

Photolysis processes and how we model them



<https://www.ncdc.noaa.gov>

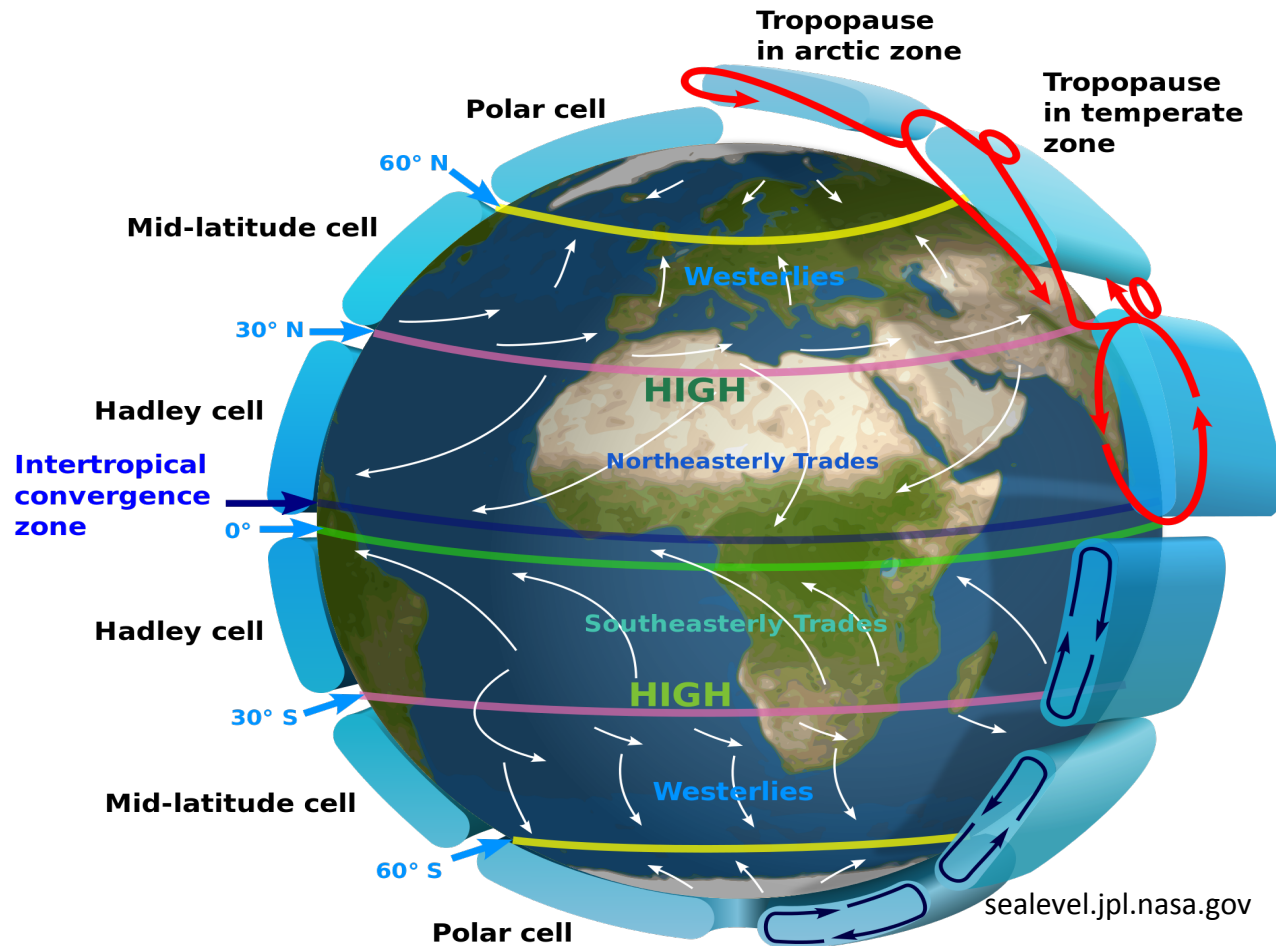
by Apostolos Voulgarakis, Imperial College London, UK

UKCA Training Course, Cambridge, 10th of January 2017

Aims & Objectives

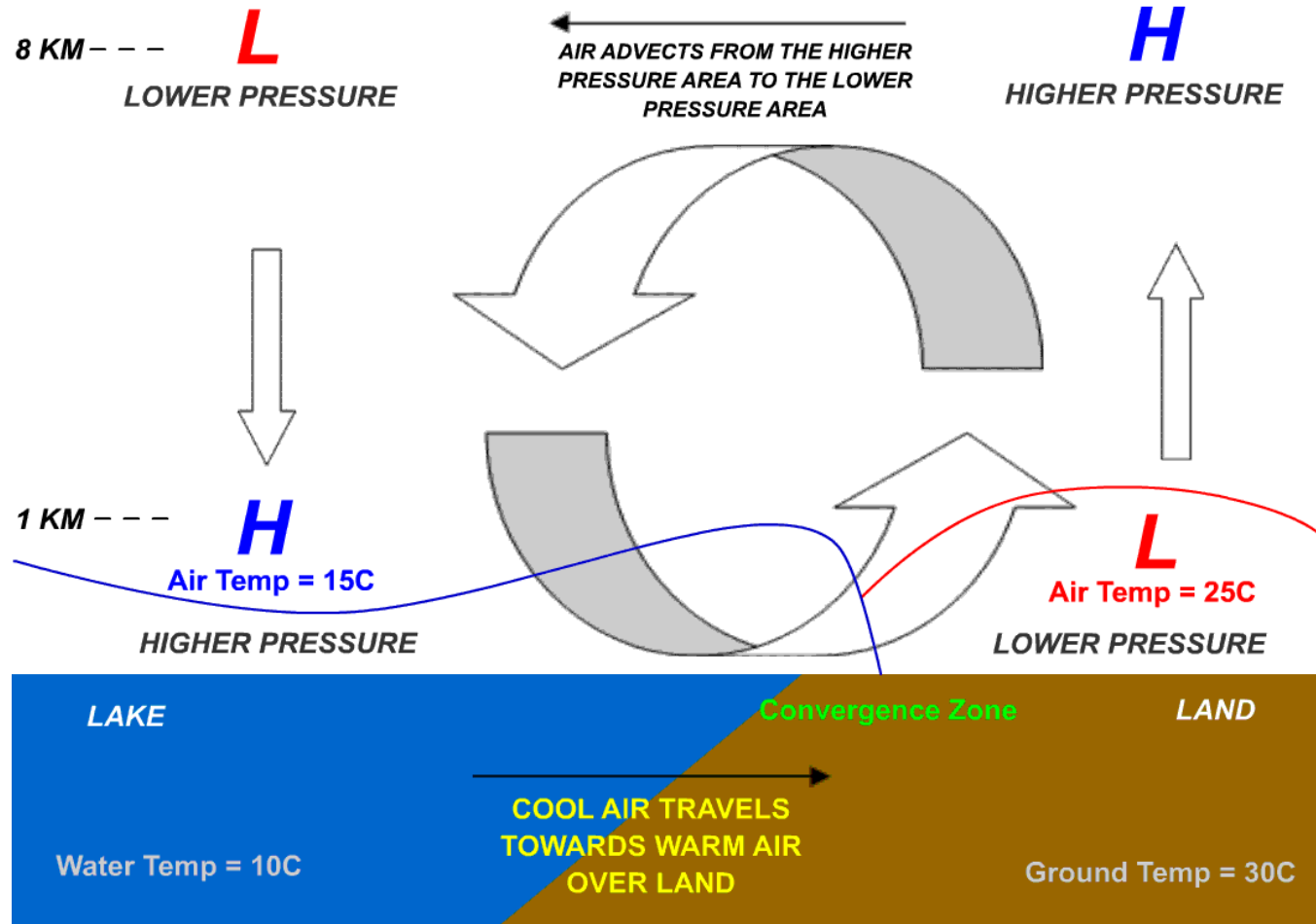
- Establish why photolysis processes are of **central importance** in atmospheric chemistry.
- Describe the main **quantities needed** for calculating photolysis rates of constituents.
- Provide a basic overview of the features of the **Fast-JX photolysis scheme**, used in UKCA.
- Describe some **photolysis-focused science** that has been pursued using the Fast-J family of modules, either in UKCA or in other global models.

Solar Radiation: The driving force behind **global circulation and large-scale weather**



- Meridional insolation & temperature gradients drive the zonal mean atmospheric circulation, the position of storm tracks, and, thus, weather.

Solar Radiation: The driving force behind regional/local circulation



en.wikipedia.org/wiki/Sea_breeze

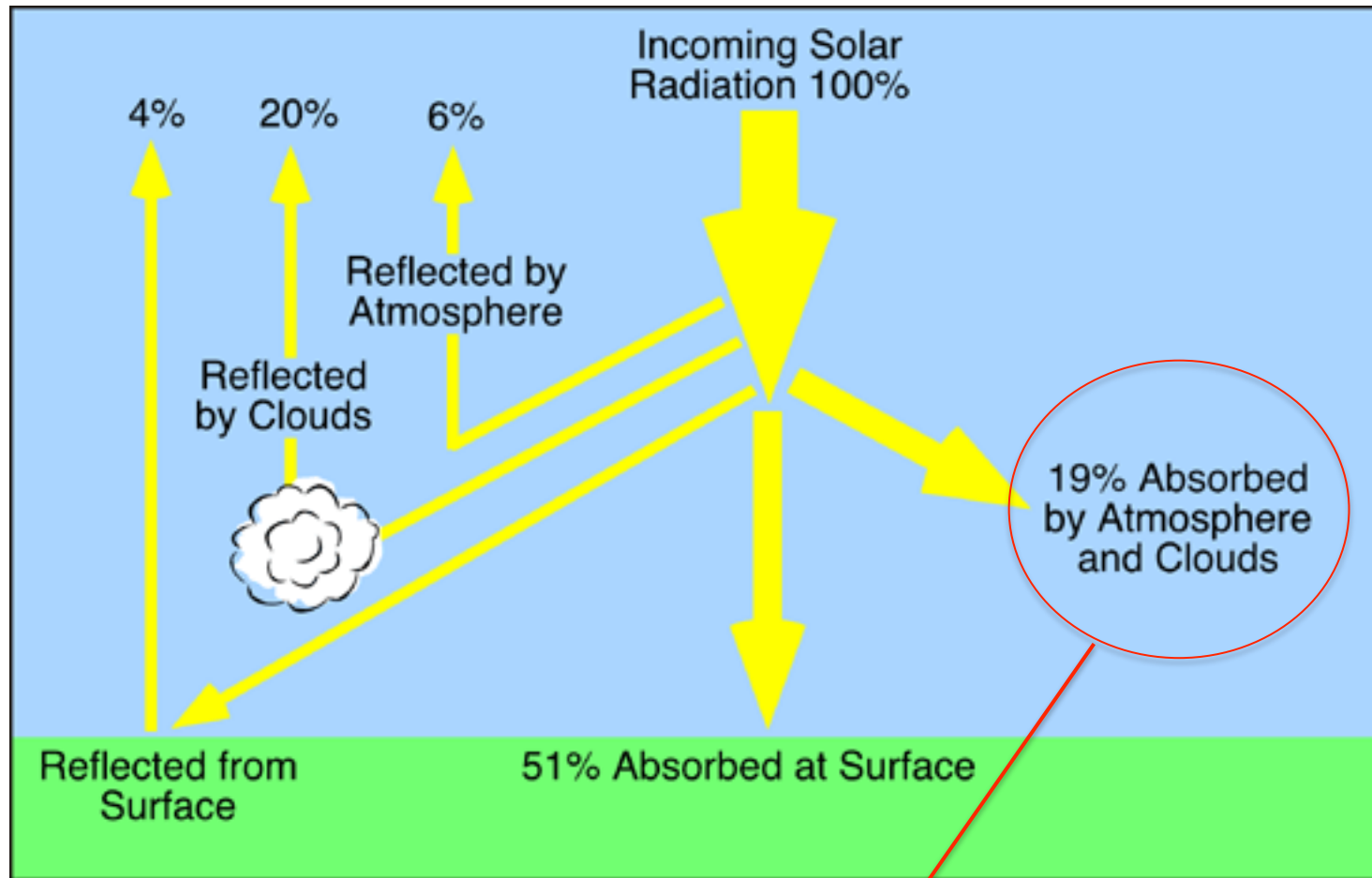
- Land-sea thermal contrasts drive regional circulations such as monsoons, and local circulations such as sea breezes.

***But simultaneously*: Solar radiation is the driving force behind atmospheric chemistry**

$$\frac{\partial E}{\partial t} = -\nabla \cdot (\mathbf{U}E) + \rho_A \frac{\theta_V}{T_V} \frac{dQ}{dt}$$


- The thermodynamic equation solved for each point in space (model gridpoints) and time (model timesteps) simulates the change of heat, and eventually of temperature, which influences the **rates** of many key chemical reactions.
- Changes in temperature cause changes in other meteorological variables such as **humidity, rainfall, pressure, winds, turbulence, lightning**, all of which strongly influence atmospheric chemistry.
- But the most direct and crucial way in which solar radiation influences atmospheric chemistry is through driving **photolysis** (also called photodissociation).

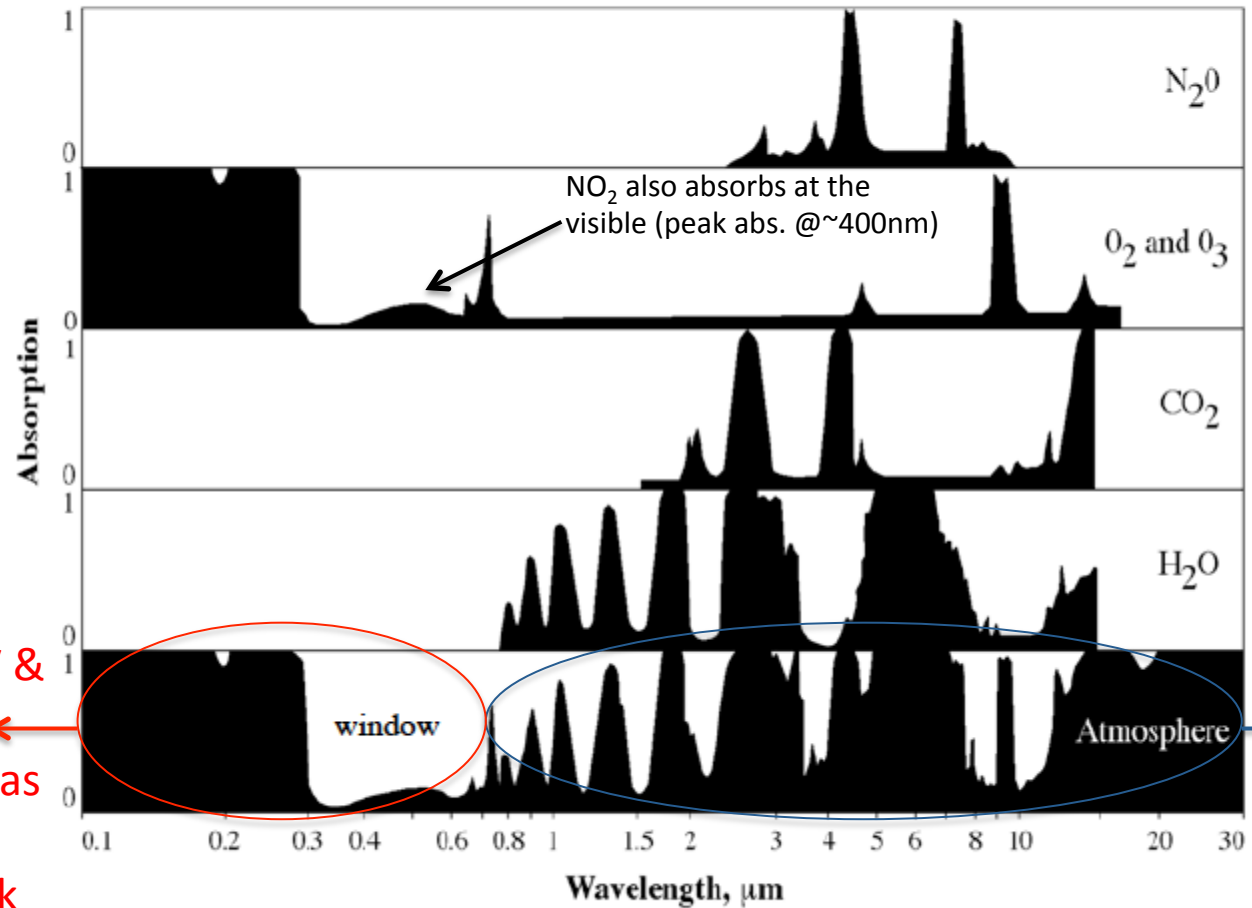
Radiative transfer in the atmosphere



www.physicalgeography.net

- This absorbed radiation is the **cause of photolysis**.
- GCMs include a radiative transfer module for climate.
- CTMs include a radiative transfer module for chemistry (photolysis scheme).
- CCMs include two codes for both (not very efficient!)

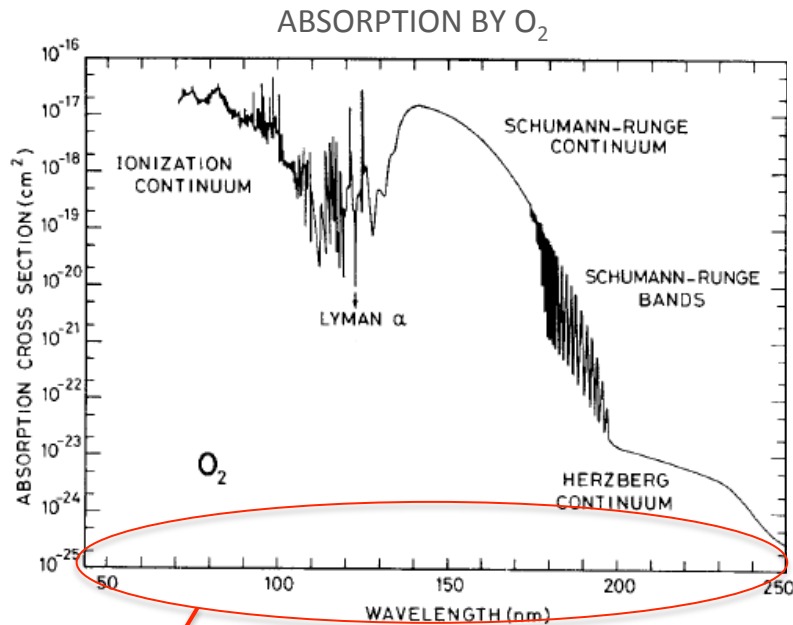
Absorption of the Sun's incident electromagnetic energy in the region from 0.1 to 30 μm (100-30,000 nm) by various atmospheric gases



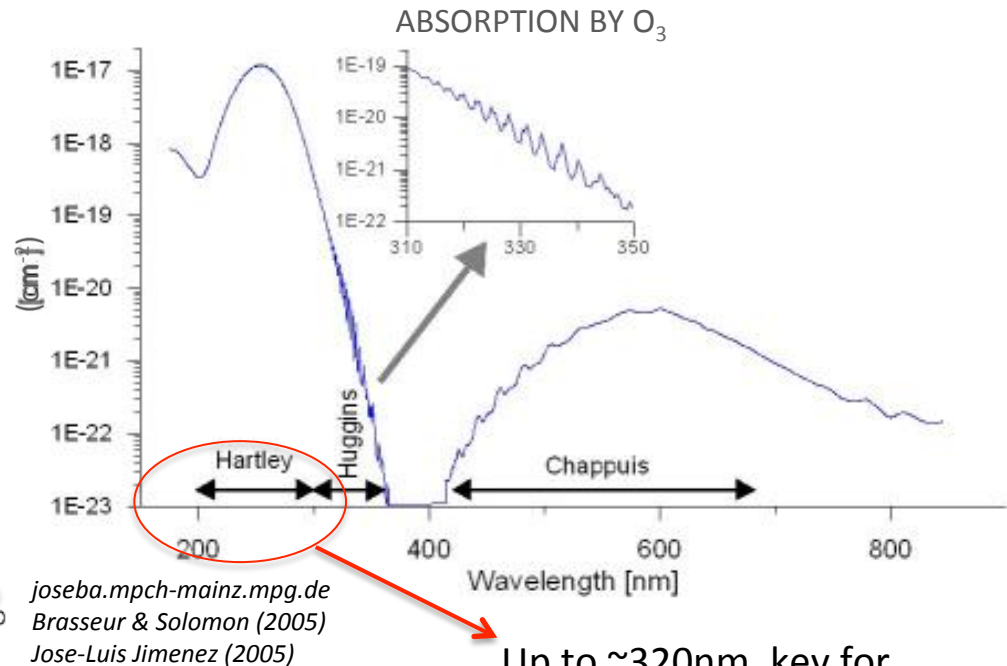
Shortwave (UV & visible): key for photolysis, as it has enough energy to break down molecules.

Longwave (solar + thermal IR): directly climate-relevant (esp. through coupling with vibrational modes).

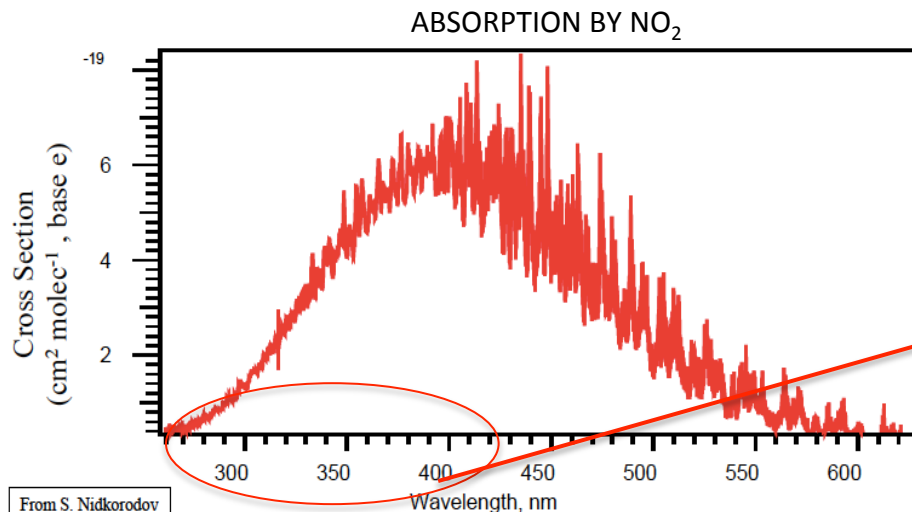
Absorption by key gases that can undergo photolysis



Very energetic wavelengths – not found in the troposphere (only slightly in the UT), but key for O_2 photolysis in **stratosphere & mesosphere**.



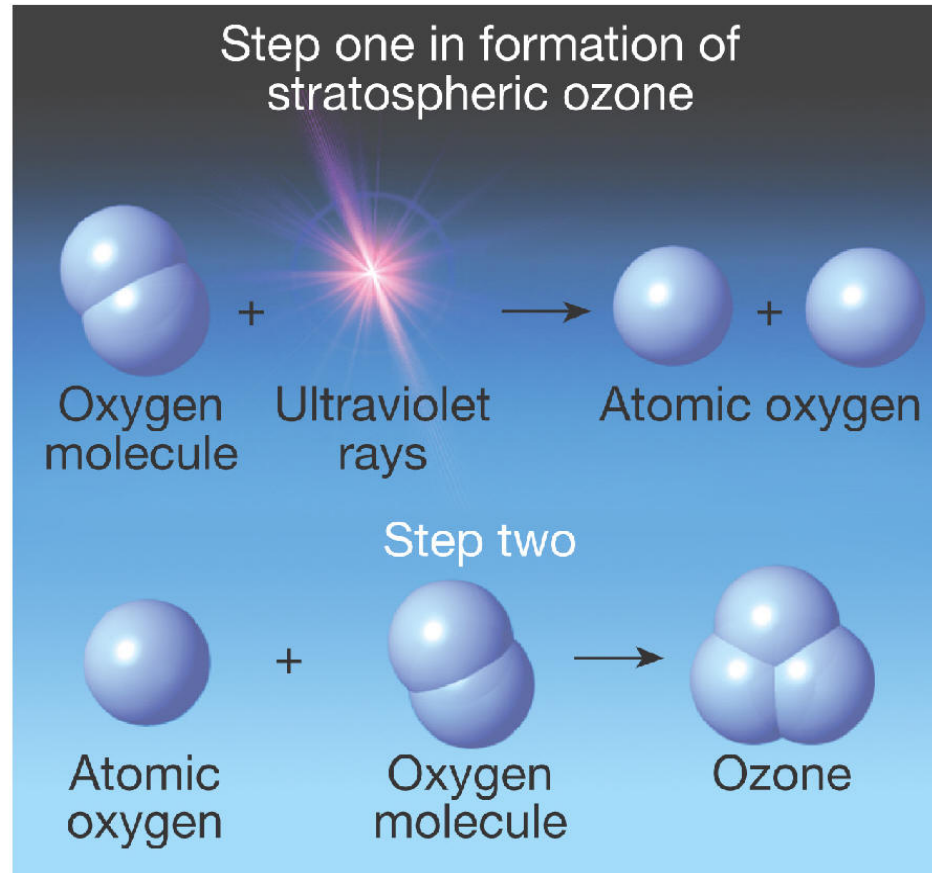
Up to ~ 320 nm, key for ozone (O_3) photolysis in the **troposphere & stratosphere**.



Up to ~ 420 nm, key for NO_2 photolysis in **troposphere & stratosphere**.

(*Note that x-sections are typically temperature dependent.)

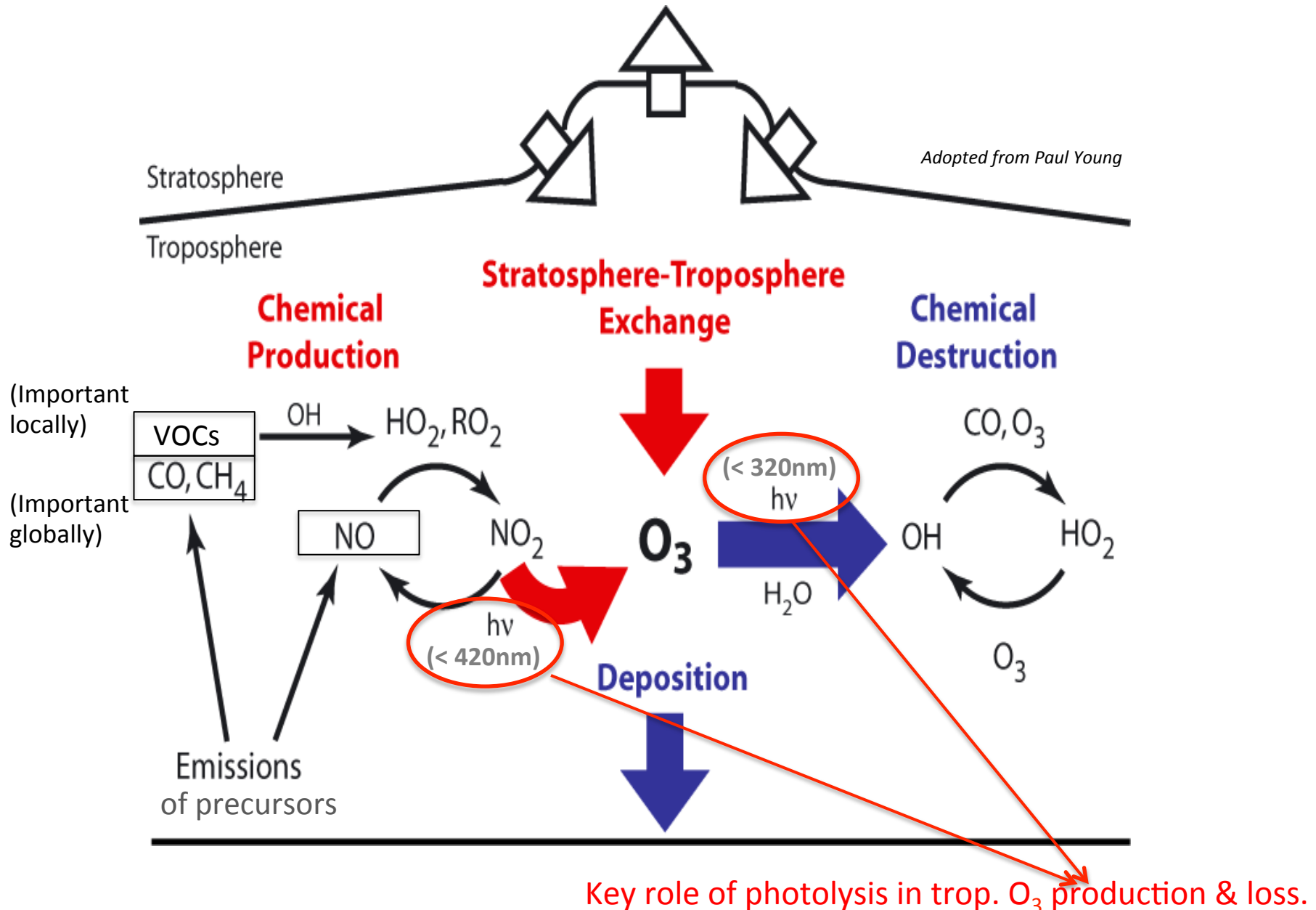
Photolysis and stratospheric ozone



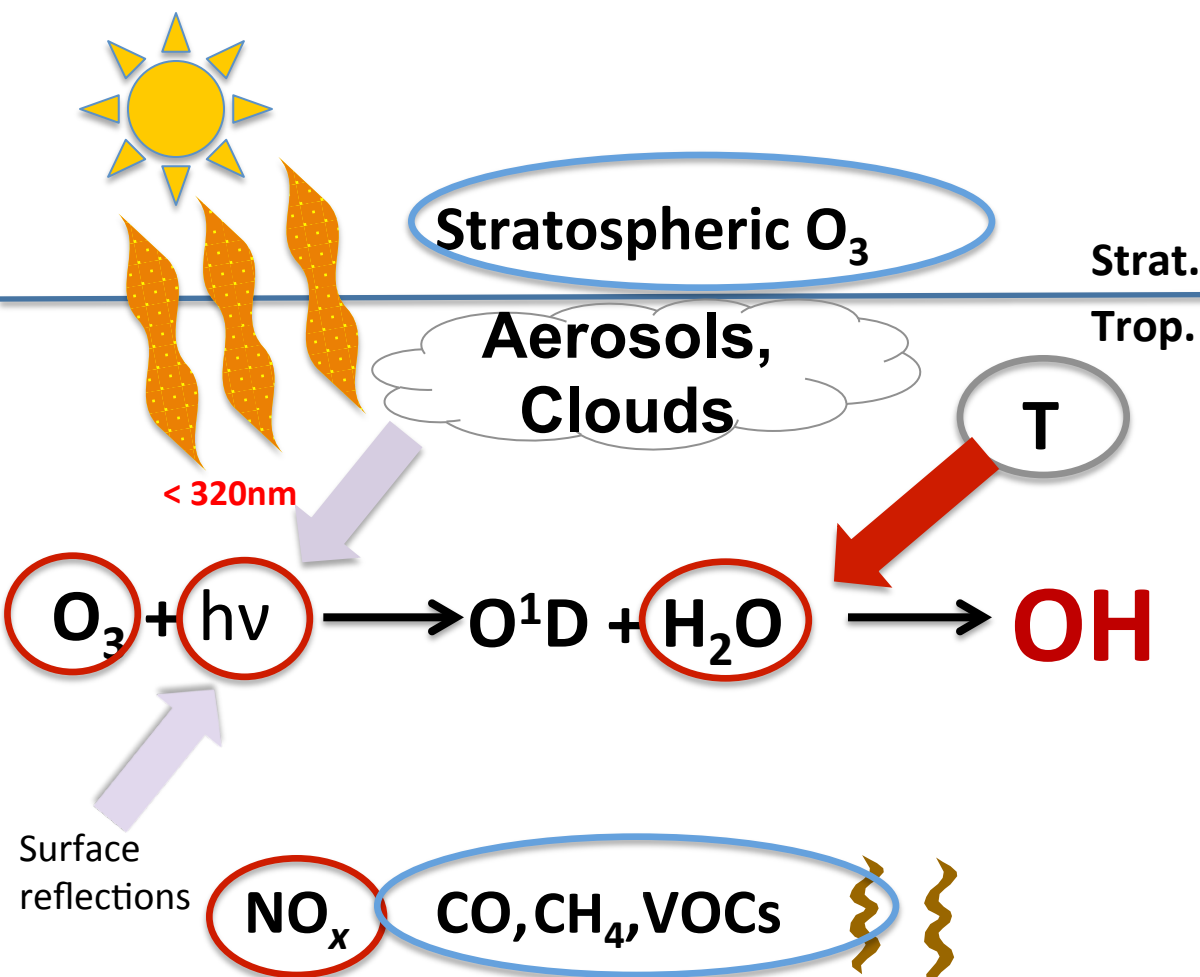
www.geography.hunter.cuny.edu

- Highly energetic photons (<240 nm) **break down O_2** .
- Subsequently, atomic oxygen reacts with oxygen molecules to yield O_3 .
- These two reactions are part of the **Chapman mechanism**.
- Photolysis is also key for **catalytic ozone destruction** (see later).

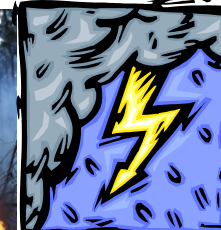
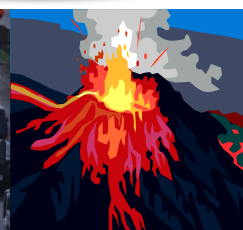
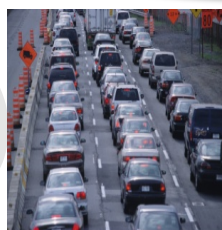
Photolysis and the tropospheric ozone budget



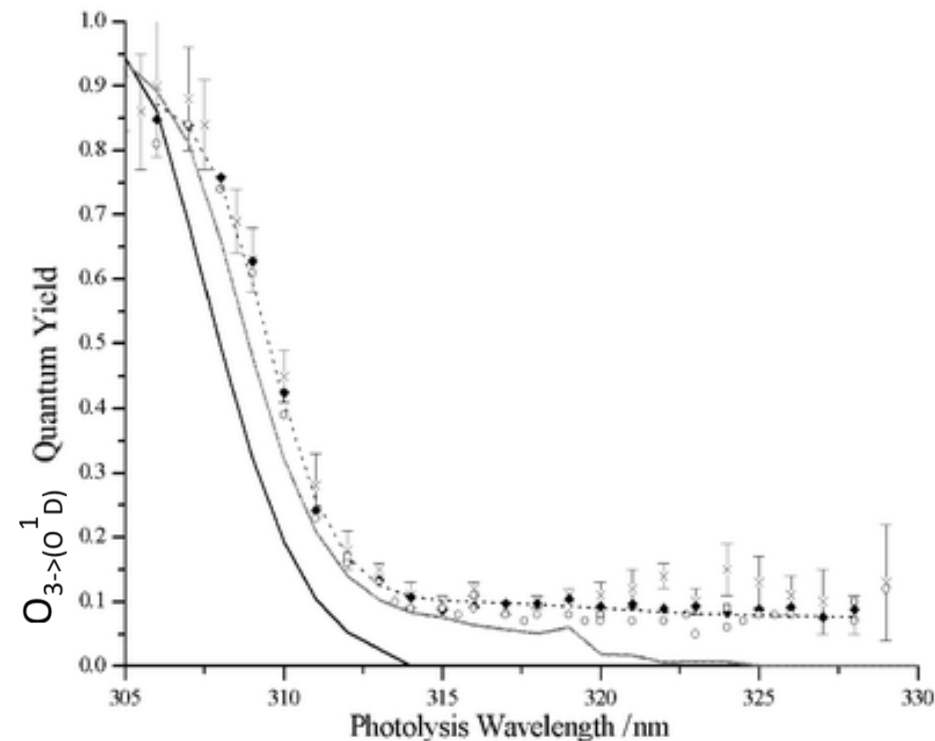
Photolysis and the hydroxyl radical (OH)



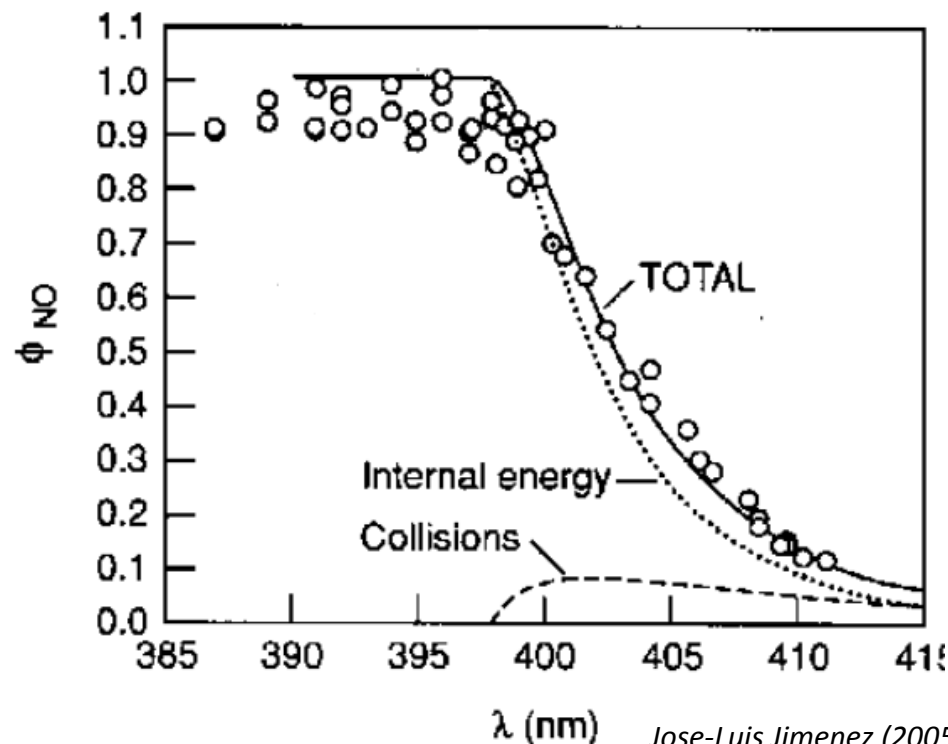
- OH is a major tropospheric **oxidant** (detergent of the troposphere).
- It **removes CO/VOCs**, is involved in tropospheric **ozone (O_3)** production, and in **aerosol formation**.
- It is the major **sink of CH_4** in the atmosphere: OH determines CH_4 **lifetime**.



How many molecules are photolysed per photon absorbed (the $\text{O}_3 \rightarrow \text{O}(^1\text{D})$ and $\text{NO}_2 \rightarrow \text{NO}$ quantum yields (ϕ))



Hancock & Tyley (2001)



Jose-Luis Jimenez (2005)

- The “cut-off” for O_3 photolysis to produce $\text{O}(^1\text{D})$ is $\sim 320\text{-}330\text{nm}$, and for NO_2 photolysis to produce NO is $\sim 420\text{nm}$.
- Thus, upper wavelength **limit** set by quantum yield rather than by absorption cross section.
- For O_2 photolysis it is absorption that sets the upper limit (see Slide 8).

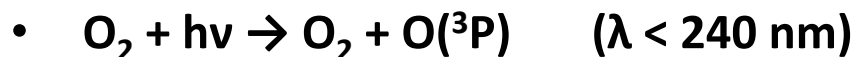
Table 4.1 Spectral regions of photochemical importance in the atmosphere

Wavelength	Atmospheric absorbers
121.6 nm	Solar Lyman α line, absorbed by O_2 in the mesosphere; no absorption by O_3
100 to 175 nm	O_2 Schumann Runge continuum. Absorption by O_2 in the thermosphere. Can be neglected in the mesosphere and stratosphere.
175 to 200 nm	O_2 Schumann Runge bands. Absorption by O_2 in the mesosphere and upper stratosphere. Effect of O_3 can be neglected in the mesosphere, but is important in the stratosphere.
200 to 242 nm	O_2 Herzberg continuum. Absorption by O_2 in the stratosphere and weak absorption in the mesosphere. Absorption by the O_3 Hartley band is also important; both must be considered.
242 to 310 nm	O_3 Hartley band. Absorption by O_3 in the <u>stratosphere</u> leading to the formation of $O(^1D)$.
310 to 400 nm	O_3 Huggins bands. Absorption by O_3 in the stratosphere and troposphere leads to the formation of $O(^3P)$.
400 to 850 nm	O_3 Chappuis bands. Absorption by O_3 in the troposphere induces photodissociation even at the surface.

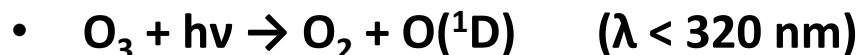
Summary of O_2 & O_3 Photochem.

(and to some extent in the troposphere).

Summary of important photolysis reactions



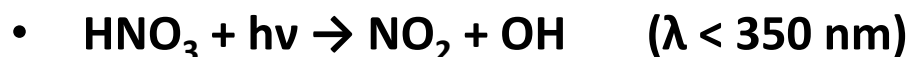
Initiates ozone production in stratosphere (and slightly in the upper trop.).



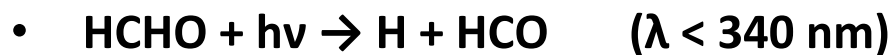
Leads to ozone destruction and OH production.



Initiates ozone production in troposphere.



Main loss process of HNO_3 (which is a “NO_x reservoir”).



Contributes to HO_x production (similar for CH₃CHO and higher aldehydes).



Can contribute to OH production.



Destroys N₂O; Subsequently, N₂O+O(¹D) produces NO_x in the stratosphere.



Releases Cl that destroys ozone in the stratosphere (similarly for other Cl species).

The photolysis rate

- For a given molecule A being photolysed ($A+h\nu \longrightarrow B+C$):

$$d[A]/dt = -J_A[A] = -\int \sigma_A(\lambda) \varphi_A(\lambda) F(\lambda) d\lambda \times [A]$$

- J_A : First order **photolysis rate constant** (or frequency) of A (s^{-1}).
- $\sigma_A(\lambda)$: Absorption **cross section**, i.e. probability of a photon to be absorbed ($cm^2/molec.$).
- $\varphi_A(\lambda)$: **Quantum yield**, i.e. number of molecules photolysed per photon absorbed ($molec./quanta$).
- $F(\lambda)$: Solar **actinic flux**, i.e. radiative flux incident on molecule from all directions ($quanta\ cm^{-2}\ s^{-1}$).

Lifetime with respect to photolysis

- The rate at which a chemical species A (with concentration $[A]$) is lost from the atmosphere is characterised by its **e-folding lifetime** τ_A .

- It is the time required by a gas to decrease to $1/e$ of its original concentration due to chemical reaction. Lifetimes are **independent** of emission/production rates.

- For example, for **photolysis** reaction:
$$\tau_A = \frac{1}{J_A} = \frac{[A]}{d[A]/dt}$$

- If concentration of a constituent is determined by multiple processes (1, 2,..., n), the overall lifetime is:

$$\tau_A = \frac{1}{\frac{1}{\tau_{A1}} + \frac{1}{\tau_{A2}} + \dots + \frac{1}{\tau_{An}}}$$

The FAST- JX photolysis scheme *(Wild et al., 2000; Bian and Prather, 2002; Neu et al., 2007)*, used in UKCA

- Calculates photolysis rates in the presence of an arbitrary mix of **cloud and aerosol layers** (handles multiple layers as well).
 - Enables tropospheric chemistry simulations to include **directly** the physical properties of scattering and absorbing particles (and clouds) in the column.
 - The code is fast (obviously!) and can be applied to 3D global CTMs or CCMs with relatively **low computational cost**.
- It is a sufficiently **accurate and efficient** scheme to apply to global models.

Unique features of Fast-JX

- Phase functions calculated using **Mie theory** (except for ice-clouds).
- Optimization of the phase function expansion (8 terms).
- Radiative transfer equation is solved using the **finite-difference** method. Additional levels are inserted for thick clouds.
- **Optimisation** of the integration over wavelength (18 bins, from 177 to 850 nm).
- JPL and IUPAC **cross-sections** for various temperatures reapportioned onto the scheme's wavelength bins.

Modelling photolysis rate constants: σ & φ

$$J_A = \int \sigma_A(\lambda) \varphi_A(\lambda) F(\lambda) d\lambda$$

- The x-sections (σ) and quantum yields (φ) for different constituents have been **measured in the lab** for different wavelengths, temperatures, and sometimes pressures (JPL & IUPAC reports).
- **Tabulated values** are then typically used in atmospheric models (e.g. see FJX_spec_Nov11.dat for UKCA).
- **Real-time, simulated** temperatures at different points in space and time can modify σ and φ .

**In UKCA, cross sections and quantum yields are tabulated
in file FJX_spec_Nov11.dat (its top part is shown below)**

w-eff (nm)		187.	191.	193.	196.	202.	208.
		211.	214.	261.	267.	277.	295.
		303.	310.	316.	333.	380.	574.
SOL#/cm2/s		1.391E+12	1.627E+12	1.664E+12	9.278E+11	7.842E+12	4.680E+12
		9.918E+12	1.219E+13	6.364E+14	4.049E+14	3.150E+14	5.889E+14
		7.678E+14	5.045E+14	8.902E+14	3.853E+15	1.547E+16	2.131E+17
Raylay cm2		5.073E-25	4.479E-25	4.196E-25	3.906E-25	3.355E-25	2.929E-25
		2.736E-25	2.581E-25	1.049E-25	9.492E-26	8.103E-26	6.131E-26
		5.422E-26	4.923E-26	4.514E-26	3.643E-26	2.087E-26	3.848E-27
jo2	180	1.727E-21	1.989E-22	3.004E-23	9.833E-24	7.306E-24	6.835E-24
		6.243E-24	5.804E-24	8.662E-26	5.040E-25	4.163E-25	0.000E+00
		0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
jo2	260	2.273E-21	3.070E-22	4.943E-23	1.408E-23	7.688E-24	6.835E-24
		6.243E-24	5.886E-24	8.662E-26	5.040E-25	4.163E-25	0.000E+00
		0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
jo2	300	2.763E-21	4.269E-22	7.478E-23	2.100E-23	8.350E-24	6.835E-24
		6.243E-24	5.992E-24	8.662E-26	5.040E-25	4.163E-25	0.000E+00
		0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
jo3b	180	5.849E-19	4.708E-19	4.154E-19	3.549E-19	3.230E-19	4.555E-19
		6.287E-19	9.126E-19	8.846E-18	3.467E-18	1.495E-18	7.561E-19
		2.367E-19	8.756E-20	3.690E-20	4.256E-21	1.806E-23	1.625E-21
jo3b	260	5.916E-19	4.794E-19	4.246E-19	3.651E-19	3.332E-19	4.610E-19
		6.325E-19	8.750E-19	8.857E-18	3.565E-18	1.555E-18	8.016E-19
		2.572E-19	9.710E-20	4.136E-20	5.409E-21	2.784E-23	1.625E-21
jo3b	300	5.884E-19	4.736E-19	4.183E-19	3.557E-19	3.302E-19	4.688E-19
		6.372E-19	8.993E-19	8.863E-18	3.597E-18	1.597E-18	8.391E-19
		2.778E-19	1.079E-19	4.720E-20	6.725E-21	4.845E-23	1.625E-21
jo3a	180	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01
		9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01
		8.926E-01	4.516E-01	8.621E-02	7.740E-02	0.000E+00	0.000E+00
jo3a	260	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01
		9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01
		8.934E-01	5.091E-01	1.472E-01	8.632E-02	0.000E+00	0.000E+00
jo3a	300	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01
		9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01	9.000E-01
		8.954E-01	5.723E-01	2.362E-01	9.937E-02	0.000E+00	0.000E+00

Modelling photolysis rate constants: F

$$J_A = \int \sigma_A(\lambda) \varphi_A(\lambda) F(\lambda) d\lambda$$

- Typically, actinic fluxes are simulated online for every point in space and time, accounting for modelled **clouds, surface albedo, gas** (e.g. O₂, O₃, NO₂) absorption, **aerosol** scattering and absorption, and of course for TOA spectral fluxes and the solar zenith angle.
- There are two terms that need to be summed in order to calculate the actinic flux:
 - a) the **direct** solar flux, obtained from the Beer-Lambert law:

$$I_{DIR}(z, \lambda) = I_{TOA}(\lambda) * \exp(-\tau(z, \lambda))$$

- b) the 4π integrated mean specific intensity originating **from all directions** after undergoing multiple scattering by surrounding particles.

Modelling photolysis rate constants: F (cont.)

$$J_A = \int \sigma_A(\lambda) \varphi_A(\lambda) F(\lambda) d\lambda$$

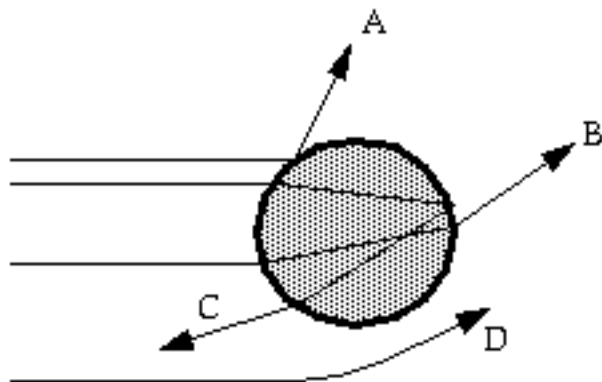
- Discrimination between the role of scattering and absorption is given by the **single scattering albedo (ω)**, the ratio of scattering/total extinction.
- The **scattering phase function (P)** gives the angular distribution of light around a particle following scattering.
- In the **Rayleigh scattering regime** (small particles), forward- and backward-scattered radiation are **symmetric**. For larger particles, the forward peak becomes stronger.
- P & ω of different aerosol/cloud types are **pre-calculated** for five wavelengths using an offline code that is based on **Mie theory** for particle types with given refractive indices and sizes (see FJX_scat.dat for UKCA).

Aerosol & cloud radiative effects

Absorption

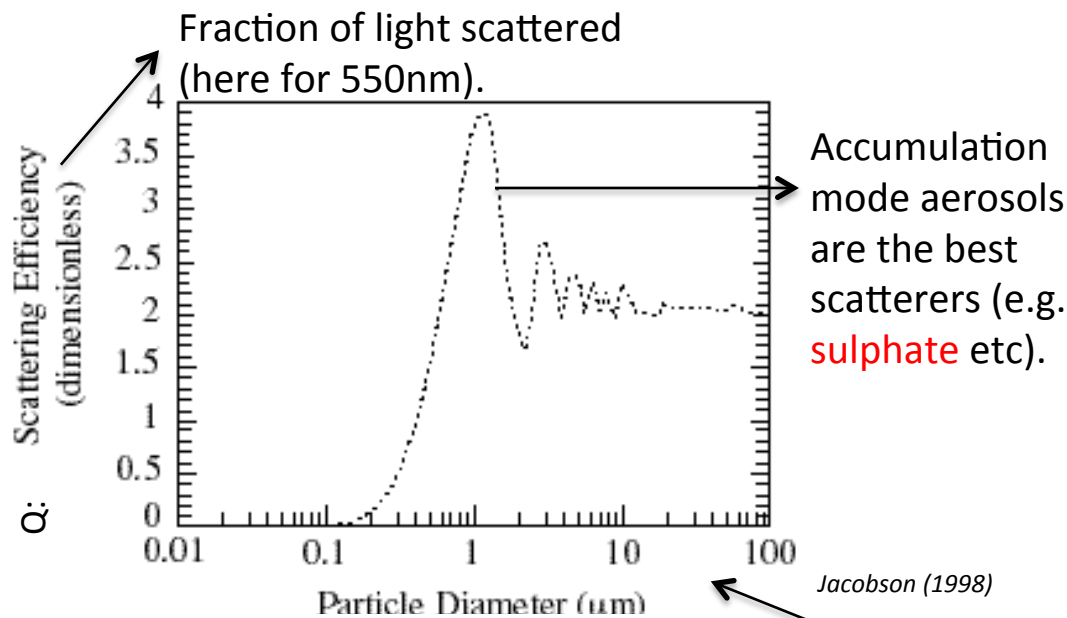
- **Black carbon**: the main aerosol absorber in all **solar** wavelengths (then re-emits in thermal). Also, some absorption by dust and a bit by organic carbon.
- **Dust & sea-salt** absorb substantially in **thermal** wavelengths (3,000-15,000 nm).
- **Clouds** absorb radiation, but how much is absorbed depends on the cloud type.

Scattering (only for solar)



- A:** Reflection **B:** Refraction
C: Refraction & internal reflection
D: Diffraction

(Their combination results in scattering)



$$\tau_{\lambda} = \int_0^z k_{\lambda}(z) \rho(z) dz = \int_0^z \alpha_{\lambda}(z) dz$$

$$\tau_{\lambda} = \int_0^z n(z) \pi r^2 Q_{\lambda}(z) dz = \int_0^z n(z) \sigma_{\lambda}(z) dz$$

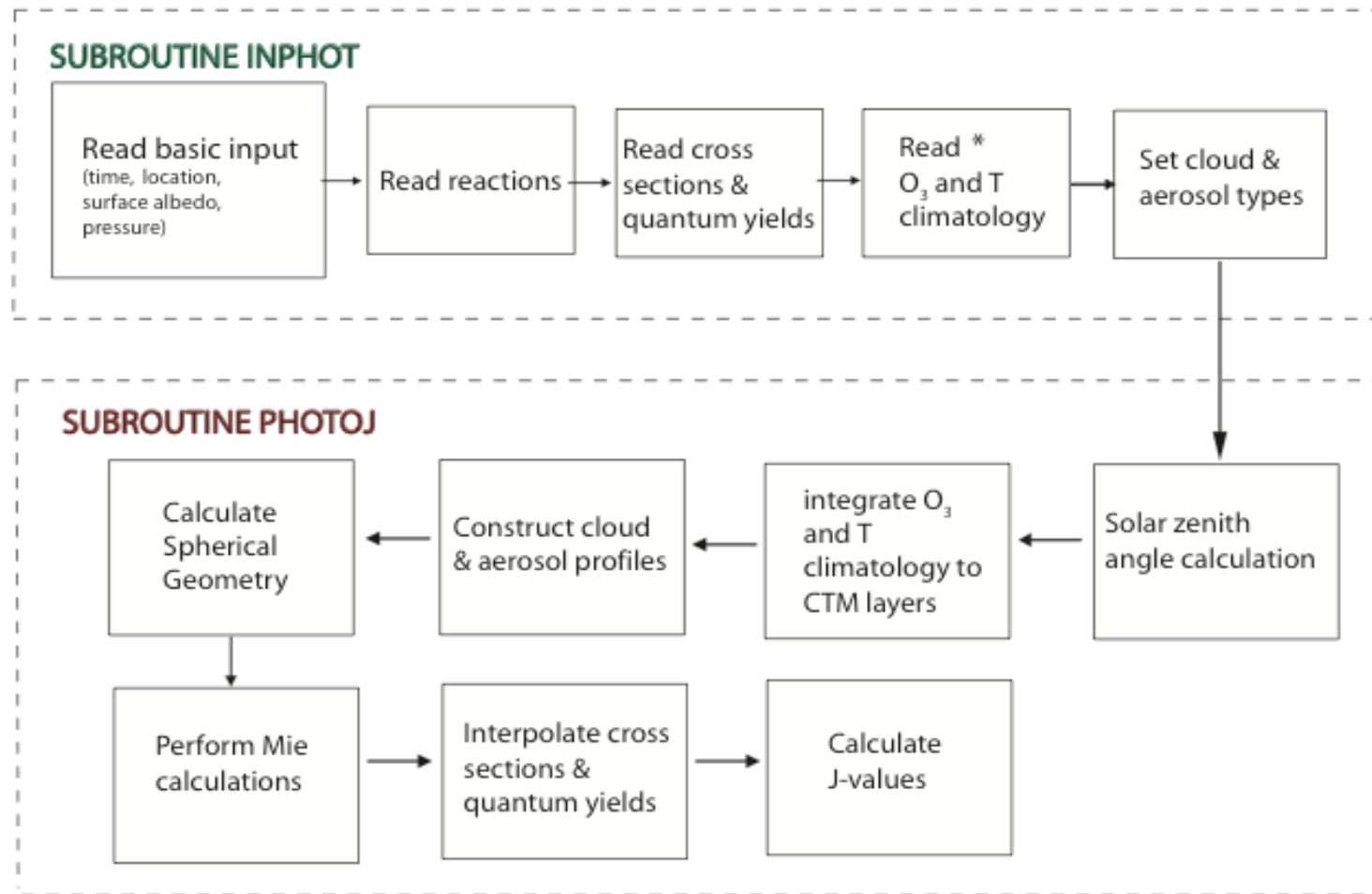
$$\alpha_{\lambda} = n \pi r^2 Q_{\lambda}$$

Aerosol and cloud optical properties are tabulated in file FJX_scatt.dat (its top part is shown below)

w(nm)	Q	ss-alb	pi(1)	pi(2)	pi(3)	pi(4)	pi(5)	pi(6)	pi(7)
01 RAYLEIGH Rayleigh phase 1/w^4 reff=2142.____G=1.000_rho=1000.									
200	2.102	1.0000	0.0	0.500	0.0	0.0	0.0	0.0	0.0
300	.3360	1.0000	0.0	0.500	0.0	0.0	0.0	0.0	0.0
400	.1000	1.0000	0.0	0.500	0.0	0.0	0.0	0.0	0.0
600	.0190	1.0000	0.0	0.500	0.0	0.0	0.0	0.0	0.0
999	.00242	1.0000	0.0	0.500	0.0	0.0	0.0	0.0	0.0
02 ISOTROPIC reff=0.150____G=1.000_rho=1.000									
200	1.0	1.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
300	1.0	1.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
400	1.0	1.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
600	1.0	1.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
999	1.0	1.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
03 ABSORBING reff=0.150____G=1.000_rho=1.000									
200	1.0	0.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
300	1.0	0.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
400	1.0	0.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
600	1.0	0.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
999	1.0	0.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0
04 W_H01 (H1/Deir)GAMMA:r-m=0.1/alf=2 n=1.335 reff=0.250____G=.0940_rho=1.000									
200	2.8983	1.0000	2.399	3.372	3.681	3.789	3.705	3.551	3.340
300	2.8438	1.0000	2.454	3.376	3.624	3.608	3.300	2.911	2.526
400	2.3497	1.0000	2.431	3.235	3.355	3.108	2.686	2.180	1.690
600	1.4037	1.0000	2.328	2.789	2.593	2.062	1.492	1.013	0.632
999	0.5034	1.0000	1.916	1.870	1.233	0.704	0.338	0.154	0.062
05 W_H04 (H1/Deir)GAMMA:r-m=0.4/alf=2 n=1.335 reff=1.000____G=1.508_rho=1.000									
200	2.2550	1.0000	2.462	3.730	4.305	4.935	5.430	5.923	6.449
300	2.2995	1.0000	2.433	3.625	4.104	4.645	5.020	5.409	5.802
400	2.4743	1.0000	2.341	3.475	3.863	4.330	4.589	4.878	5.125
600	2.6719	1.0000	2.325	3.334	3.624	3.896	3.939	3.968	3.964
999	2.9565	1.0000	2.434	3.393	3.685	3.709	3.528	3.213	2.903
06 W_H40 (H1/Deir)GAMMA:r-m=4.0/alf=2 n=1.335 reff=10.00____G=146.4_rho=1.000									
200	2.0493	1.0000	2.623	4.019	4.809	5.487	6.248	6.890	7.808
300	2.0642	1.0000	2.611	3.999	4.772	5.451	6.196	6.829	7.720
400	2.0785	1.0000	2.598	3.978	4.734	5.415	6.145	6.771	7.636
600	2.1045	1.0000	2.577	3.942	4.669	5.347	6.051	6.661	7.483
999	2.1478	1.0000	2.540	3.875	4.551	5.223	5.877	6.458	7.197

Flowchart of standalone version of the Fast-J scheme

(that presented in Wild et al. (2000) - somewhat earlier than the Fast-JX version used in UKCA)



Photolysis reactions included in the UKCA implementation of Fast-JX

Telford et al. [2012], GMD

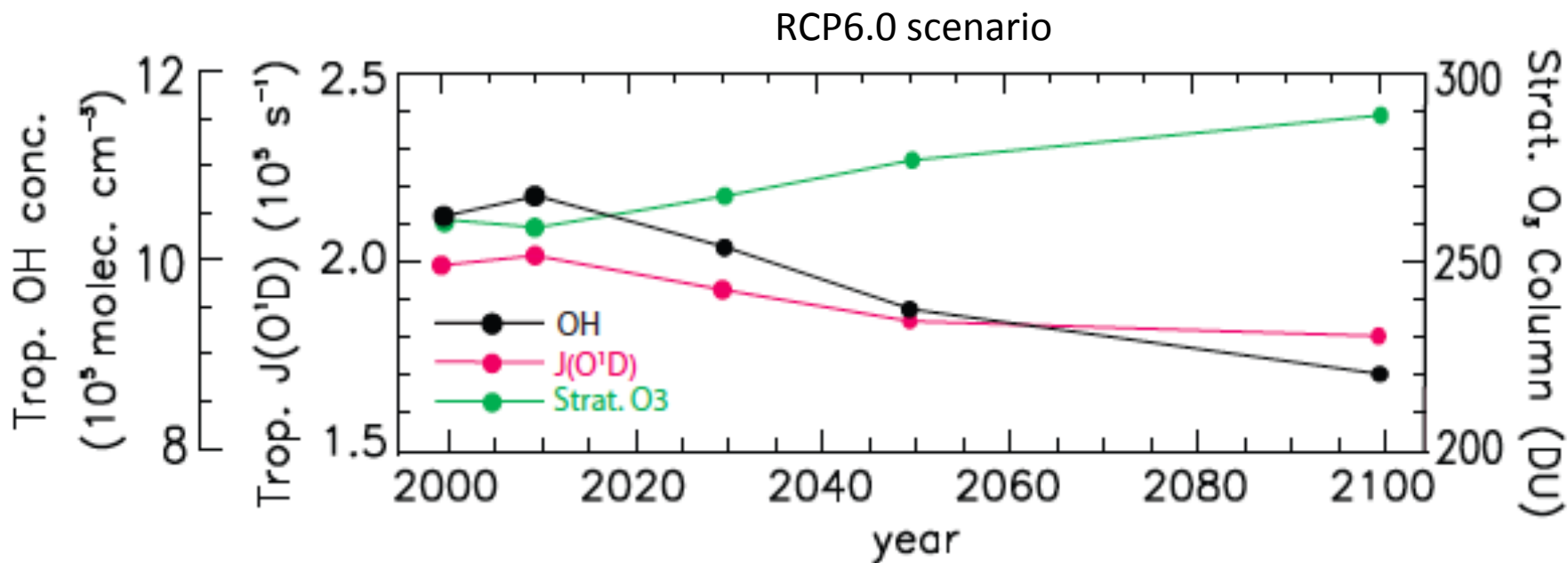
Reaction	Notes	Reference
1. $\text{O}_2 \rightarrow \text{O}(3\text{P}) + \text{O}(1\text{D})$	Cross section 0 in Fast-JX wavelengths.	
2. $\text{O}_2 \rightarrow \text{O}(3\text{P}) + \text{O}(3\text{P})$	T -dependence between 180 and 300 K.	Prather et al. (2010).
3. $\text{O}_3 \rightarrow \text{O}_2 + \text{O}(1\text{D})$	T -dependence between 180 and 300 K.	Prather et al. (2010).
4. $\text{O}_3 \rightarrow \text{O}_2 + \text{O}(3\text{P})$	T -dependence between 180 and 300 K.	Prather et al. (2010).
5. $\text{NO} \rightarrow \text{N} + \text{O}(3\text{P})$		Prather et al. (2010).
6. $\text{NO}_2 \rightarrow \text{NO} + \text{O}(3\text{P})$	T -dependence between 220 and 298 K.	Prather et al. (2010).
7. $\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$	T -dependence between 190 and 300 K.	Sander et al. (2006).
8. $\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}(3\text{P})$	T -dependence between 190 and 300 K.	Sander et al. (2006).
9. $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$	T -dependence between 230 and 300 K.	Sander et al. (2006).
10. $\text{HONO} \rightarrow \text{OH} + \text{NO}$		Sander et al. (2006).
11. $\text{HONO}_2 \rightarrow \text{OH} + \text{NO}_2$	T -dependence between 200 and 300 K.	Sander et al. (2006).
12. $\text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$	T -dependence between 200 and 300 K. Includes IR photolysis of Jiménez et al. (2005).	Sander et al. (2006).
13. $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}(1\text{D})$	T -dependence between 200 and 300 K.	Prather et al. (2010).
14. $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$		Sander et al. (2006).
15. $\text{CH}_4 \rightarrow \text{CH}_3\text{OO} + \text{H}$	Cross section 0 in Fast-JX wavelengths.	
16. $\text{CO}_2 \rightarrow \text{CO} + \text{O}(3\text{P})$	T -dependence between 195 and 295 K.	Parkinson et al. (2003).
17. $\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$	T -dependence between 200 and 300 K.	Prather et al. (2010).
18. $\text{HCHO} \rightarrow \text{HO}_2 + \text{HO}_2 + \text{CO}$	T -dependence between 223 and 293 K.	Prather et al. (2010).
19. $\text{HCHO} \rightarrow \text{H}_2 + \text{CO}$	T -dependence between 223 and 293 K.	Prather et al. (2010).
20. $\text{CH}_3\text{OOH} \rightarrow \text{HO}_2 + \text{HCHO} + \text{OH}$		Sander et al. (2006).
21. $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{OO} + \text{HO}_2 + \text{CO}$		Sander et al. (2006).
22. $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$		Sander et al. (2006).
23. $\text{C}_2\text{H}_5\text{CHO} \rightarrow \text{C}_2\text{H}_5\text{OO} + \text{HO}_2 + \text{CO}$		Sander et al. (2006).
24. $\text{C}_2\text{H}_5\text{CHO} \rightarrow \text{CH}_3\text{OH} + \text{HO}_2 + \text{OH}$		Sander et al. (2006).
25. $\text{CH}_3\text{O}_3\text{H} \rightarrow \text{CH}_3\text{OO} + \text{OH}$		Sander et al. (2006).

Photolysis reactions included in the UKCA implementation of Fast-JX (cont.)

Telford et al. [2012], GMD

26.	$(\text{CH}_3)_2\text{CO} \rightarrow \text{CH}_3\text{CO}_3 + \text{CH}_3\text{OO}$	Using scheme of Blitz et al. (2004).	Prather et al. (2010).
27.	$\text{n-PrOOH} \rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{HO}_2 + \text{OH}$	Use cross sections from reaction 20.	
28.	$\text{i-PrOOH} \rightarrow (\text{CH}_3)_2\text{CO} + \text{HO}_2 + \text{OH}$	Use cross sections from reaction 20.	
29.	$\text{CH}_3\text{COCH}_2\text{OOH} \rightarrow \text{CH}_3\text{CO}_3 + \text{HCHO} + \text{OH}$	Use cross sections from reaction 20.	
30.	$\text{HACET} \rightarrow \text{CH}_3\text{CO}_3 + \text{HCHO} + \text{HO}_2$	Lumped species of C3 carbonyls, including hydroxyacetone. Use hydroxyacetone cross sections.	Sander et al. (2006).
31.	$\text{MGLY} \rightarrow \text{CH}_3\text{CO}_3 + \text{CO} + \text{HO}_2$	Lumped species of C3 aldehydes, including methyl glyoxal. Use methylglyoxal cross sections.	IUPAC datasheet P6 ^a
32.	$\text{MACR} \rightarrow \text{CH}_3\text{CO}_3 + \text{HCHO} + \text{CO} + \text{HO}_2$	Lumped species of C4 carbonyls, including methacrolein. Use methacrolein cross sections.	Prather et al. (2010).
33.	$\text{MACROOH} \rightarrow 0.5\text{HACET} + 0.5\text{CO} + 0.5\text{MGLY} + 0.5\text{HCHO} + \text{OH} + \text{HO}_2$	Use cross sections from reaction 20.	
34.	$\text{iSOOH} \rightarrow \text{MACR} + \text{HO}_2 + \text{HCHO} + \text{OH}$	Use cross sections from reaction 20.	
35.	$\text{CH}_3\text{ONO}_2 \rightarrow \text{HO}_2 + \text{HCHO} + \text{NO}_2$	T -dependence between 240 and 300 K.	Prather et al. (2010).
36.	$\text{PAN} \rightarrow \text{CH}_3\text{CO}_3 + \text{NO}_2$	T -dependence between 250 and 300 K.	Prather et al. (2010).
37.	$\text{PPAN} \rightarrow \text{C}_2\text{H}_5\text{CO}_3 + \text{NO}_2$	Use cross sections from reaction 36.	
38.	$\text{MPAN} \rightarrow \text{MACRO}_2 + \text{NO}_2$	Use cross sections from reaction 36.	
39.	$\text{NALD} \rightarrow \text{HCHO} + \text{CO} + \text{NO}_2 + \text{CO}_2$	Use cross sections from reaction 21.	
40.	$\text{ISON} \rightarrow \text{NO}_2 + \text{MACR} + \text{HCHO} + \text{NO}_2$	Lumped species. Use $i - \text{C}_3\text{H}_7\text{ONO}_2$ T -dependence between 230 and 360 K.	IUPAC datasheet P17 ^b
41.	$\text{CH}_3\text{Br} \rightarrow \text{Br} + \text{H}$	T -dependence between 196 and 296 K.	Prather et al. (2010).
42.	$\text{BrCl} \rightarrow \text{Br} + \text{Cl}$	T -dependence between 190 and 300 K.	Sander et al. (2006).
43.	$\text{BrO} \rightarrow \text{Br} + \text{O}(3\text{P})$		Sander et al. (2006).
44.	$\text{HOBr} \rightarrow \text{Br} + \text{OH}$		Prather et al. (2010).
45.	$\text{BrNO}_3 \rightarrow \text{Br} + \text{NO}_3$		Sander et al. (2006).
46.	$\text{BrNO}_3 \rightarrow \text{BrO} + \text{NO}_2$		Sander et al. (2006).
47.	$\text{CFCl}_3 \rightarrow \text{Cl} + \text{Cl} + \text{Cl}$		Prather et al. (2010).
48.	$\text{CF}_2\text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}$		Prather et al. (2010).
49.	$\text{HCl} \rightarrow \text{H} + \text{Cl}$		Sander et al. (2006).
50.	$\text{HOCl} \rightarrow \text{Cl} + \text{OH}$		Prather et al. (2010).
51.	$\text{OCIO} \rightarrow \text{ClO} + \text{O}(3\text{P})$		Sander et al. (2006).
52.	$\text{Cl}_2\text{O}_2 \rightarrow \text{Cl} + \text{Cl} + \text{O}_2$		Sander et al. (2006).
53.	$\text{ClNO}_3 \rightarrow \text{Cl} + \text{NO}_3$		Prather et al. (2010).
54.	$\text{ClNO}_3 \rightarrow \text{ClO} + \text{NO}_2$		Prather et al. (2010).

Example: Stratospheric ozone, tropospheric photolysis, and trop. OH (in GISS CCM with Fast-J2)

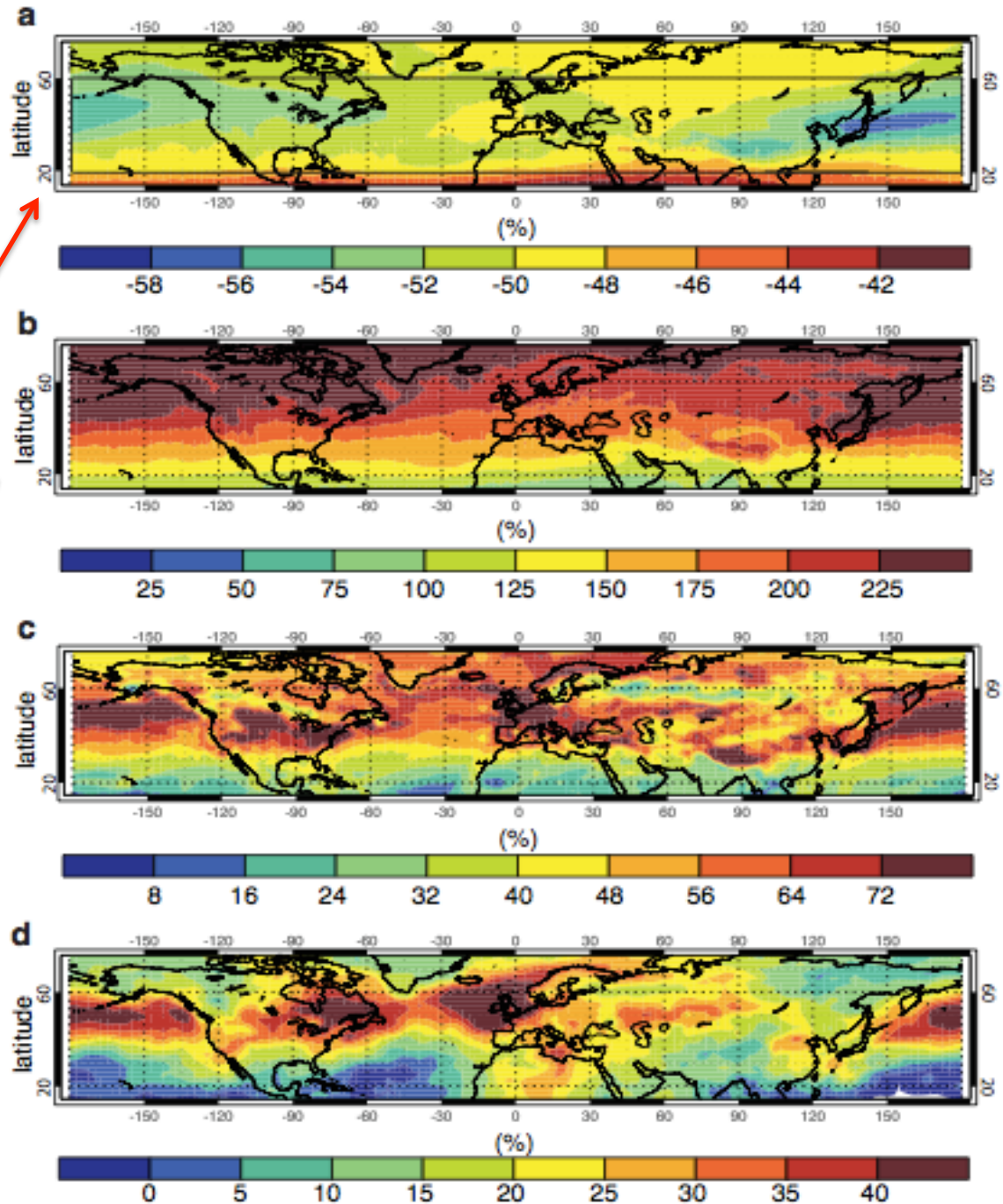


Voulgarakis et al. (2013a), ACP

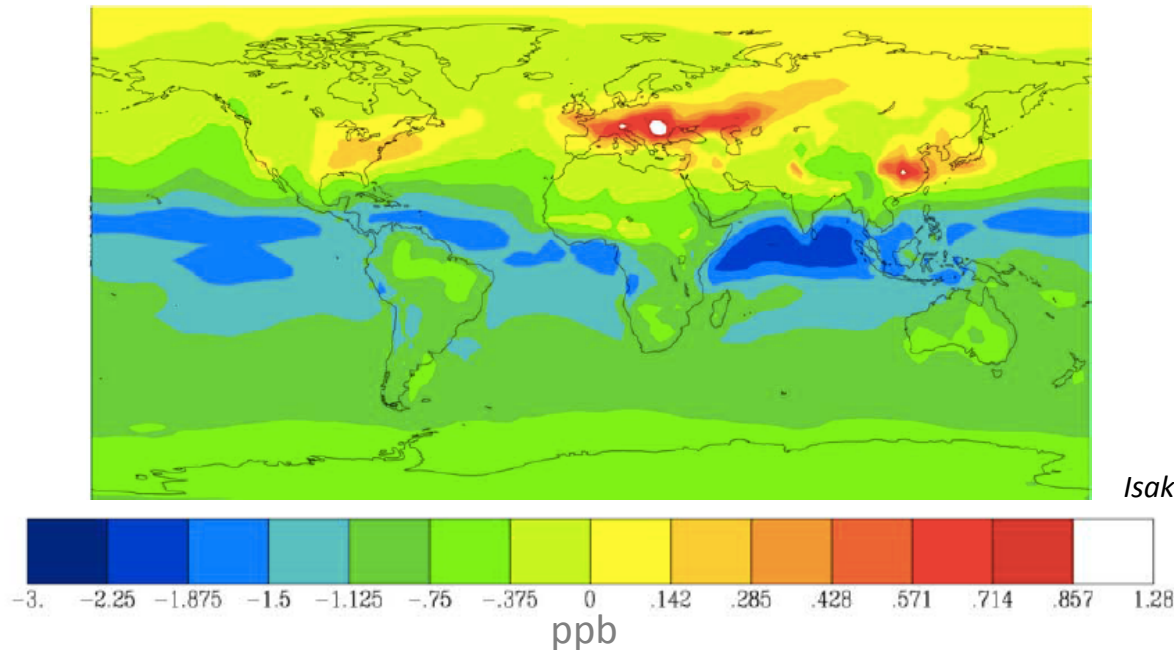
- Strat. O_3 recovery → less solar radiation in the troposphere → slower photolysis ($J(\text{O}^1\text{D})$) → less OH

Example: Changes in “world avoided” scenario due to photolysis (in GISS CCM with Fast-J2)

- Ozone column
- JO(¹D)
- OH
- Sulphate aerosol



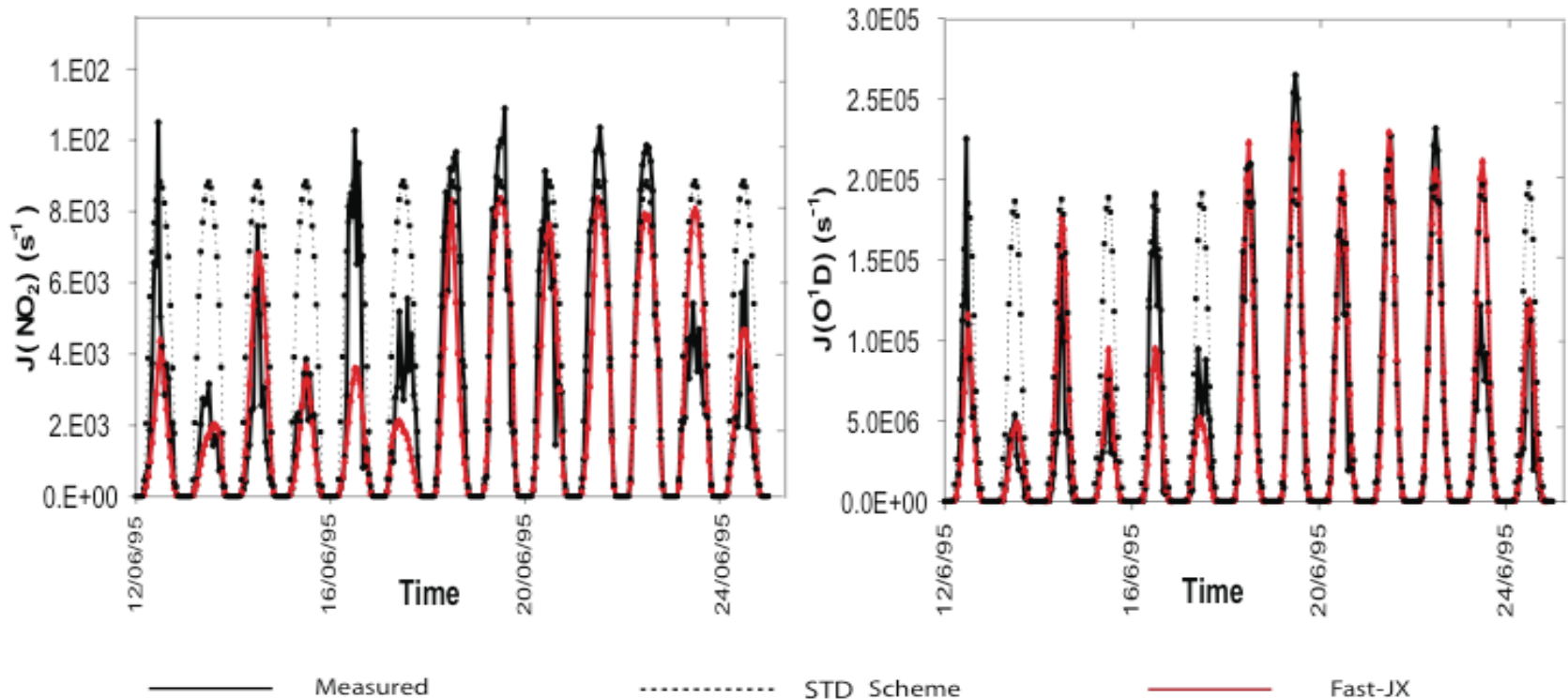
Example: Changes in surface O_3 due to 10% reduction in column O_3 in January (in OsloCTM2 with Fast-J)



- Faster photolysis favours both O_3 **production** (JNO_2) and **destruction** ($JO(^1D)$).
- **In the net**, the O_3 production perturbation wins in polluted regions, and the ozone destruction wins in remote regions.

Example: Effect of clouds on photolysis

(in the *p*-TOMCAT CTM using Fast-JX)



Photolysis rates for a measurement site (Weybourne).

Black: measured.

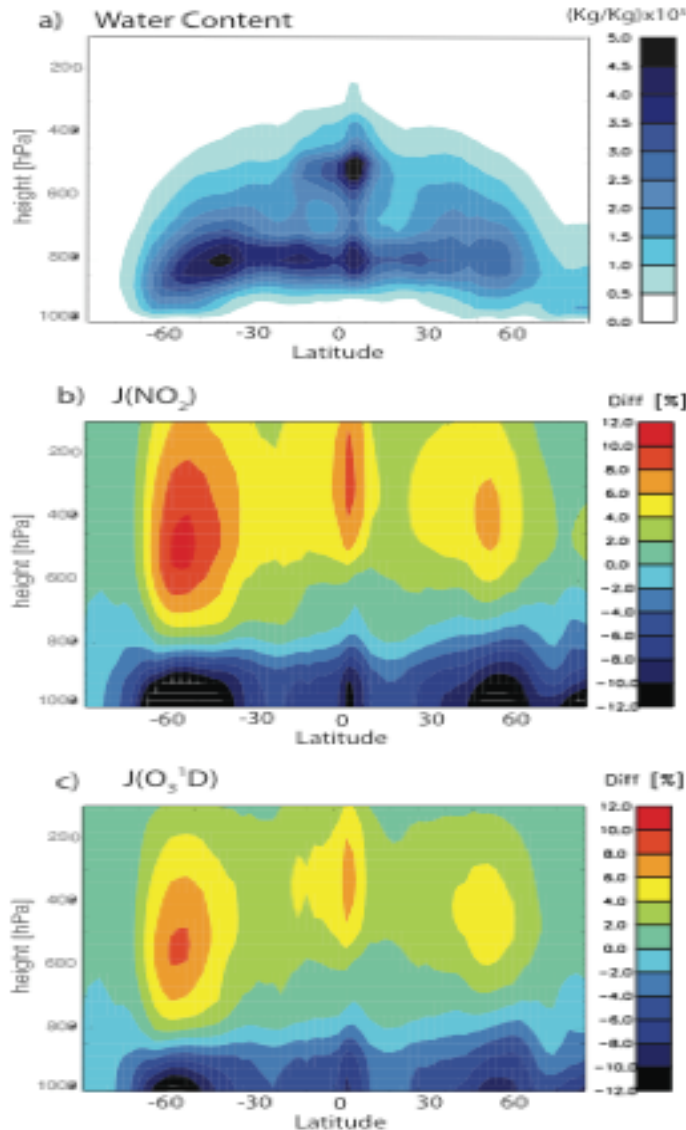
Dotted: modeled with no cloud variations.

Red: modeled with cloud variations.

→ **Clouds** drive the day-to-day variability in photolysis.

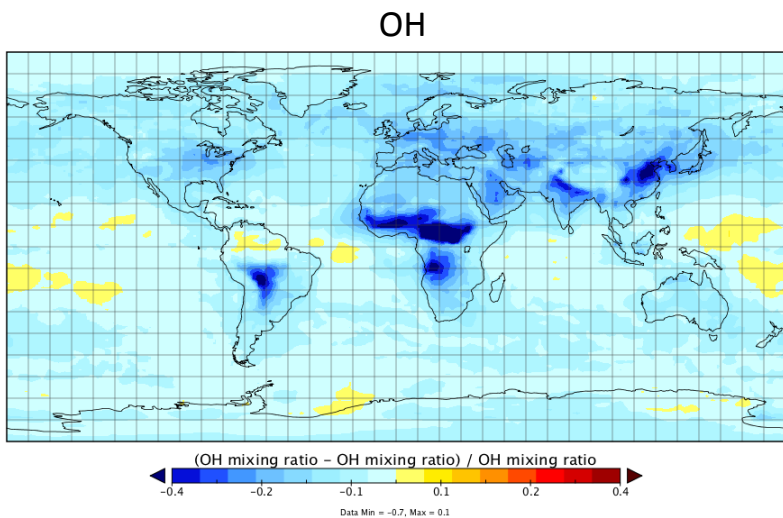
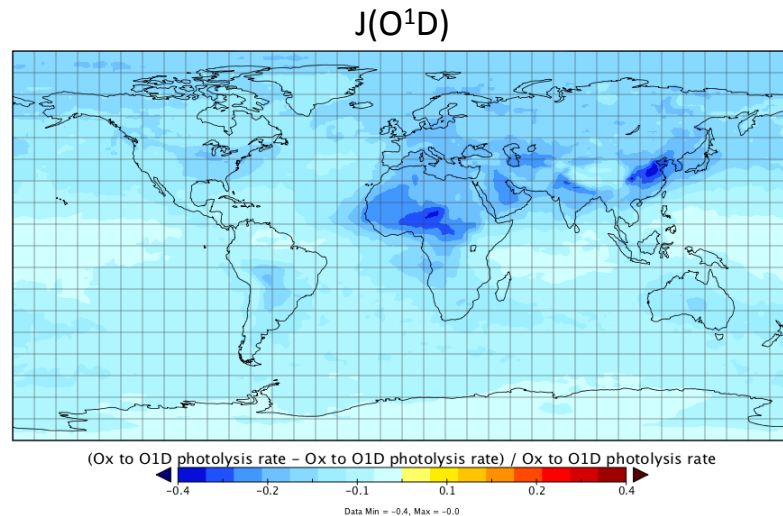
Example: Effect of clouds on photolysis (cont.)

(in the *p*-TOMCAT CTM using Fast-JX)



- Distribution of cloud water content shows the multi-layered cloud structure in the tropics and the large cloud amounts in the southern midlatitudes.
- Photolysis rates are **increased above** clouds, **decreased below** them and remain intact where the main masses of clouds are.
- These results are in agreement with Liu et al. (2006), who used Fast-J.

Example: Effect of aerosols on photolysis & OH (in the GISS CCM with Fast-J2)



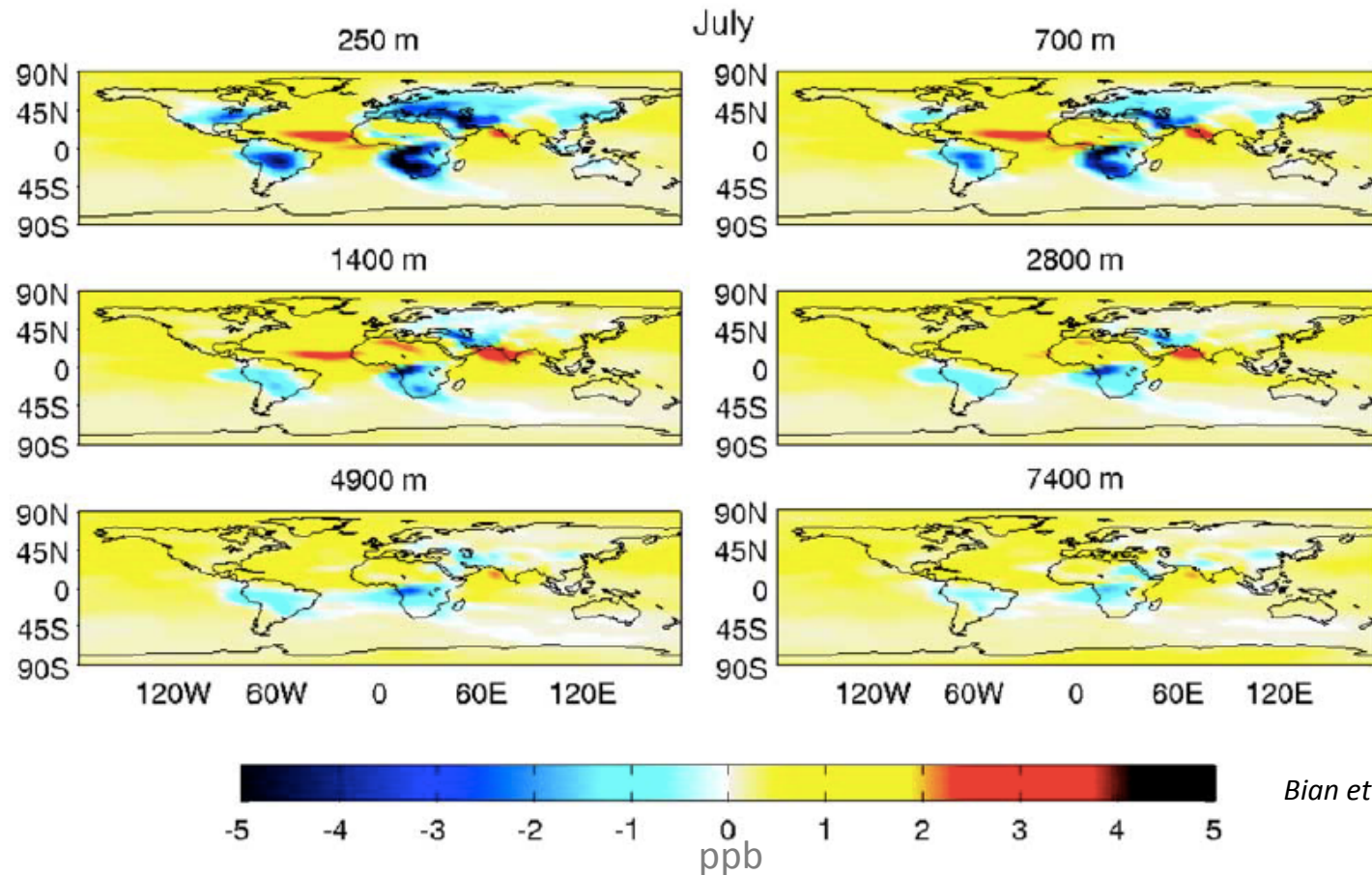
- Maps show relative change of $J(\text{O}^1\text{D})$ and OH at the surface due to **the presence of aerosols** in the atmosphere.

- **Strong effects**, especially over regions with heavy anthropogenic (East & South Asia) and biomass burning (Africa, South America) pollution.

- Possible **implications** for ozone, methane, CO, VOCs, aerosols over those regions.

Example: Effect of aerosols on photolysis & O₃

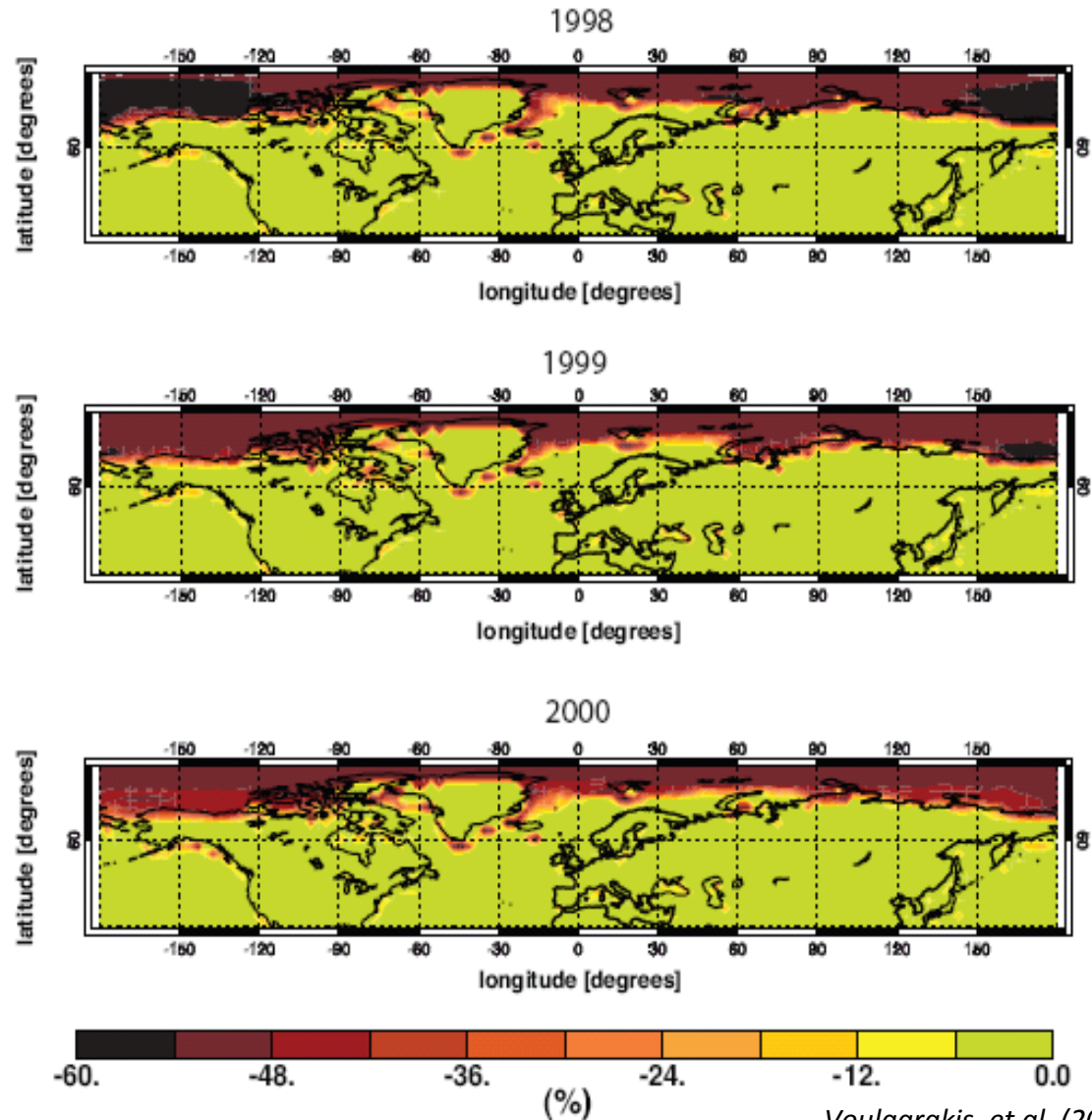
(in UCI CTM with Fast-J2)



- Attenuation of solar radiation by aerosols leads to **slower photochemical O₃ production** over polluted regions, an effect that weakens with height.

Example: Effect of surf. albedo on photolysis & OH (in the *p*-TOMCAT CTM with Fast-JX)

- Removing Arctic sea ice changes summer OH drastically (decreases of up to 60%).
- The changes are mainly confined to polar latitudes (due to short OH lifetime).
- Possibly important implications in a future, ice-free Arctic.

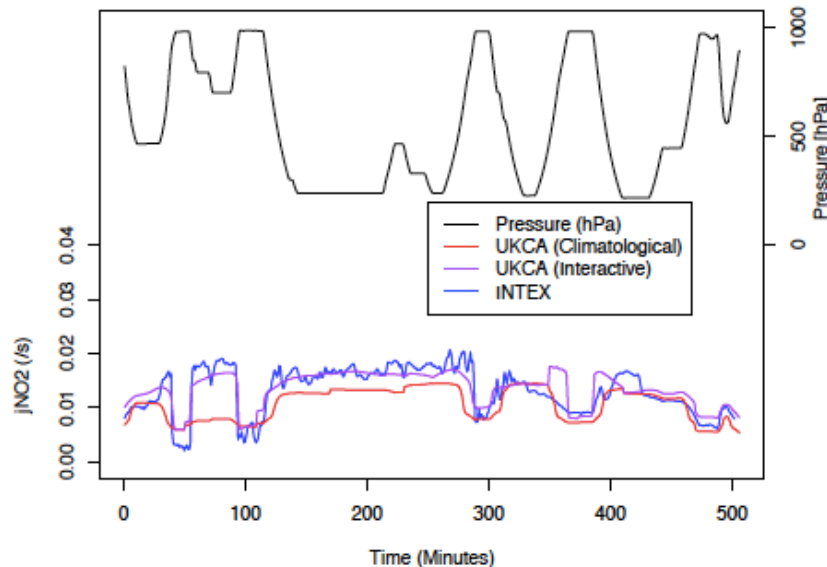
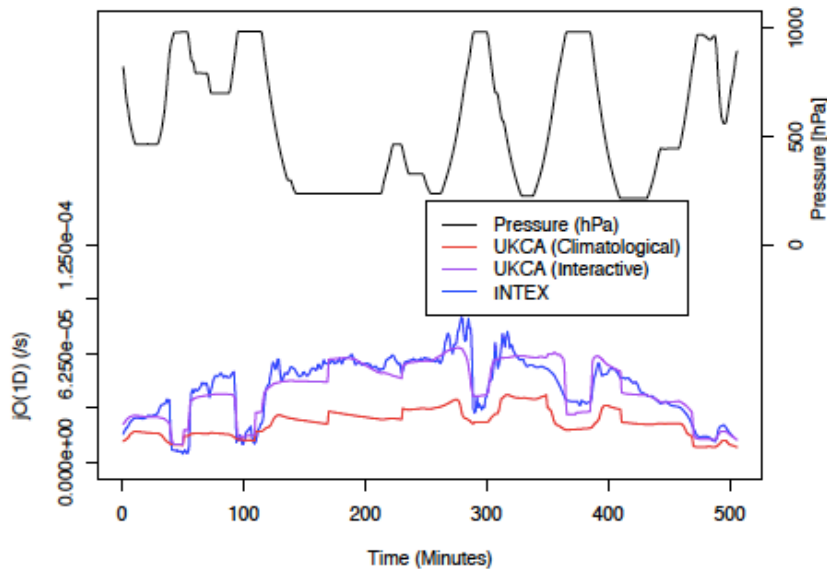


Evaluation of UKCA with Fast-JX (interactive) vs UKCA with offline (climatological) photolysis

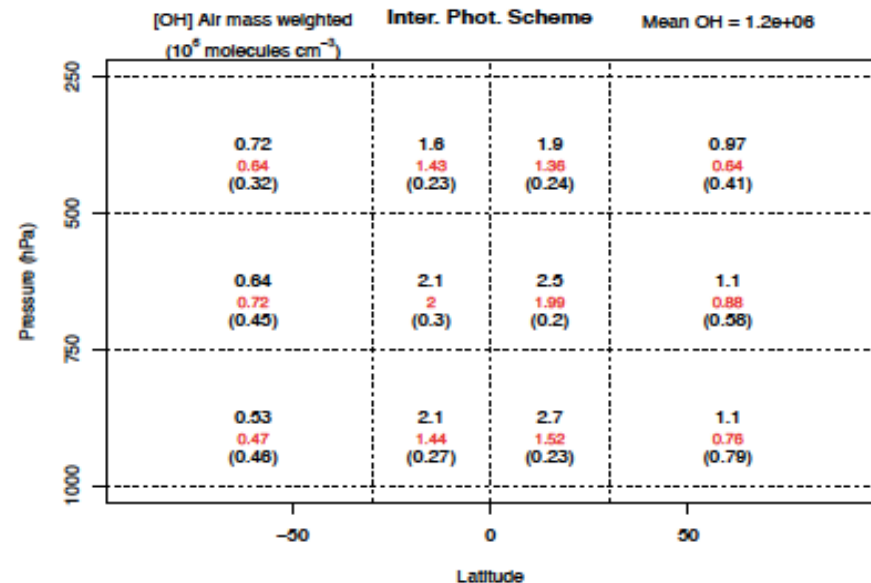
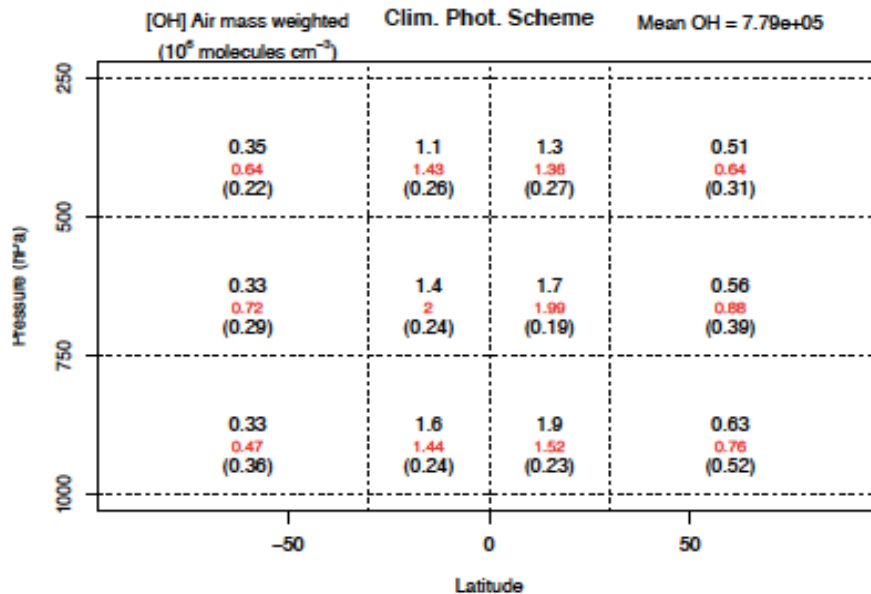
- An example of performance of photolysis rates ($\text{JO}(^1\text{D})$ and JNO_2) against **aircraft** observations.

- Including Fast-JX (interactive) makes the simulation **much more realistic**.

- The offline scheme gives a much **“flatter”** evolution of photolysis during the flights, as real-time **clouds** are not represented.



Effect of UKCA photolysis handling on OH



- Black is modelled, red is from observation-based climatology of Spivakovsky et al. (2000), and brackets are stddev within box.
- The use of the interactive photolysis scheme (Fast-JX) **increases the total OH burden**, which leads to decreased CO concentrations and CH_4 lifetimes (not shown).
- Found that the increases in HO_x (incl. OH) are **dominated** by increases in its production via $\text{O}(^1\text{D}) + \text{H}_2\text{O}$.

Summary

- Photolysis is **central** in tropospheric and stratospheric chemistry, initiating the production of ozone and OH, the destruction of ozone, and numerous other processes.
- To model it, we use **tabulated** cross sections/quantum yields and aerosol optical properties, but **online** calculated actinic fluxes.
- Fast-JX is a state-of-the-art, **accurate and efficient** photolysis scheme designed for global models, currently used in UKCA.
- **Important scientific insight** has been provided using Fast-JX in conjunction with UKCA or other global models, when it comes to the influence of clouds, aerosols, ozone column, and surface albedo on photolysis and oxidants.
- Fast-JX will be **a key tool** for studying a range of interactions as the UKCA model becomes part of the larger UKESM1 framework.