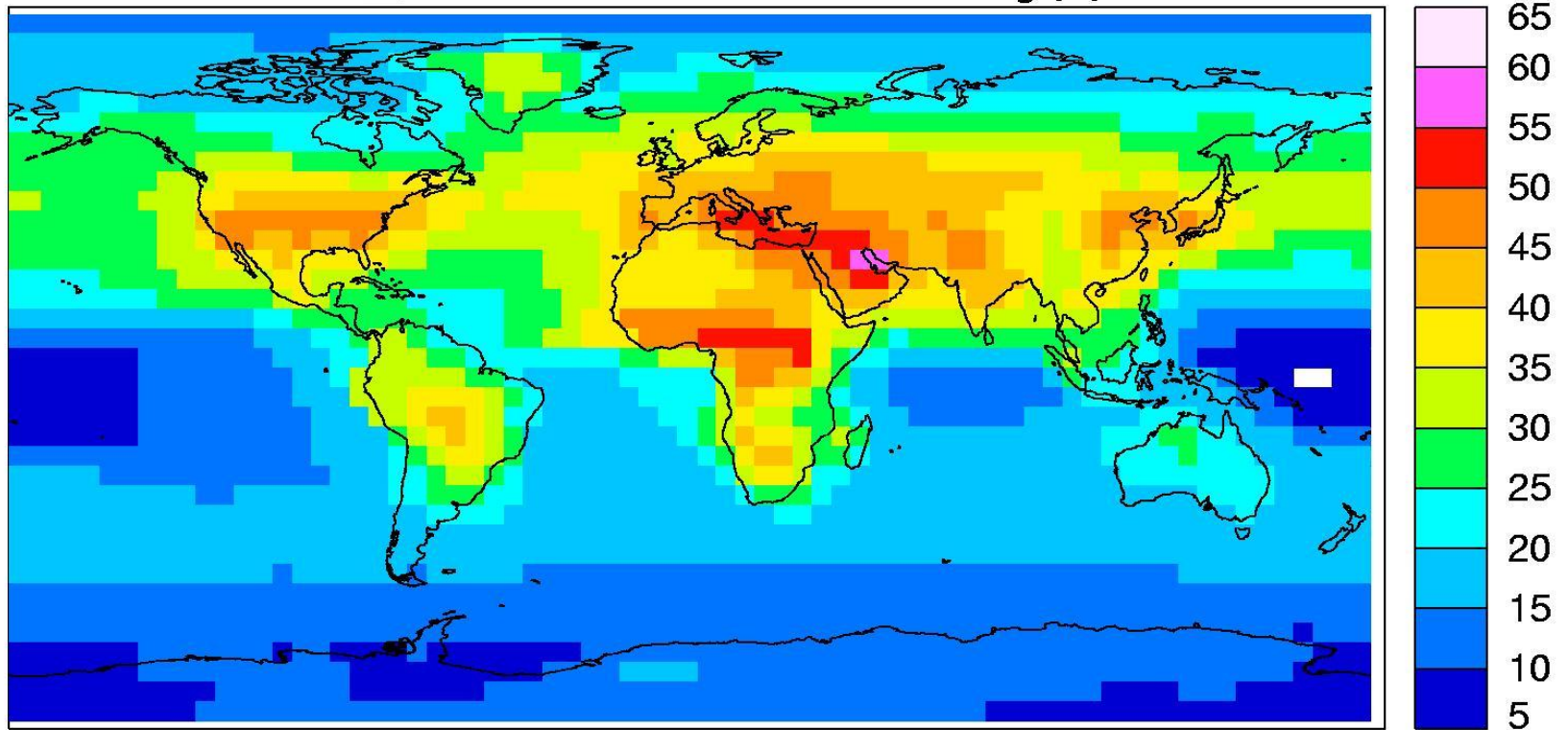


Predicted global temperature rise for different scenarios



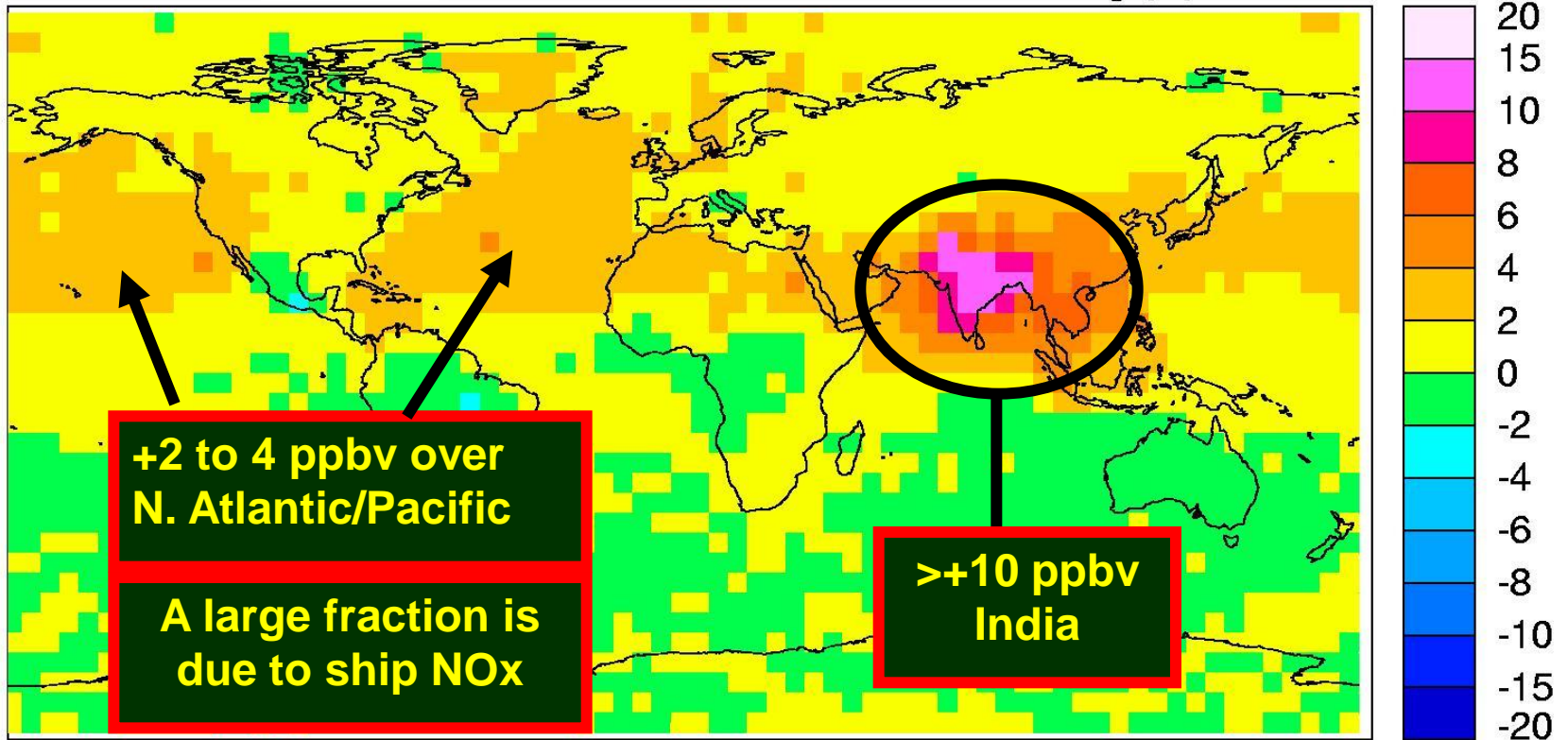
Surface O₃ (ppbv) 1990s

IIASA_BAU 1990s Surface O₃/ppbv



Change in surface O₃, CLE 2020s-1990s No climate change

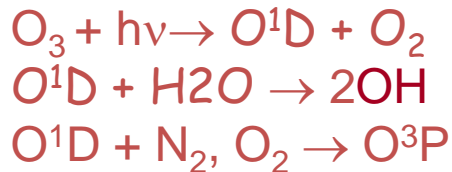
IIASA **CLE** 2020s-1990s Surface O₃/ppbv



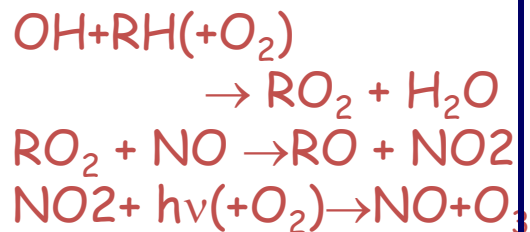
ΔO_3 from climate change

2020s CLEcc-
2020s CLE

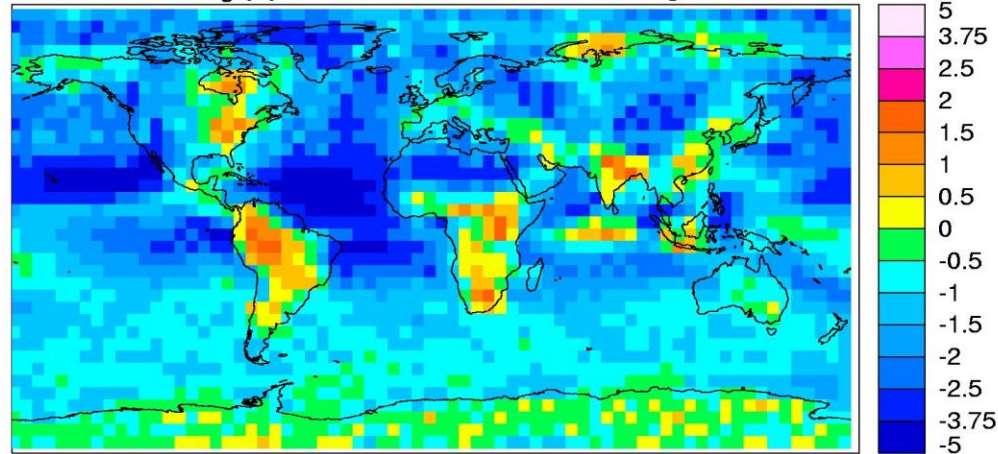
Warmer temperatures
& higher humidities
increase O_3 destruction
over the oceans



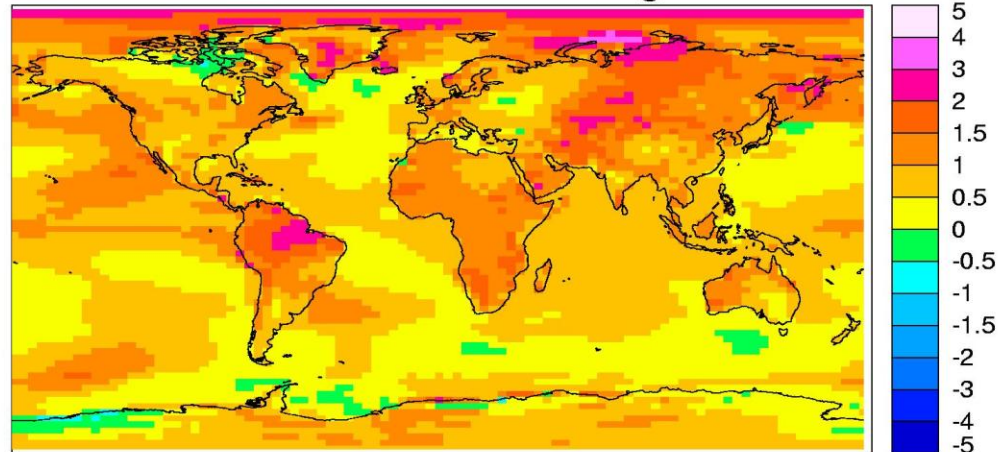
But also a role from
increases in isoprene
emissions from
vegetation & changes in
lightning NO_x

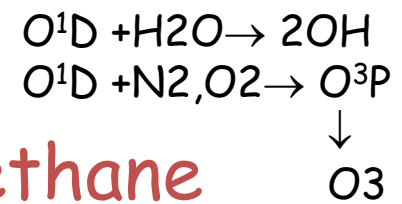


ΔO_3 /ppbv from climate change

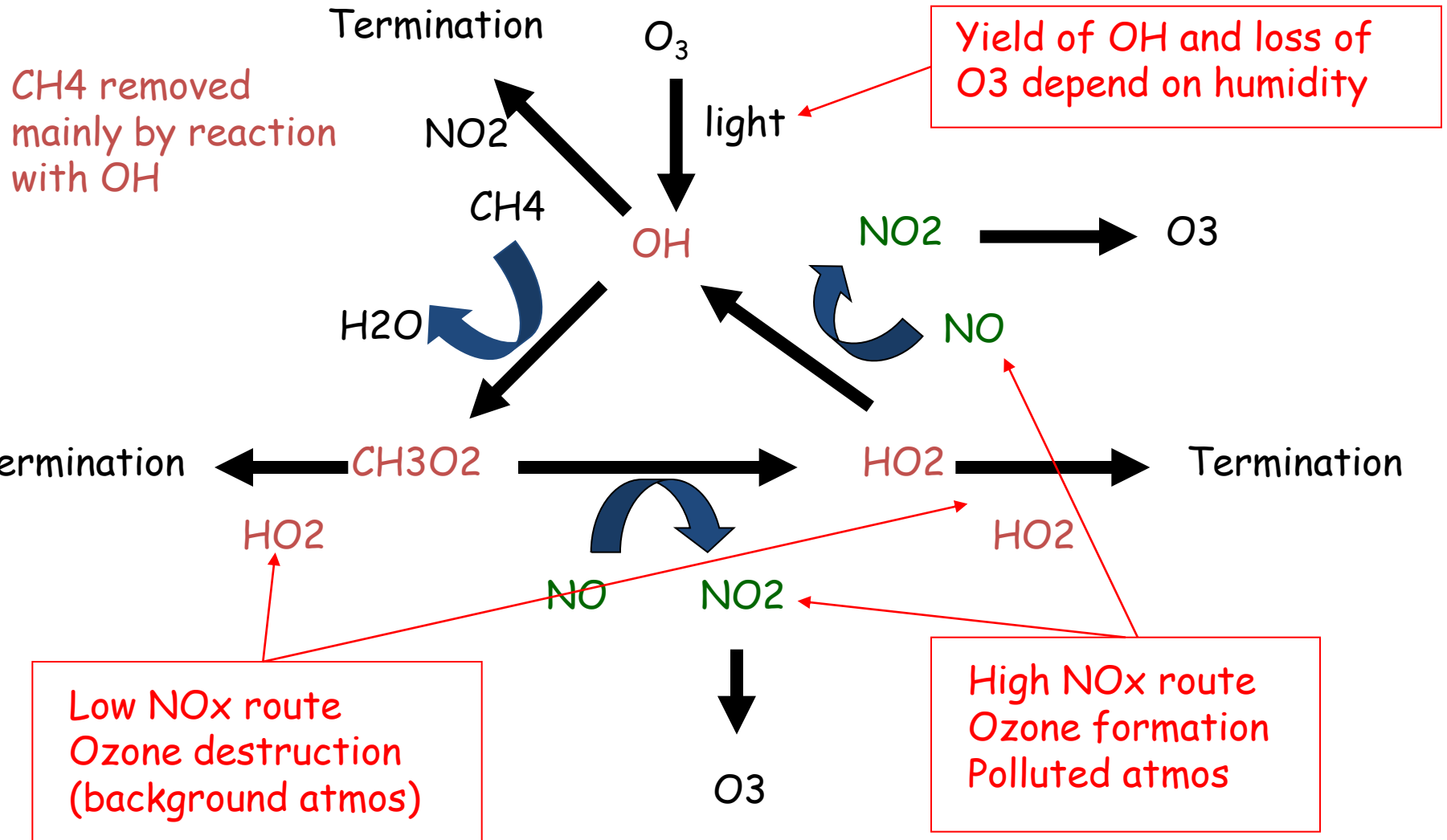


ΔT_0 /K from climate change



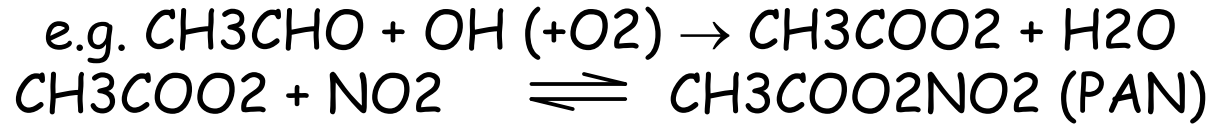


Atmospheric oxidation of methane

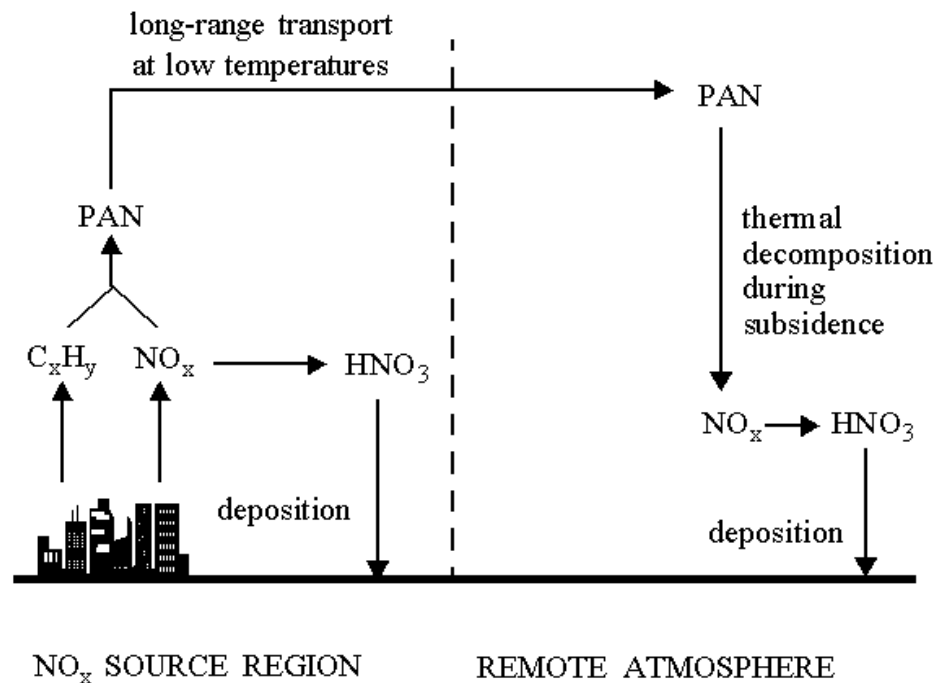


PAN - peroxy acetyl nitrate - reminder

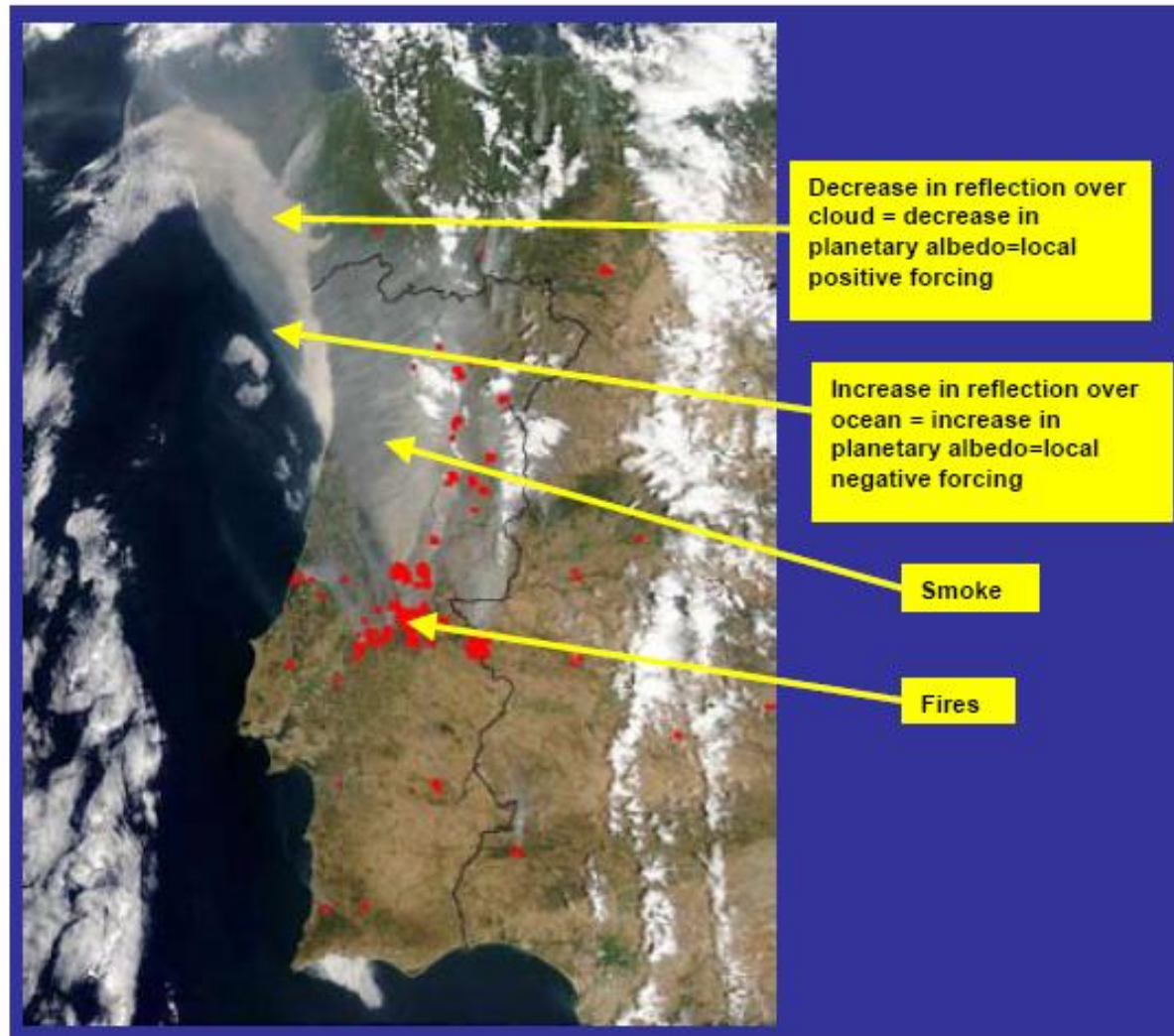
PAN is formed from reactions of the acetyl peroxy radical and NO₂:



PAN is a **reservoir** compound for nitrogen oxides and provides a mechanism for their transport, especially in the upper troposphere. It provides a means of carrying nitrogen oxides from polluted to less polluted regions. It is a major player in the intercontinental transport of pollutants

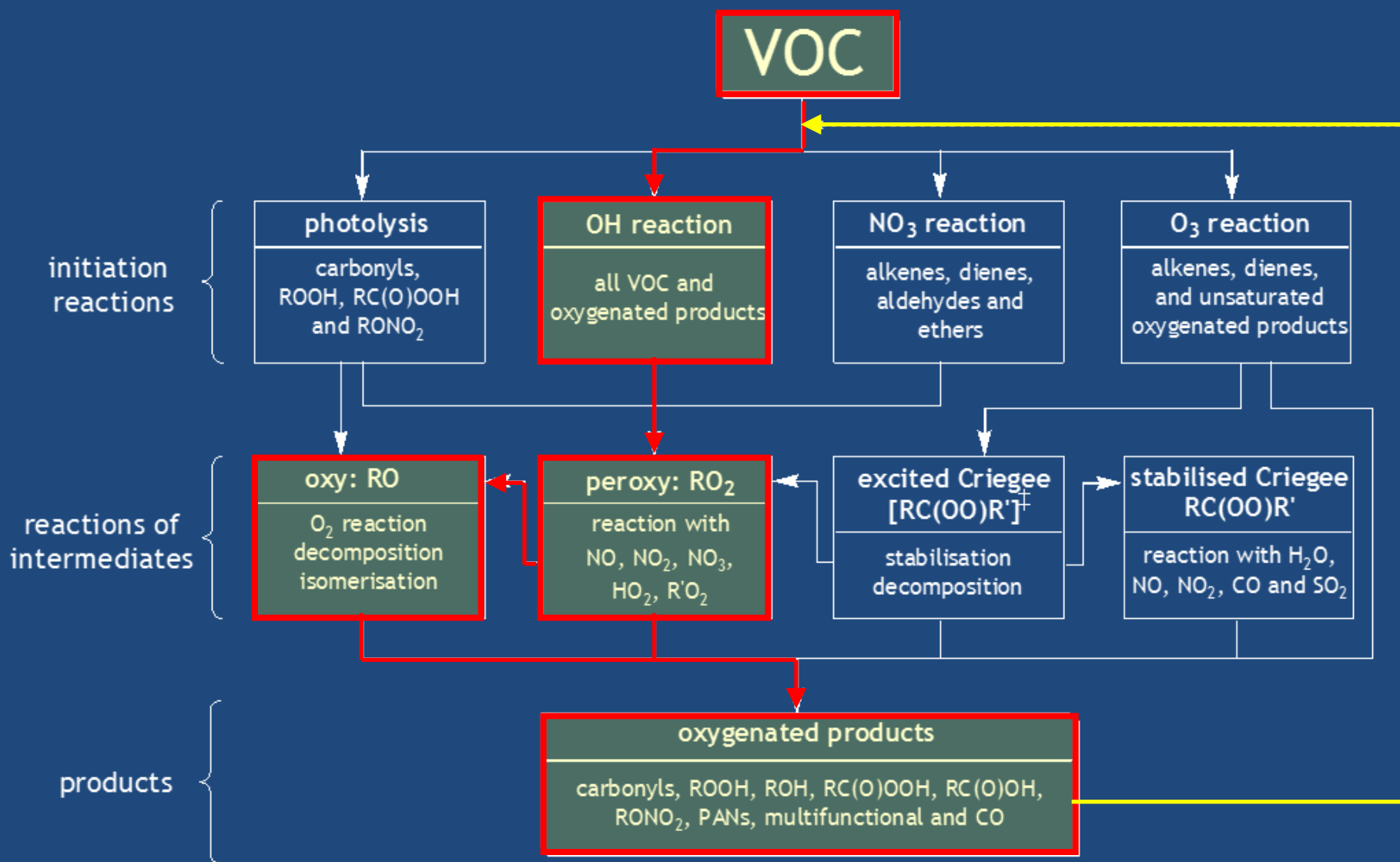


Emission of biomass smoke from Portugal in August 2003: effects on local albedo



Chemical mechanisms and their evaluation

General description of a chemical mechanism



Explicit chemical mechanisms - the MCM

<http://mcm.leeds.ac.uk/MCM/>

MCM Website - Windows Internet Explorer provided by MaPS Faculty

http://mcm.leeds.ac.uk/MCM/ master chemical mechanism

File Edit View Favorites Tools Help

MCM Website

The Master Chemical Mechanism

VERSION 3.2 [What's new?](#)

[MCMv3.1 Archive site](#)

search

Home Browse Search Extract Download Construction method AtChem Tools Feedback Links Citation Contributors Funding MCMv3.1

Mark List
No species are marked.

Welcome to the MCM website

The Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism which describes the detailed gas-phase chemical processes involved in the tropospheric degradation of a series of primary emitted volatile organic compounds (VOCs). Currently, the degradation of methane and 142 non-methane VOCs is represented.

Done Internet 100%

Start Michael Pilling - Outl... MCM Website - W... 7. atmosphere atmosphere mechanism evaluation evaluation [Compati... EN 16:21

1st page of isoprene mechanism

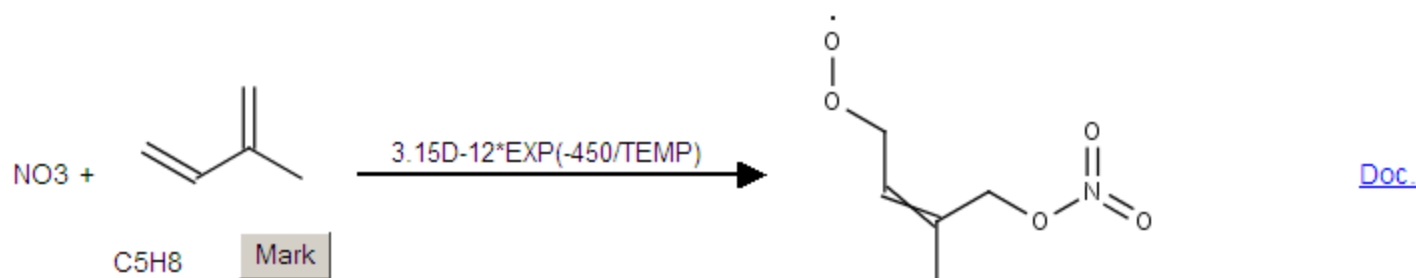
MCM Website C5H8 - Windows Internet Explorer provided by MaPS Faculty

http://mcm.leeds.ac.uk/MCM/browse.htt?species=C5H8 master chemical mechanism

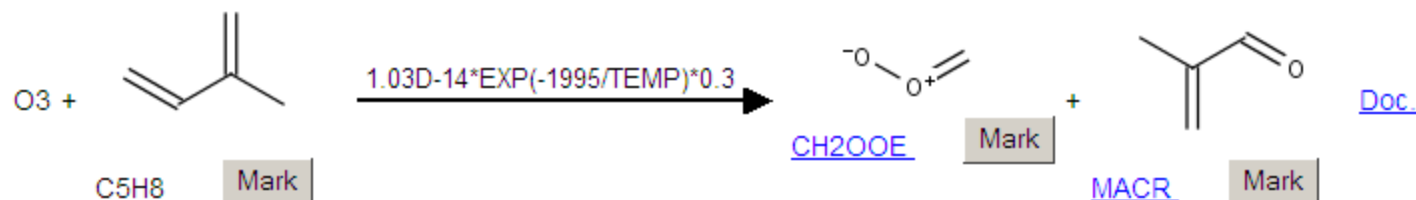
File Edit View Favorites Tools Help

MCM Website C5H8

Page

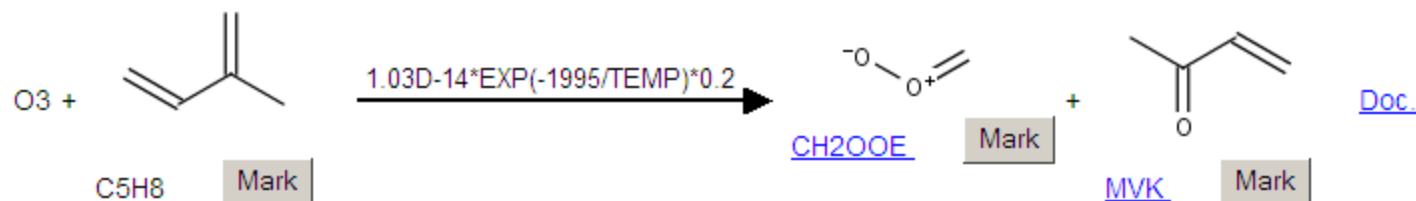


NISOP2



CH2OOE

MACR



CH2OOE

MVK

http://mcm.leeds.ac.uk/MCM/browse.htt?species=MVK

Start Microsoft Exchange... MCM Website C5... 7. atmosphere atmosphere mechanism evaluation evaluation [Compati... EN

1st few lines of extracted mechanism

MCM Website - Windows Internet Explorer provided by MaPS Faculty

http://mcm.leeds.ac.uk/MCM/extract.py

File Edit View Favorites Tools Help

MCM Website

Mark List

☐ C5H8 Delete Clear

Mechanism subset for marked species

Each product species is linked to the point in the subset where that species reacts. Select "Goto MCM" next to the first occurrence of each reactant to browse the MCM from that point.

Goto MCM	NO3 + C5H8	→	NISOPQ2	3.15D-12*EXP(-450/TEMP)
	O3 + C5H8	→	CH2OOE + MACR	1.03D-14*EXP(-1995/TEMP)*0.3
	O3 + C5H8	→	CH2OOE + MVK	1.03D-14*EXP(-1995/TEMP)*0.2
	O3 + C5H8	→	HCHO + MACROOA	1.03D-14*EXP(-1995/TEMP)*0.3
	O3 + C5H8	→	HCHO + MVKOOA	1.03D-14*EXP(-1995/TEMP)*0.2
	OH + C5H8	→	ISOPAQ2	2.7D-11*EXP(390/TEMP)*0.148
	OH + C5H8	→	ISOPBQ2	2.7D-11*EXP(390/TEMP)*0.444
	OH + C5H8	→	ISOPCQ2	2.7D-11*EXP(390/TEMP)*0.102
	OH + C5H8	→	ISOPDQ2	2.7D-11*EXP(390/TEMP)*0.306
Goto MCM	NISOPQ2 + HO2	→	NISOPQOH	KRO2HO2*0.706
	NISOPQ2 + NO	→	NISOPQNO3	KRO2NO*0.052
	NISOPQ2 + NO	→	NISOPQ + NO2	KRO2NO*0.948

/MCM/mark.py

Internet 100%

Start Microsoft Exchange... MCM Website - W... 7. atmosphere atmosphere mechanism evaluation evaluation [Compati... EN 16:27

Atmospheric chambers and their application in mechanism evaluation

Large outdoor chamber
Valencia, Spain 200m³





Photochemical Reactor

Volume: 200 m³

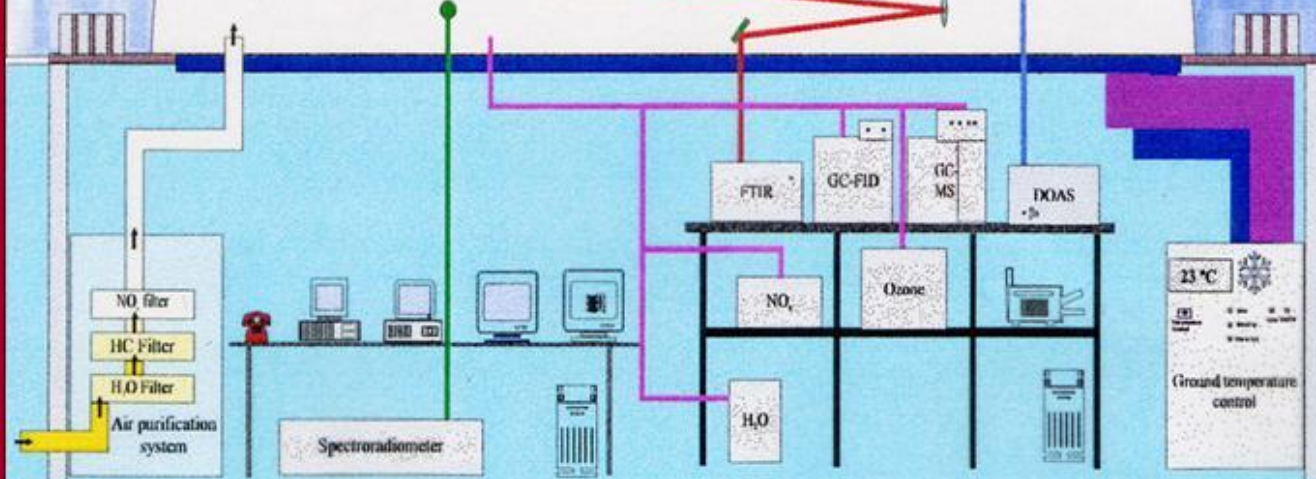
Surface material: 127 μ m Teflon film, transparent to sunlight

Ground: temperature controlled aluminum plates covered with teflon

Wind protection: automatic closing cover

Optical path for DOAS (1152 m)

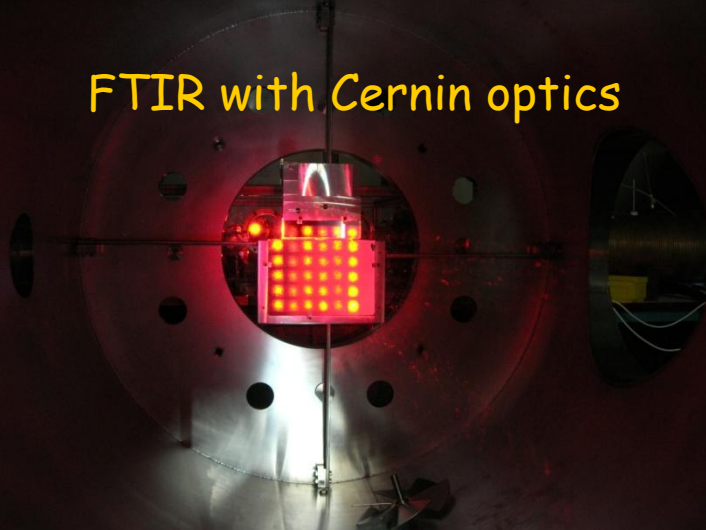
Optical path for FTIR (634 m)



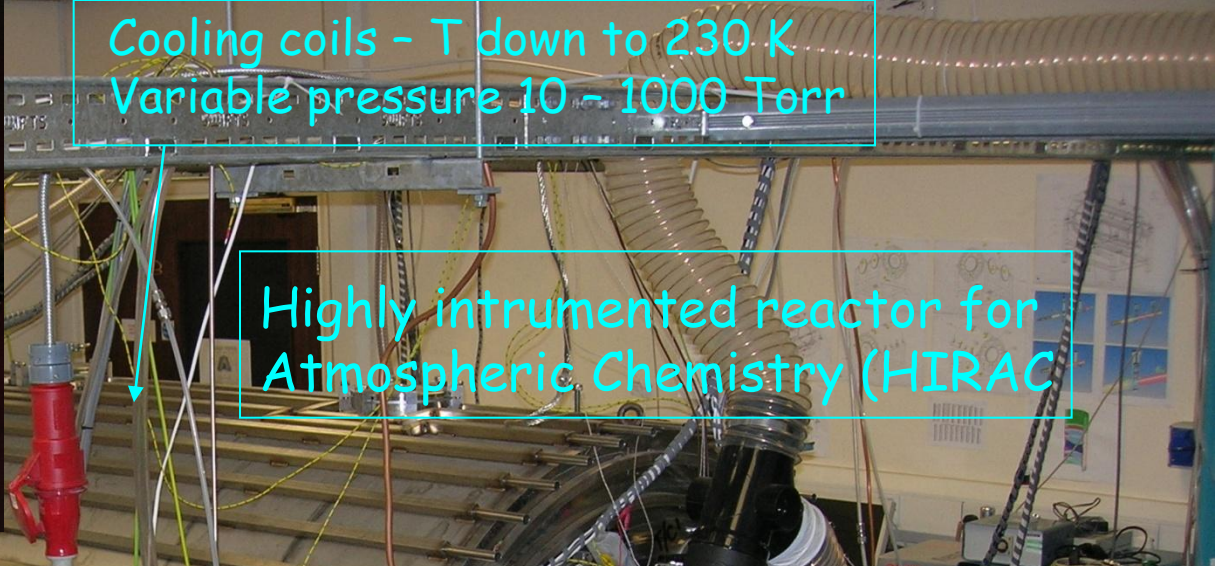
SAPHIR chamber Juelich, Germany



FTIR with Cernin optics



Cooling coils - T down to 230 K
Variable pressure 10 - 1000 Torr

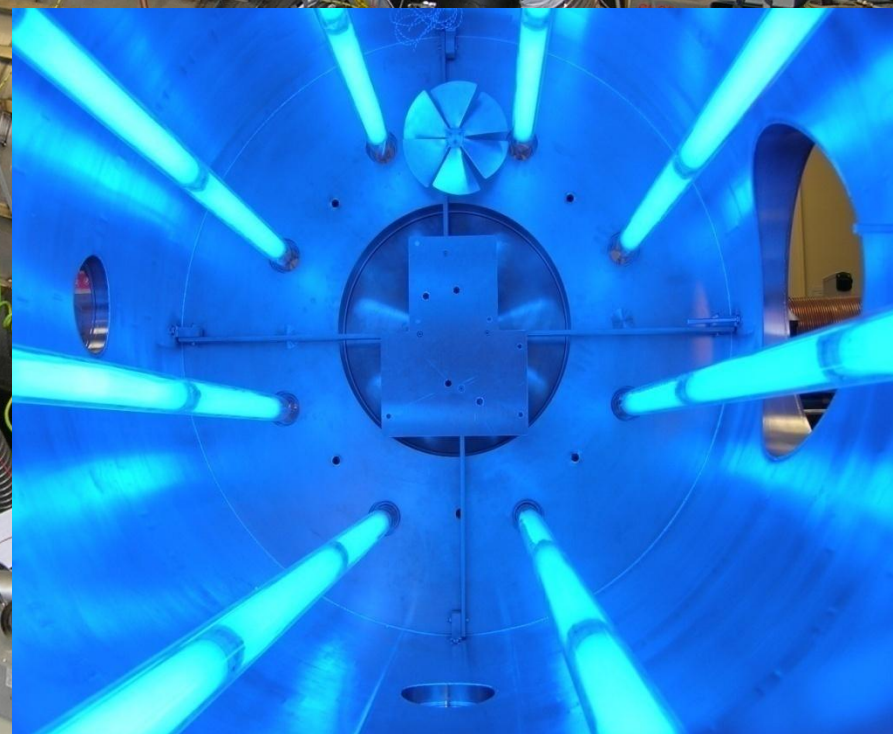


Highly instrumented reactor for
Atmospheric Chemistry (HIRAC)

FAGE Laser induced fluorescence
for detection of OH, HO₂

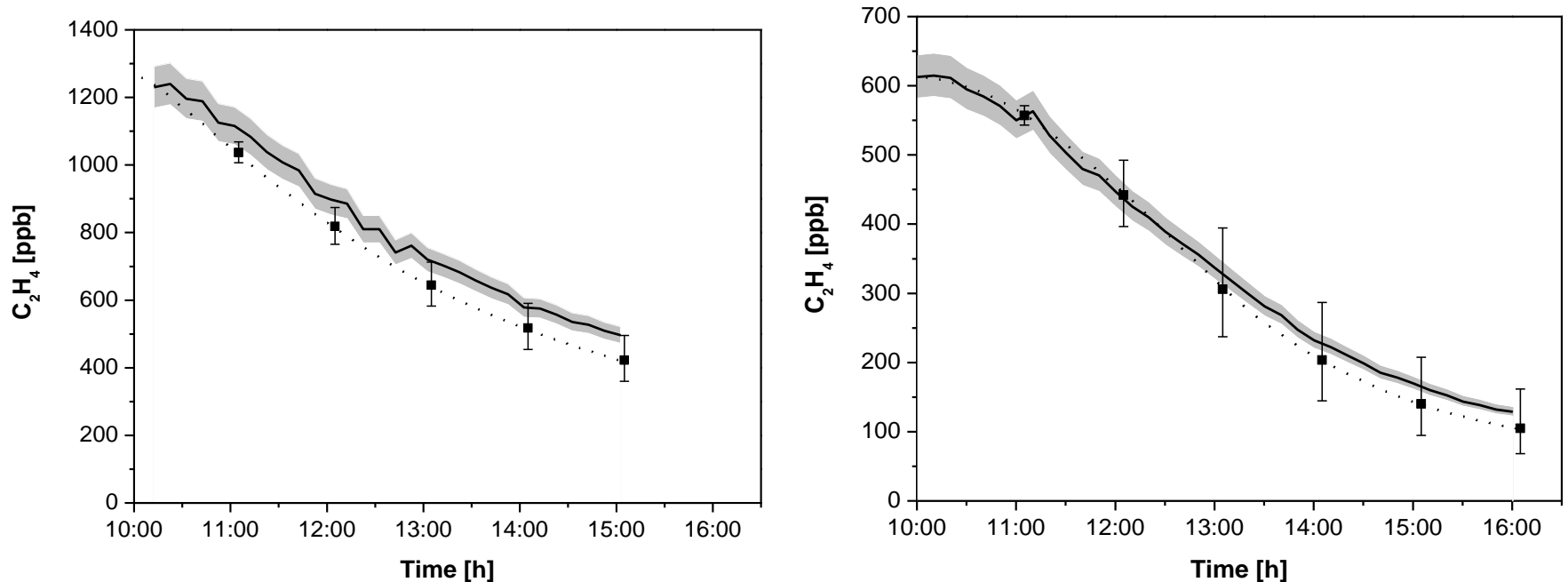
GC for hydrocarbons, oxygenates ...

NO, NO₂, O₃, CO detectors



Statistical and uncertainty analyses of chamber measurements and models

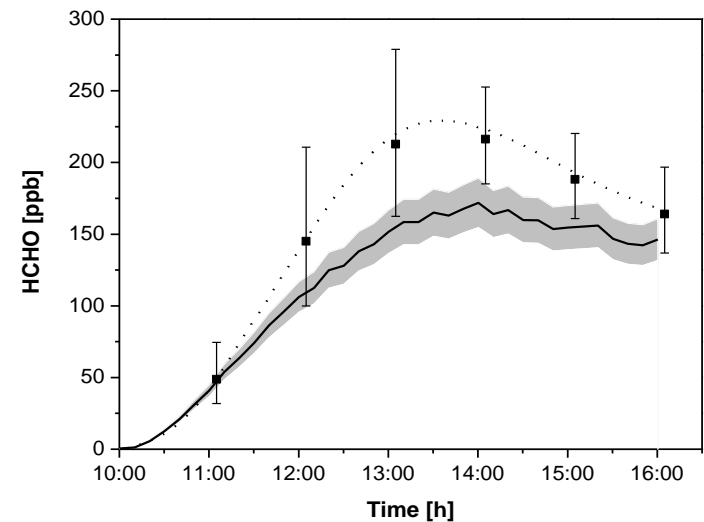
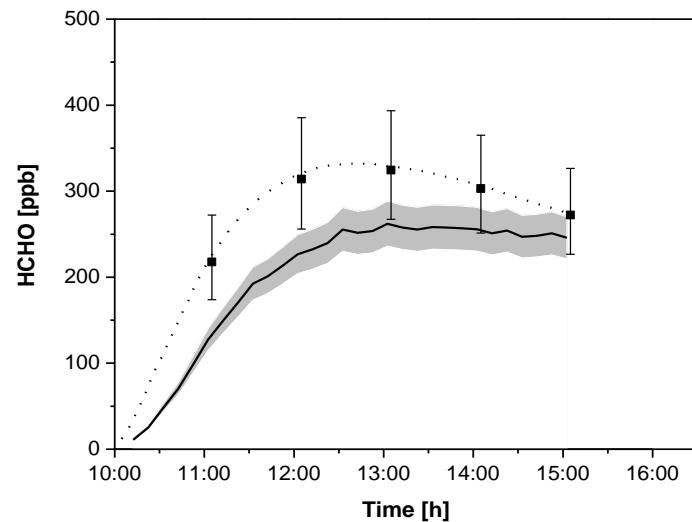
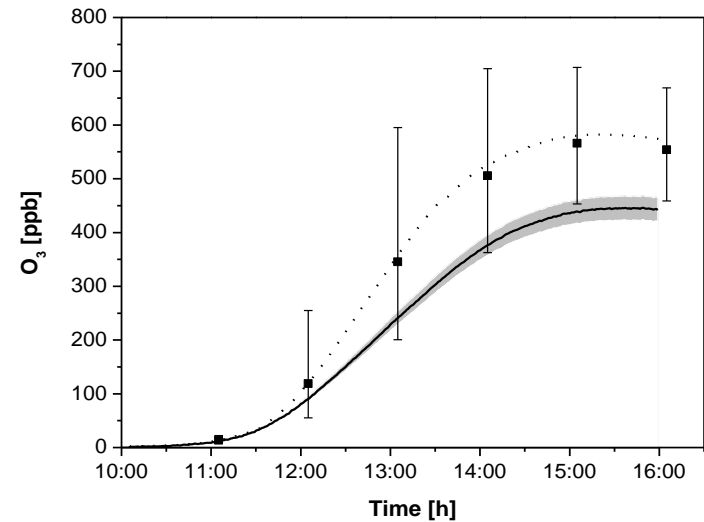
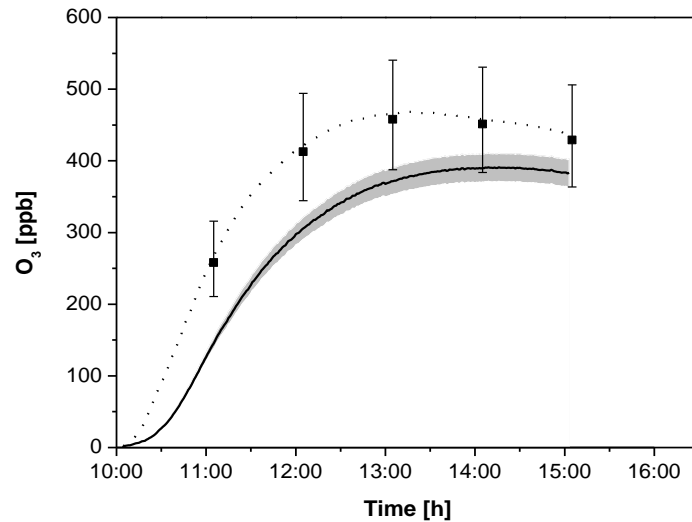
Comparison of ethene measurements and simulations



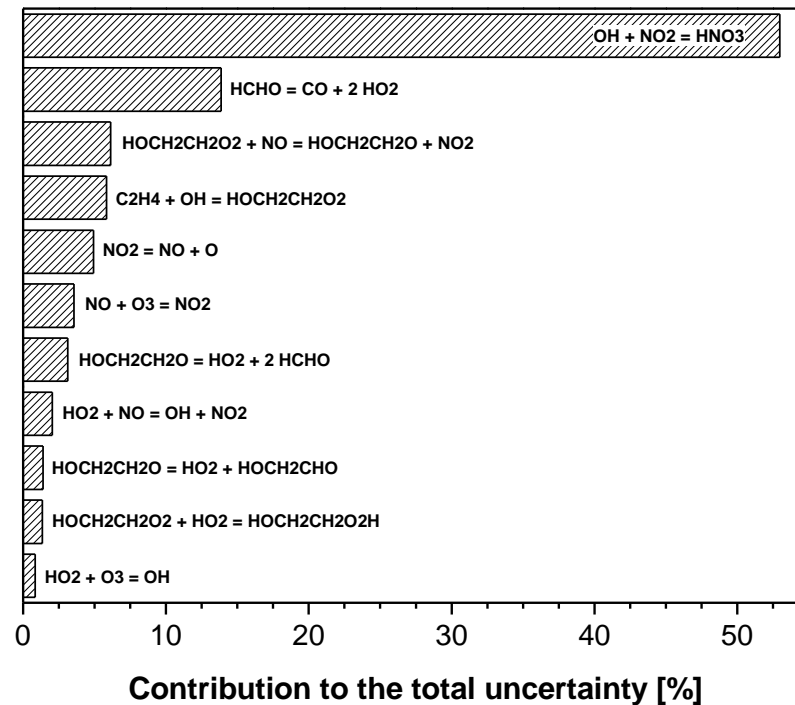
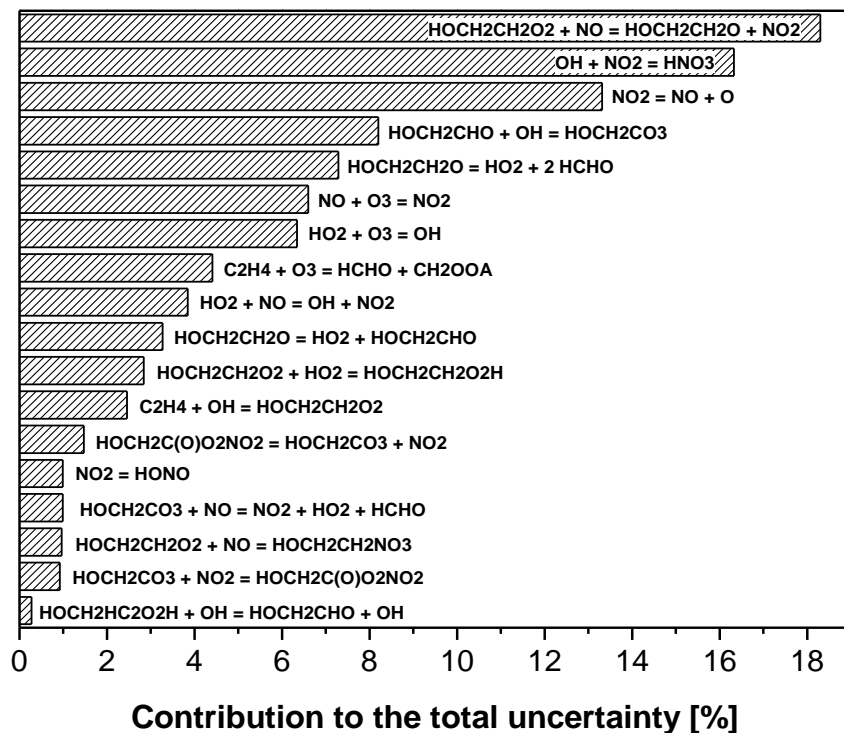
2 σ measurement uncertainty (grey bands)

2 σ uncertainties from Monte-Carlo simulations (error bars) J. Zador, et al., Atmospheric Environment, 2005, 39, 2805-2817

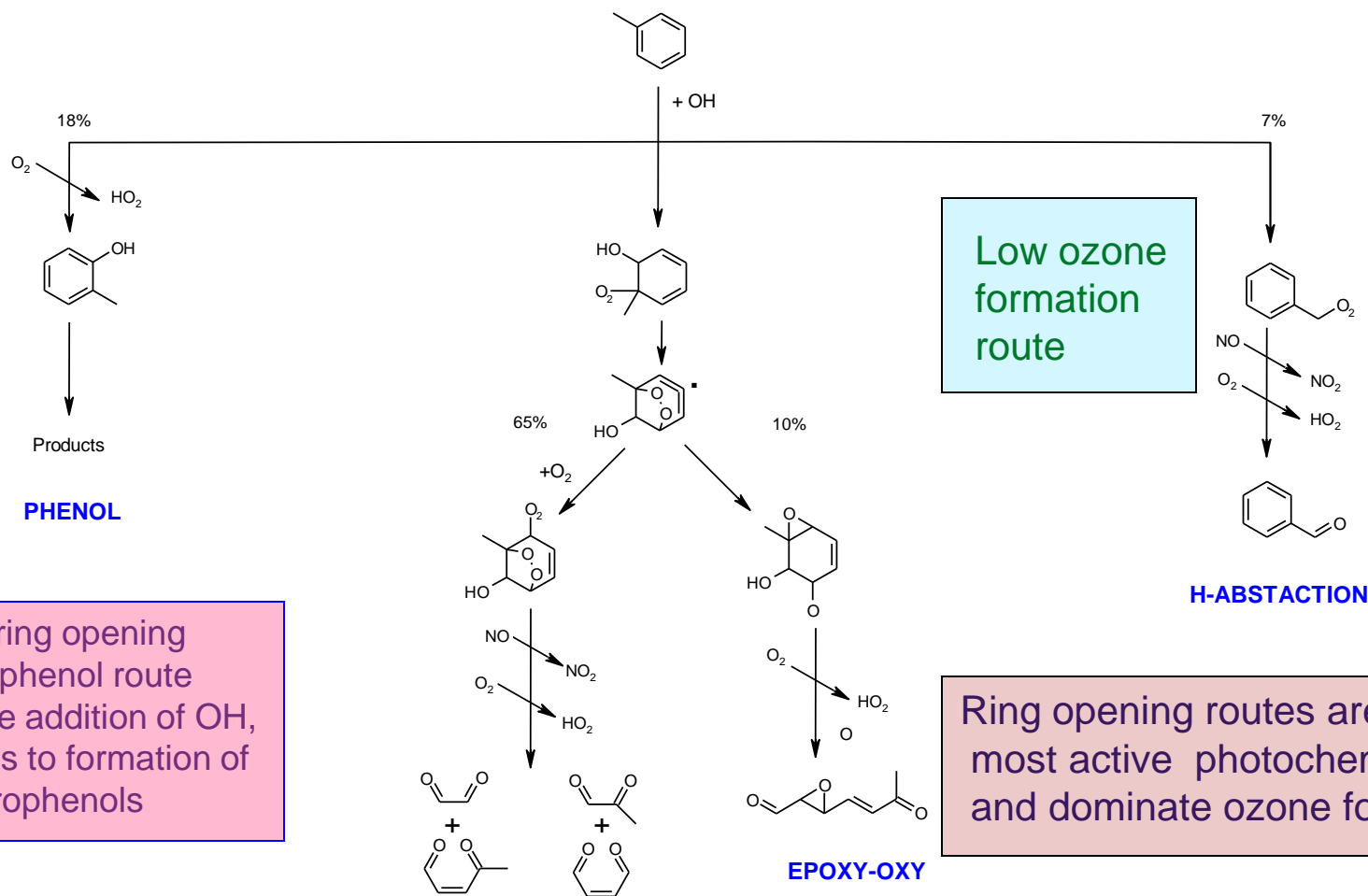
Model measurement comparisons and uncertainties



Uncertainty contributions, ethene, low and high NO_x

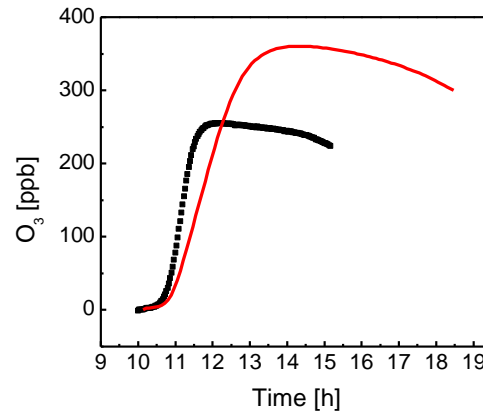
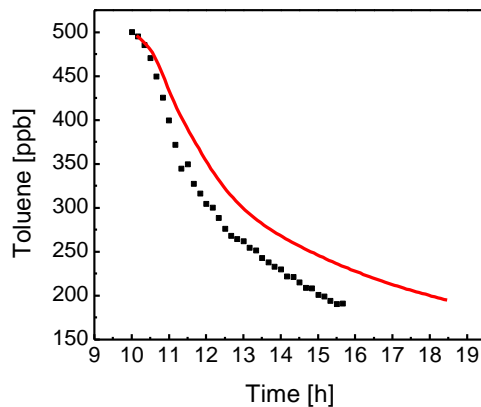


Toluene Oxidation Routes in MCMv3.2

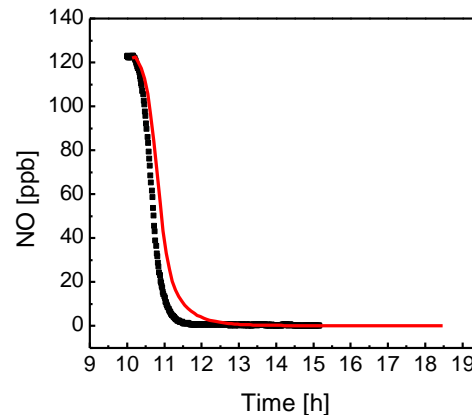
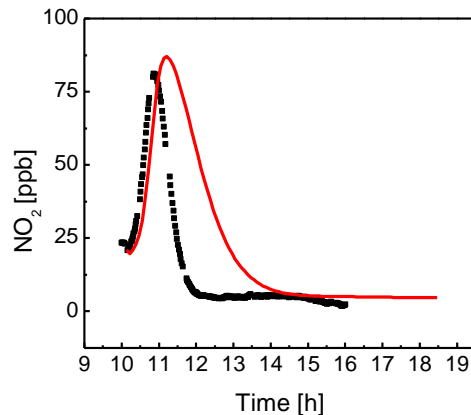


Yields for different channels determined through chamber experiments e.g. Volkamer et al. at EUPHORE using DOAS. Epoxy oxy product only observed – not fully quantified. Yield completes mass balance. Initial rate coefficients from pulsed photolysis.

Comparison of MCM3.1 to Toluene Chamber Experiment (27/09/01)



■ Experiment
— MCM3.1



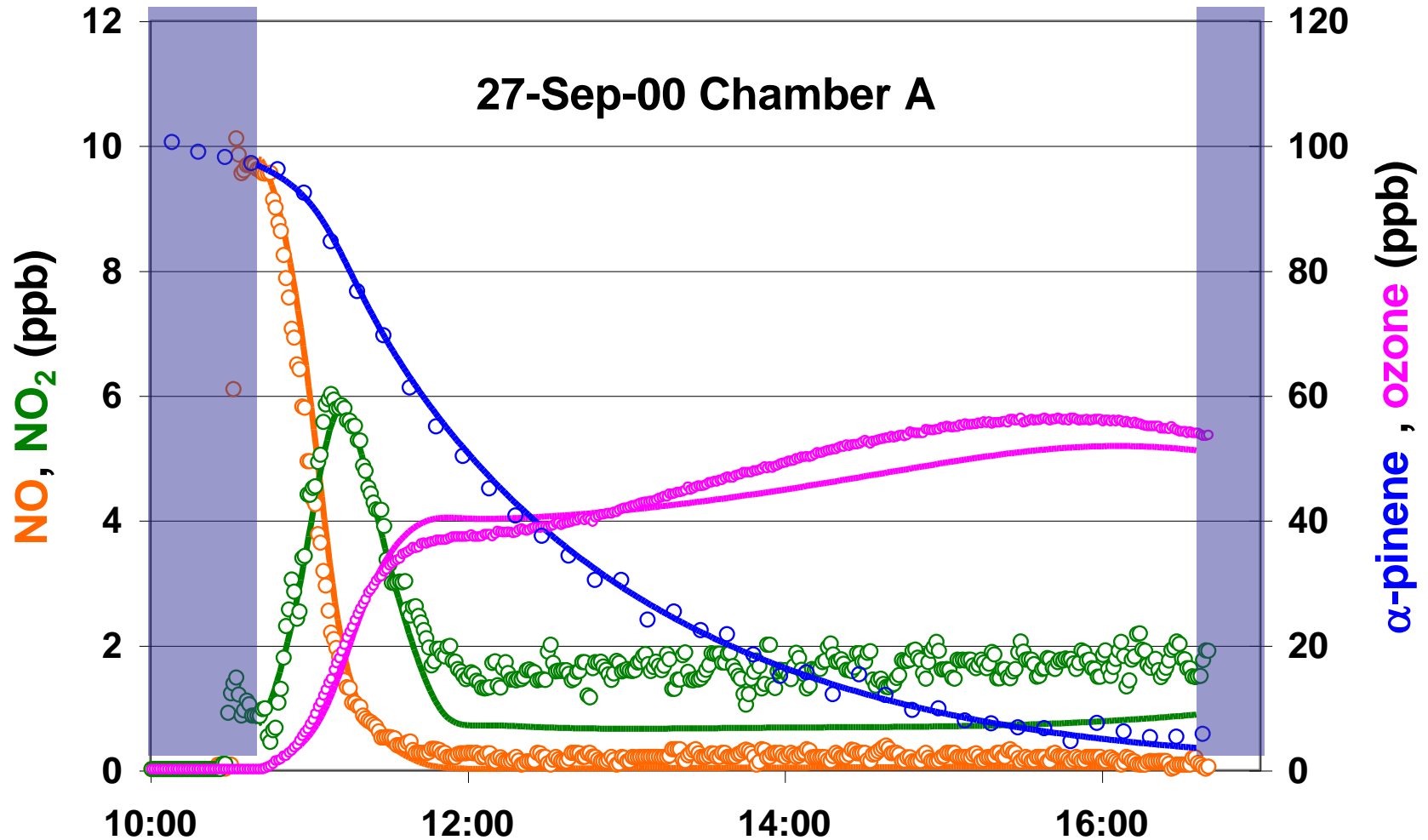
Conclusions:

- Ozone overpredicted but OH is too low. Need early OH source that doesn't produce O₃
- NO₂ is not formed or removed rapidly enough
- Co-products of glyoxal/Me glyoxal not detected in sufficient concⁿ

Photo-oxidation of α -pinene / NO_x : gas-phase simulation

$[\alpha\text{-pinene}]_0 = 97 \text{ ppb}$; $[\text{NO}]_0 = 9.7 \text{ ppb}$; $[\text{NO}_2]_0 = 0.85 \text{ ppb}$

Jenkin - OSOA project

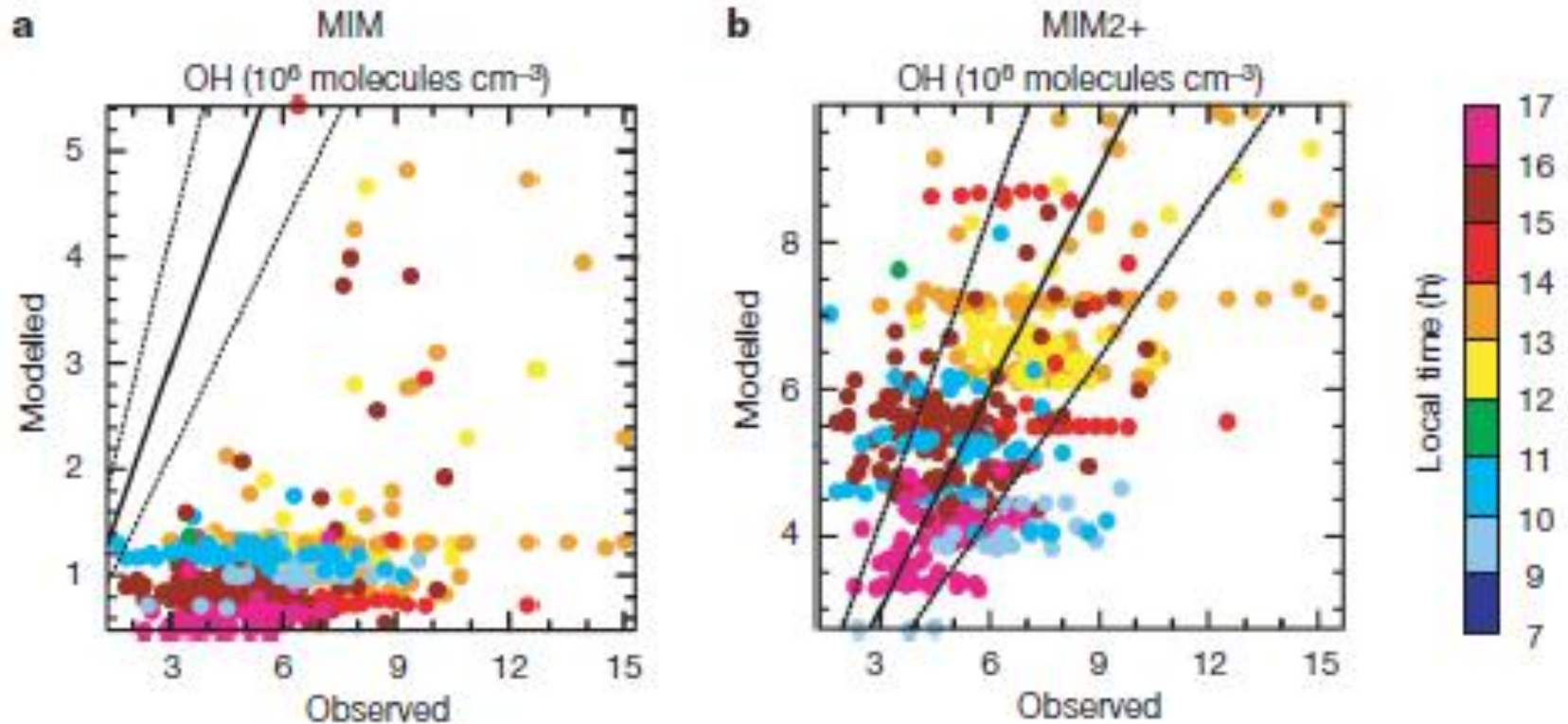


How well do we understand the general structure of oxidation mechanisms

Missing radical sources

Examples of recent observations suggesting that new sources of OH are needed.

Lieleveld et al., Gabriel campaign Guyanas, 2005.
Nature, April 2008; Atmos. Chem. Phys., 8,
4529-4546. 2008.

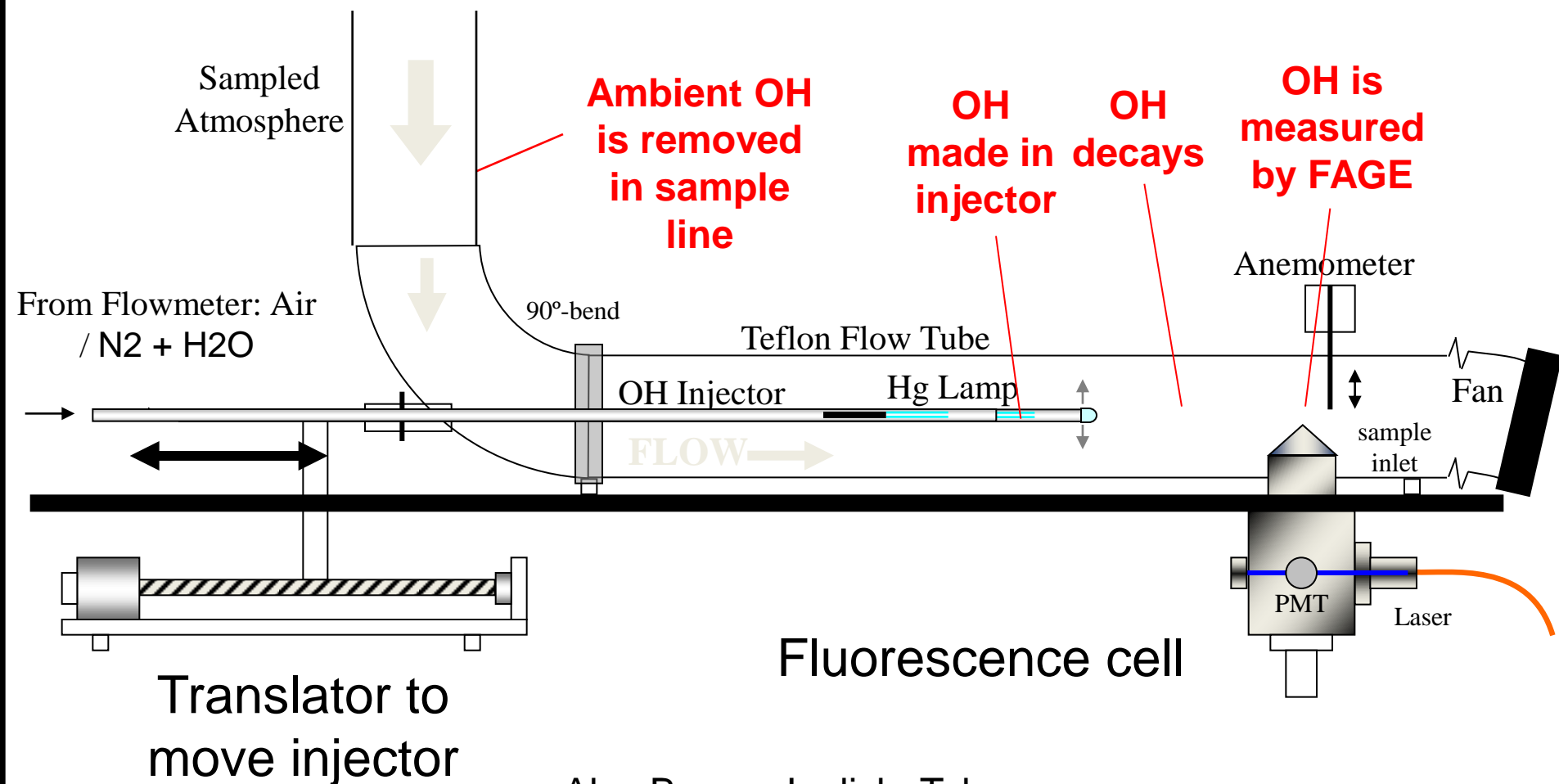


Conclusions from Gabriel analyses

"To explain the observed isoprene concentrations, the effective rate constant for the reaction of isoprene with OH be reduced by about 50% compared with the lower bound of the range recommended by IUPAC. A reasonable explanation for this lower effective rate constant could be the segregation of isoprene and OH in the mixed layer."

Measurement of OH reactivity: Leeds OH reactivity (lifetime) instrument

Flow-tube reactor with the atmosphere as the reagent



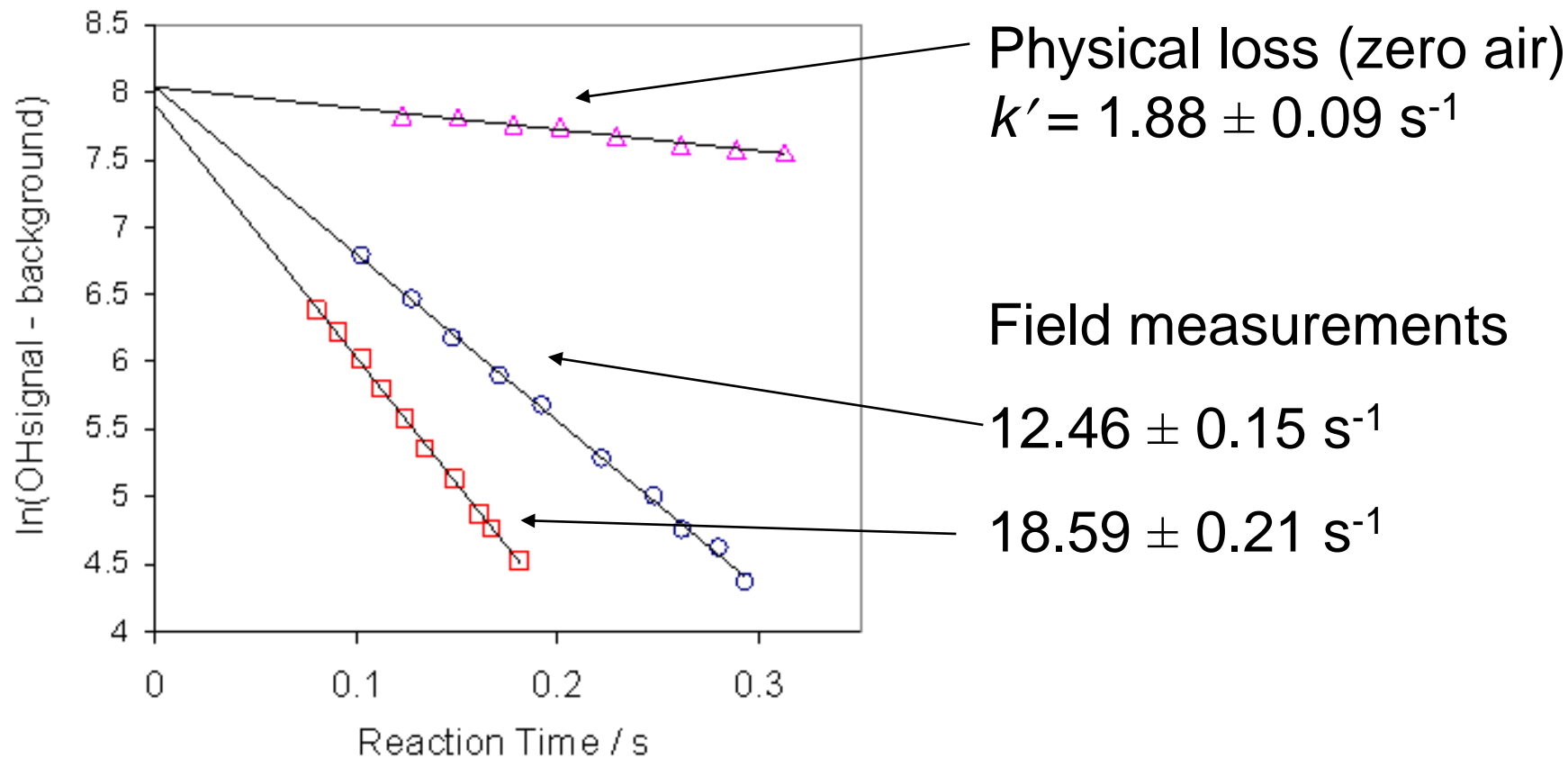
Also Brune, Juelich, Tokyo.

Semi-log decay of OH

$$k'_{\text{OH}} = \sum_i k_i [\text{VOC}]_i$$
$$= 1 / \tau_{\text{OH}}$$

$[\text{OH}] = [\text{OH}]_0 \exp(-k'_{\text{OH}} t)$. Obtain k'_{OH} from semi-log plot

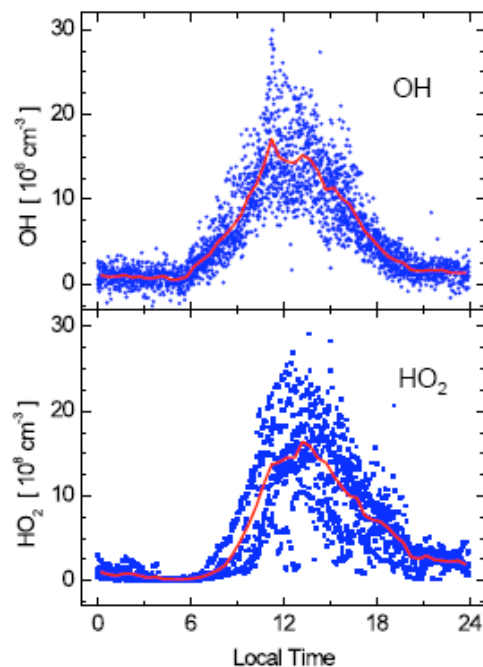
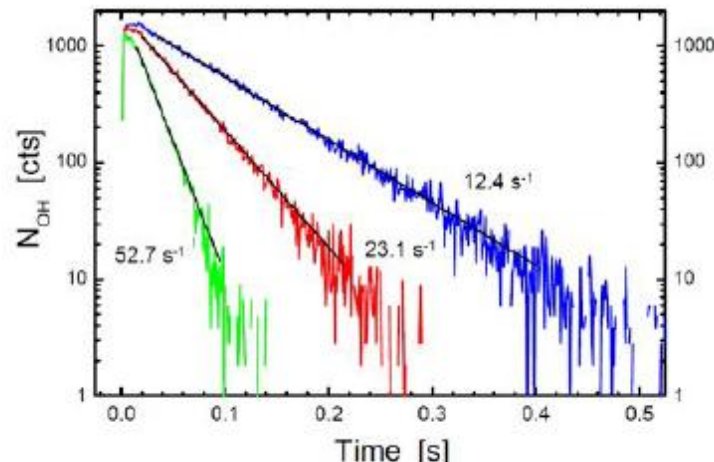
Change t by moving injector position



Combine measurement of OH reactivity with measurement of $[\text{OH}]$, $[\text{HO}_2]$ and concentrations of OH sources (ozone, HONO....). Check budget balance.

- Pearl River Delta, 3 - 30 July 2006
Photochemistry study with measurements of HOx in China (PRIDE-PRD 2006)
~ 60 km outside of Guangzhou City (23.5°N)
- Forschungszentrum Jülich, Peking University, Beijing, RCEC, Taiwan University of Tokyo
- Science. 2009; >324:1702-1704.

OH lifetime measurements:
Measure $\tau = 1/k_{OH}$
Where k_{OH} is the pseudo 1st order k for loss of OH
Rate of loss of OH = $k_{OH}[OH]$



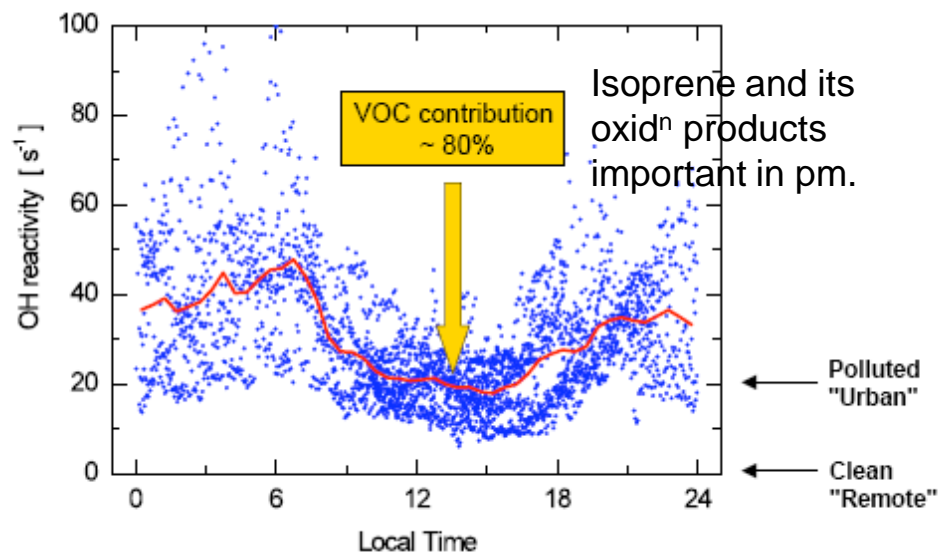
Mean Diurnal Profiles

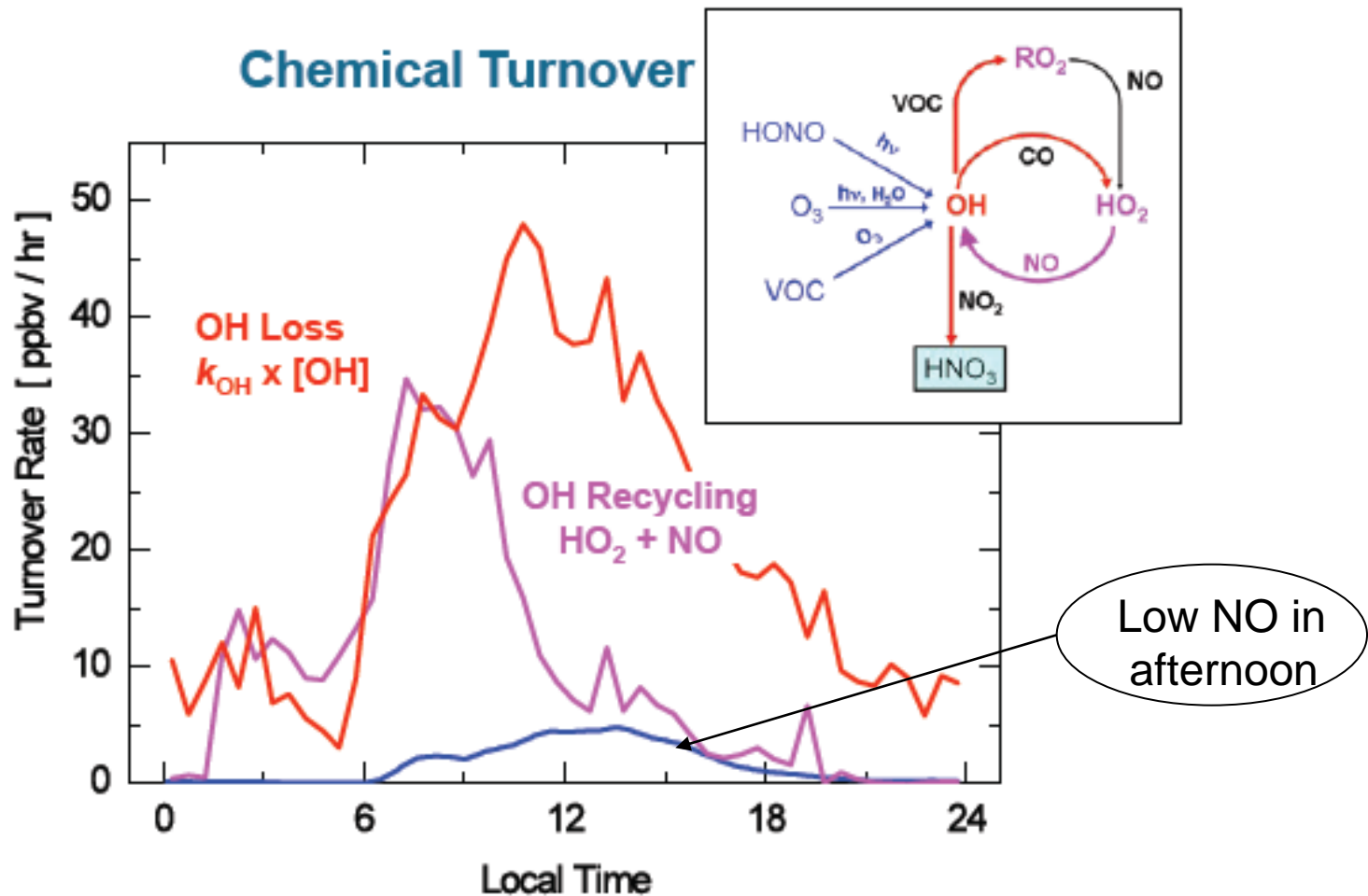
OH peak values
 2×10^7 molecules / cm³
~ 0.8 pptv

High photochemical activity !

HO₂ peak values
~ 80 pptv

— mean diurnal profiles
• individual data points





- Radical budget closed in morning - OH recycling is very efficient.
- No closure in afternoon. Since HO_2 , NO and OH loss are directly measured, observation indicates additional source of OH

HO_x radical regeneration in the oxidation of isoprene

Peeters et al., PCCP 2009

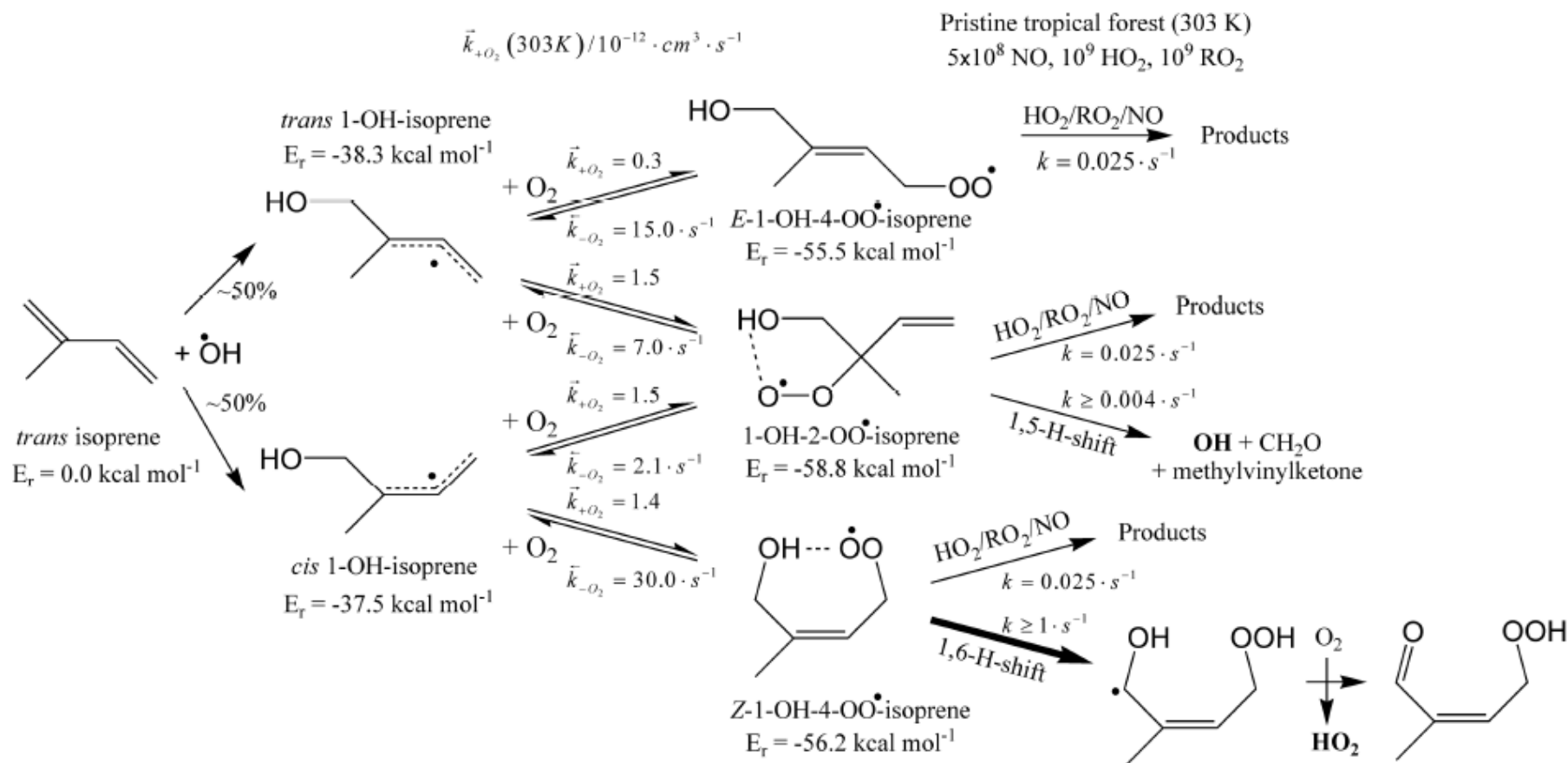
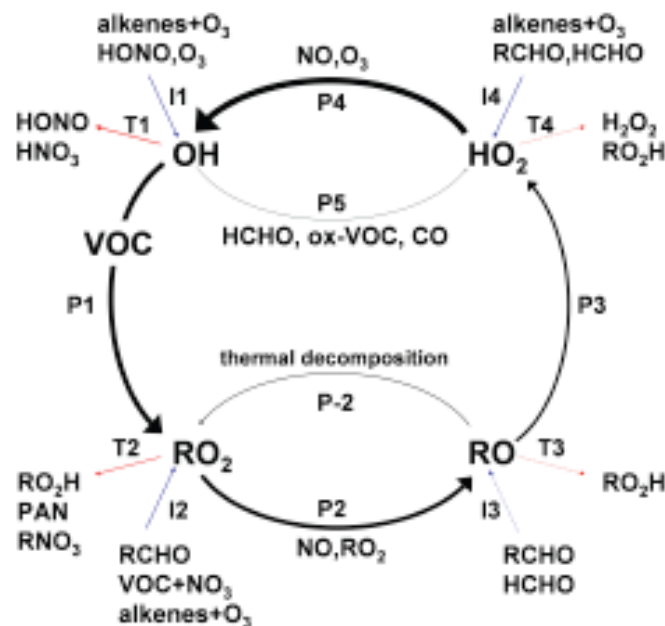
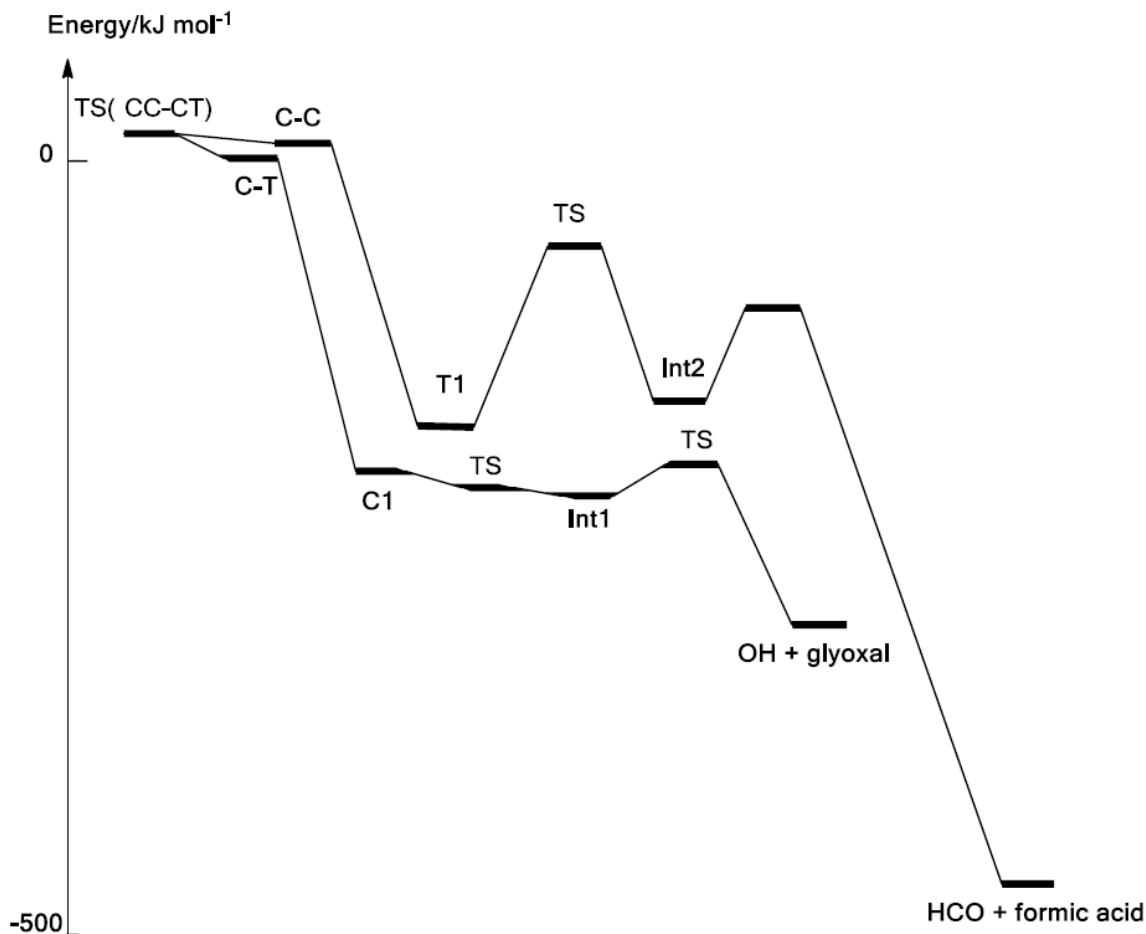


Fig. 1 Reaction scheme for OH and HO₂ radical formation following 1-OH addition to isoprene (60%), in pristine forest BL conditions, at 303 K. Note: to obtain the pseudo-first-order k'_{+O_2} , in these conditions, multiply the k_{+O_2} values listed by $5 \times 10^{18} \text{ cm}^{-3}$.

Other possible sources of OH

- The main requirement is to form OH without going through HO_2 , since that route is quantified through the measurement of $[\text{HO}_2]$ and N
- ? Unrecognised photolysis routes to OH
- $\text{RO}_2 \rightarrow \text{QOOH} \rightarrow \text{OH} + \text{products}$ the 'combustion route', via we C-H and O-H bonds, c.f. reactions in ethers and acetylene.
- $\text{RC(O)O}_2 + \text{HO}_2 \rightarrow \text{OH}$
- Both mechanisms less efficient at high NO_x





Reaction occurs to form an adduct HOC_2H_2 in which the radical is cis (CC) or trans to the OH

Addition of O_2 then generates respectively a peroxy radical that dissociates rapidly to form different products depending on the stereochemistry

Is the reaction
of vibrationally
excited species
significant in the
atmosphere

Science, 337,
1066 (2012)

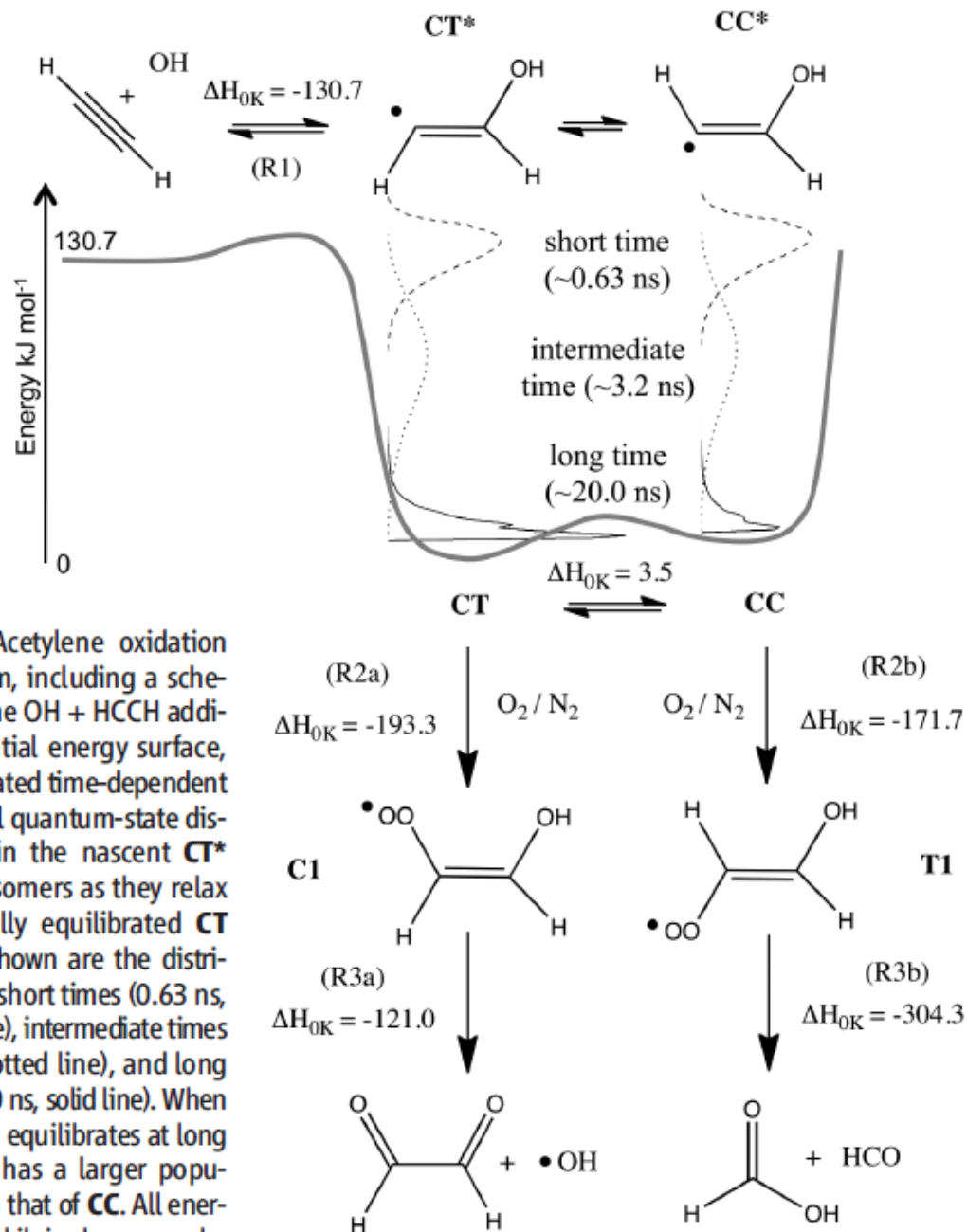


Fig. 1. Acetylene oxidation mechanism, including a schematic of the $\text{OH} + \text{HCCH}$ addition potential energy surface, and calculated time-dependent vibrational quantum-state distribution in the nascent CT^* and CC^* isomers as they relax to thermally equilibrated CT and CC . Shown are the distributions at short times (0.63 ns, dashed line), intermediate times (3.2 ns, dotted line), and long times (20.0 ns, solid line). When the system equilibrates at long times, CT has a larger population than that of CC . All energies are in kilojoules per mole. Reaction energies shown are taken from this work and previous work (21, 23).

The future?

How will global energy markets evolve to 2035?

(International Energy Agency)

<http://www.iea.org/weo/docs/weo2011/factsheets.pdf>

- Energy-related CO₂ emissions increase by 20%, consistent with a long-term rise in the average global temperature.
- 90% of projected growth from non-OECD economies .
30% from China
- The share of fossil fuels in global primary energy consumption falls slightly from 81% in 2010 to 75% in 2035
- On planned policies, rising fossil energy use will lead to irreversible and potentially catastrophic climate change
- China, responsible for nearly half of global coal use in 2009, holds the key to the future of the coal market with an ambitious 12th Five-Year Plan for 2011-2015 to reduce energy and carbon intensity through enhanced energy efficiency and diversifying the energy mix.

Reading

Some more general reading in addition to the specific references given in the lectures

- General kinetics: Pilling and Seakins, Reaction Kinetics.
- Radical Kinetics - a recent personal account, M J Pilling, J Phys Chem A, 2013, 117, 3697 - 3717
- Master equation: Barker, J. R. Multiple-Well, Int. J. Chem. Kinet. 2001, 33 (4), 232-245. Klippenstein, S. J.; Miller, J. A. J. Phys. Chem. A 2002, 106 (40), 9267-9277
- Autoignition chemistry: Zador, J.; Taatjes, C. A.; Fernandes, R. X. Prog. Energy Combust. Sci. 2011, 37 (4), 371-421
- Atmospheric Chemistry: R P Wayne, Chemistry of Atmospheres
- IPCC: 4th Assessment Report, 2007. 5th AR. 2013/2014