

# Atmospheric Chemistry

## Oxidizing capacity of the troposphere

Pontus Roldin  
Div. Nuclear Physics  
Dep. Physics  
Lund University

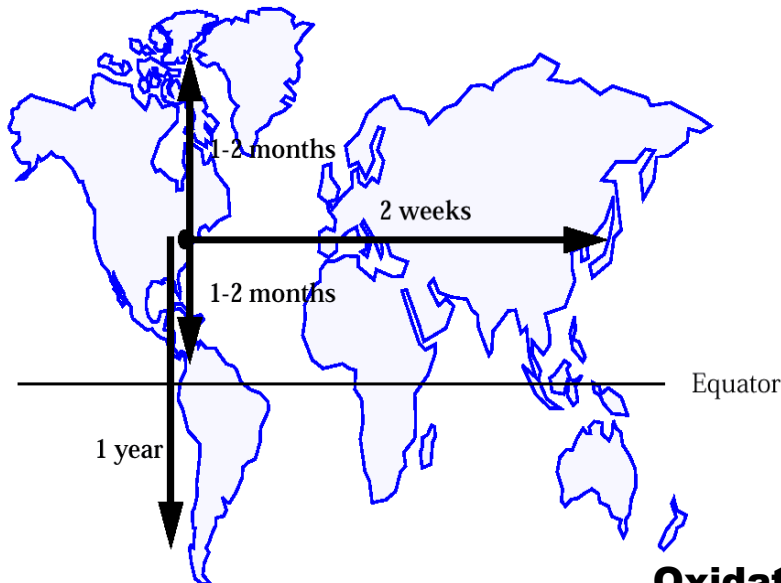
# Tropospheric chemistry

The troposphere is a chemical reservoir that is fairly well separated from the stratosphere.

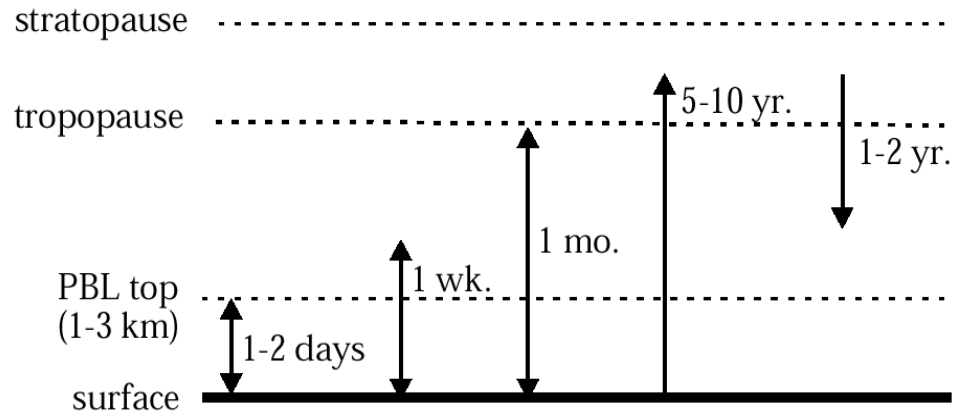
The mixing time in the troposphere is 1-2 months within each hemisphere.

Chemical substances with a lifetime shorter than ~1 year are transformed within the troposphere.

## Horizontal mixing

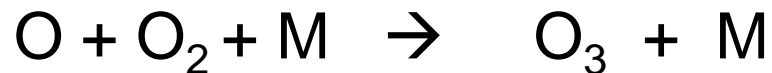


## Vertical mixing



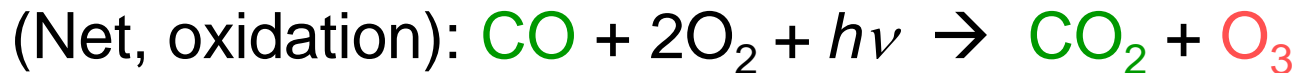
# Tropospheric chemistry

Scavenging of toxic CO by the detergent of the atmosphere, the hydroxyl radical OH.



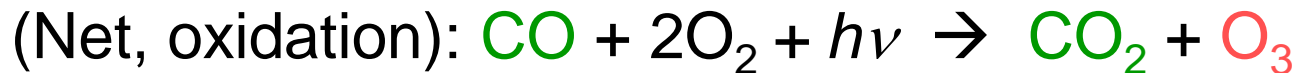
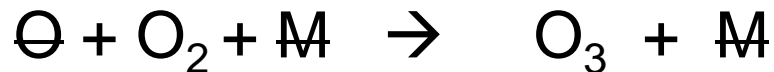
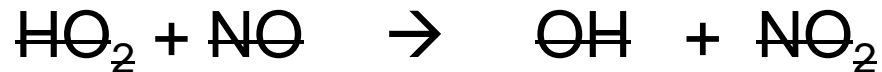
# Tropospheric chemistry

Scavenging of toxic CO by the detergent of the atmosphere, the hydroxyl radical OH.



# Tropospheric chemistry

Scavenging of toxic CO by the detergent of the atmosphere, the hydroxyl radical OH.



Tropospheric gas phase chemistry involves oxidation of CO and organic hydrocarbons ( $\text{C}_x\text{H}_y\text{O}_z$ ) in the presence of nitrogen oxides ( $\text{NO}_x$ ) and solar irradiation ( $h\nu$ ).

# Oxidants in the troposphere

The atmosphere is an **oxidizing** medium.

## Examples

(oxidation numbers)

Hydrocarbons:  $\text{CH}_4 \rightarrow \text{CO}_2$  i.e.  $\text{C}(-\text{IV}) \rightarrow \text{C}(+\text{IV})$

Sulphur species:  $\text{H}_2\text{S} \rightarrow \text{H}_2\text{SO}_4$  i.e.  $\text{S}(-\text{II}) \rightarrow \text{S}(+\text{VI})$

Nitrogen species:  $\text{NO} \rightarrow \text{HNO}_3$  i.e.  $\text{N}(+\text{II}) \rightarrow \text{N}(+\text{V})$

The most abundant oxidants ( $\text{O}_2$  and  $\text{O}_3$ ) are relatively unreactive and therefore contribute very little to the oxidation of trace gases.

Oxidation of non-radicals involves **radical** species, not  $\text{O}_2$  and  $\text{O}_3$ .

# Tropospheric chemistry

Tropospheric gas phase chemistry involves **oxidation** of organic compounds in the presence of nitrogen oxides and solar irradiation.

$h\nu$  ← 



Similar to a hot flame, the **oxidation proceeds with the aid of free radicals** (radical concentrations in the troposphere are much lower than in the flame.)

**Solar radiation** is the external **energy source** driving the "combustion".

The **organic compounds**, for instance methane, is the "fuel".

# Tropospheric oxidation of trace gases

There must be strong sinks for nearly all gases emitted from Earth to the troposphere, since the concentrations of these gases do not increase in proportion to their source strengths.

Trace gases are oxidized, often in multiple steps.

Gases containing sulphur and nitrogen are oxidized to water-soluble compounds that are eventually wet deposited (acid rain).



Tropospheric oxidation is a vital sink for trace gases and greenhouse gases (e.g.  $\text{CH}_4$  and  $\text{CO}$  that are both oxidized to  $\text{CO}_2$ ).

Without the presence of strong oxidants in the troposphere the levels of a number of toxic trace gases would have risen to lethal concentrations (e.g.  $\text{CO}$ ,  $\text{SO}_2$ ).



# Tropospheric ozone

Ozone is needed to initiate the radical production and thus also to maintain an oxidizing atmosphere.

Until the middle of the 1940-ies, it was believed that all tropospheric ozone originates from the stratosphere, where it was known to be produced via photolysis of  $O_2$  ( $\lambda < 240$  nm).

Since this UVc radiation is unable to penetrate down to Earth's surface, it was thought that no ozone could be produced in the troposphere. Earth's surface is an efficient ozone sink.

The Los Angeles smog made it apparent that **there must be other strong sources of ozone also in the lower troposphere.**

# The Los Angeles Smog



**Oxidation - troposphere**

# Ozone production in the troposphere

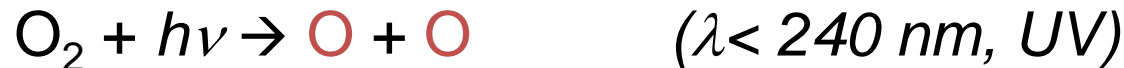
The only way to produce ozone is via



with molecular oxygen  $\text{O}_2$  and atomic oxygen  $\text{O}$  in its ground state  $\text{O}(^3\text{P})$ ,

This means that  $\text{O}$  has to be produced first.

**Photolysis of  $\text{O}_2$  does not occur in the troposphere (no UVc).**



**There must therefore be other sources of  $\text{O}$  in the troposphere.**

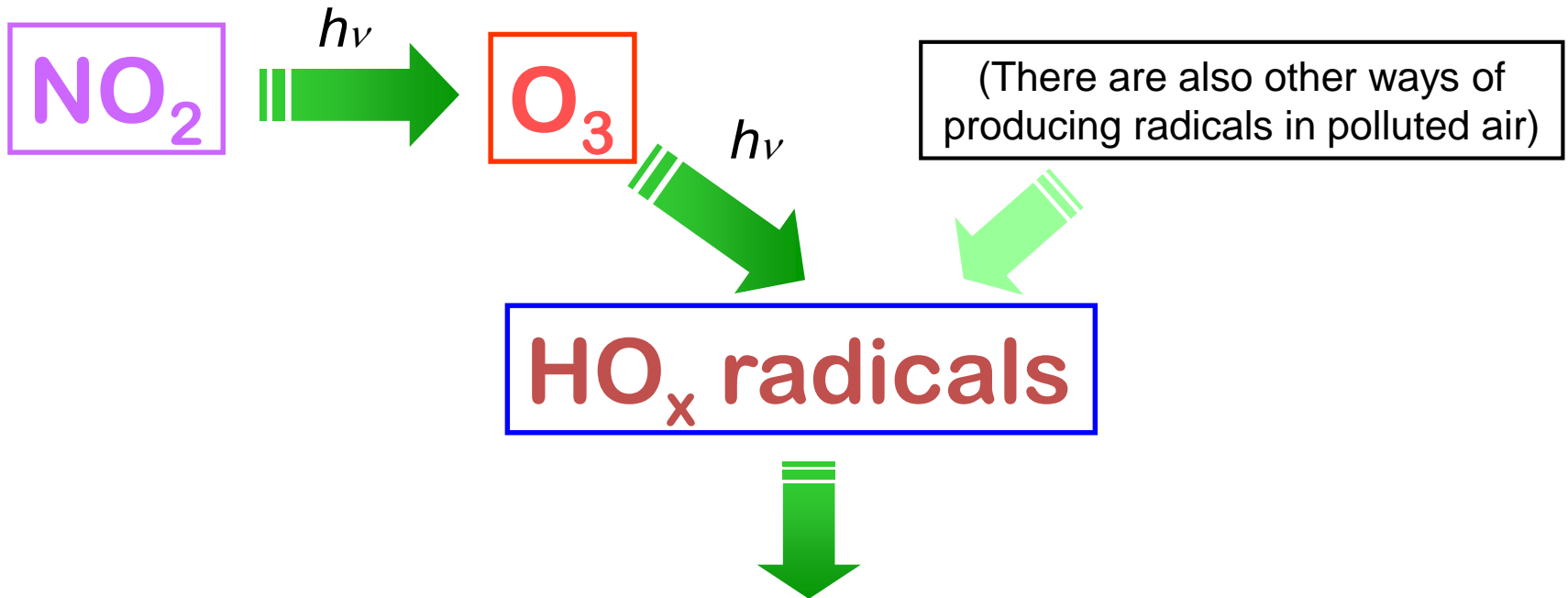
Main source of  $\text{O}$  in the troposphere is via photolysis of  $\text{NO}_2$



**This reaction is very important for the tropospheric chemistry!**

# Oxidants in the troposphere

$\text{NO}_2$  and solar radiation controls the production of  $\text{O}_3$ , which in turn controls the production of  $\text{HO}_x$  radicals, which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.



Oxidizing capacity of the troposphere

# Hydroxyl radical OH

The **hydroxyl radical** is formed by photolysis of ozone and is the **most important radical in the troposphere**.

It does not react with any of the major components of the atmosphere ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ).

**It reacts with most atmospheric trace gases.**

**The "detergent" of the atmosphere.**

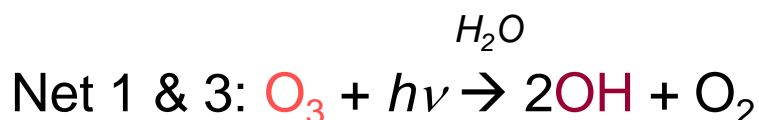
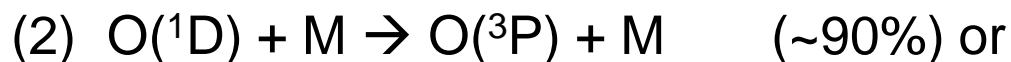
Short lifetime ( $\sim 1$  s).

Exists in very low concentrations ( $10^5$ - $10^7$  molecules/ $\text{cm}^3$ ).

Regenerated in catalytic cycles, since it would otherwise rapidly have been consumed.

# Hydroxyl radical OH

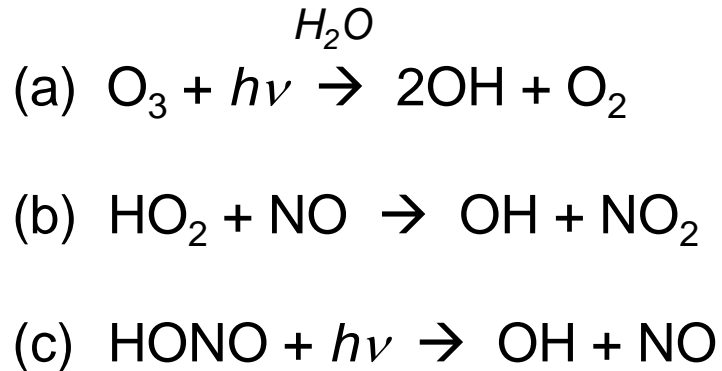
## Production of hydroxyl radicals OH via O<sub>3</sub>



**Prerequisite:** Production of excited atomic oxygen O(<sup>1</sup>D)

# Hydroxyl radical OH

Production of OH mainly proceeds via three reactions:



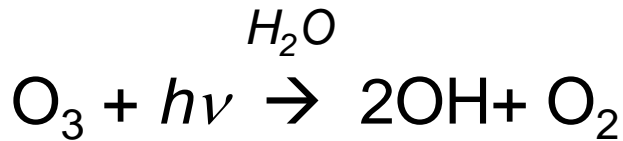
Reaction (a) dominates in background air ("low"  $\text{NO}_x$ , high RH).

Reaction (b) dominates in polluted air (high  $\text{NO}_x$ ).

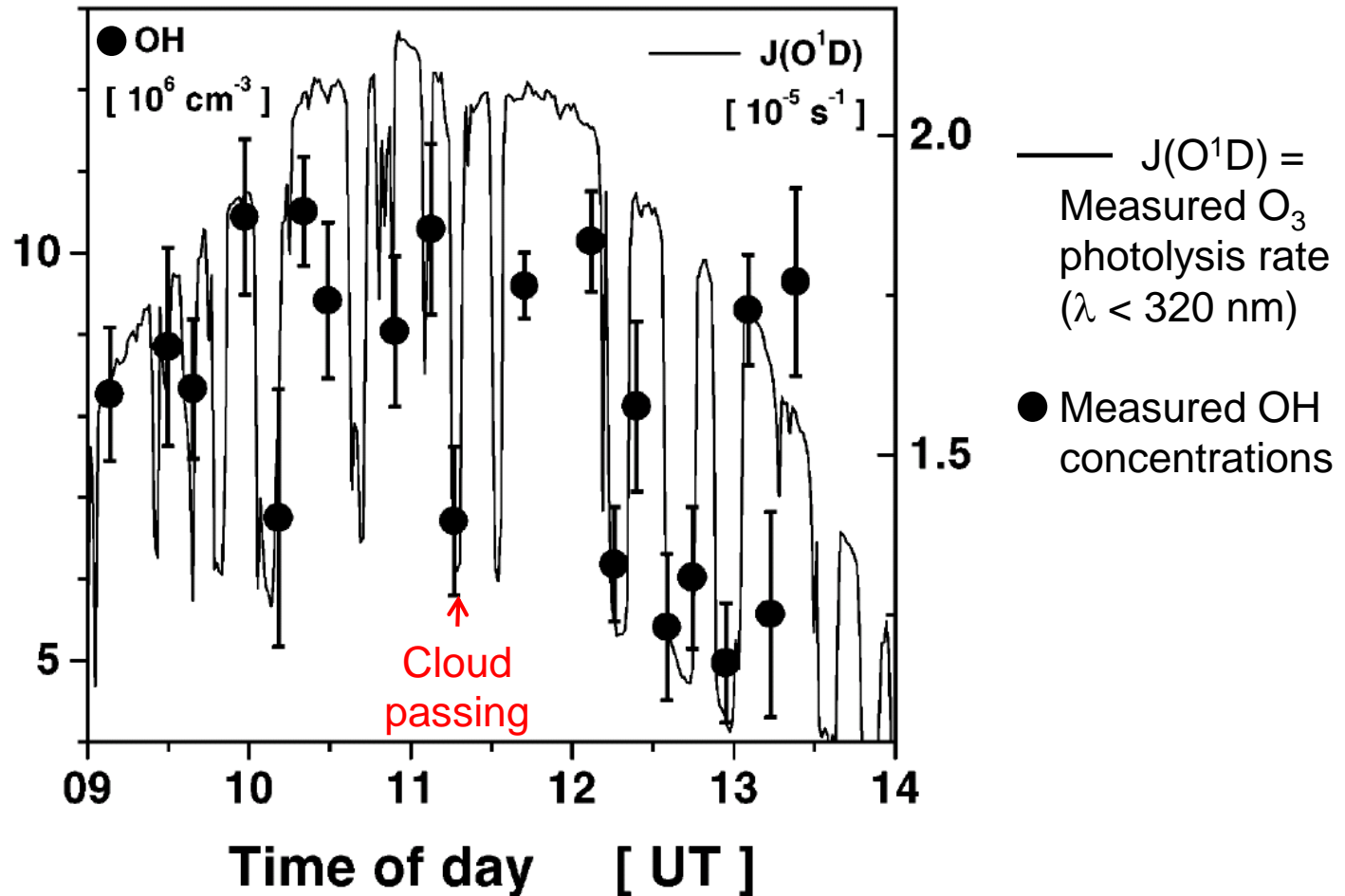
Reaction (c) from HONO only of importance at sunrise since HONO is rapidly photolyzed (within 10 min - 1 h).

Small amount of OH is also produced during the night when alkenes are oxidized by  $\text{O}_3$

# Hydroxyl radical OH responds quickly to UV



OH has short lifetime (~1 s).





# Production of the hydroxyl radical OH

Production of  $O(^1D)$  occurs in a narrow wavelength band between 300-320 nm.

Actinic Flux (Ljusflöde) :  $I$

Number of photons crossing the unit horizontal area per unit time (photons  $\cdot$  m<sup>-2</sup>  $\cdot$  s<sup>-1</sup>)

Cross Section (Absorptionstvärsnitt) :  $\sigma$

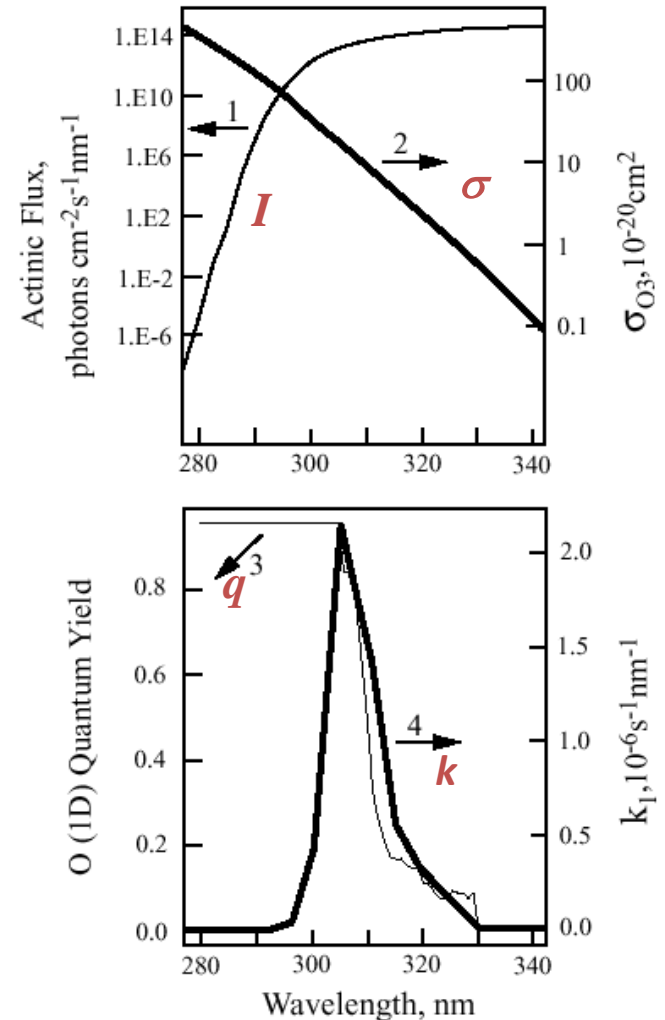
"Target area" per molecule within which the photon is absorbed (m<sup>2</sup>  $\cdot$  molecule<sup>-1</sup>)

Quantum Yield (Kvantutbyte) :  $q$

Probability that absorption of a photon will cause photolysis (molecules  $\cdot$  photon<sup>-1</sup>)

Photolysis rate constant  $k$  :

$$k = q \cdot \sigma \cdot I \quad (\text{s}^{-1}, \text{wavelength dependent})$$



# Photolysis

Absorption cross section:  $\sigma_x$  ( $\text{m}^2 \cdot \text{molecule}^{-1}$ )

Actinic Flux (Ljusflöde) :  $I$

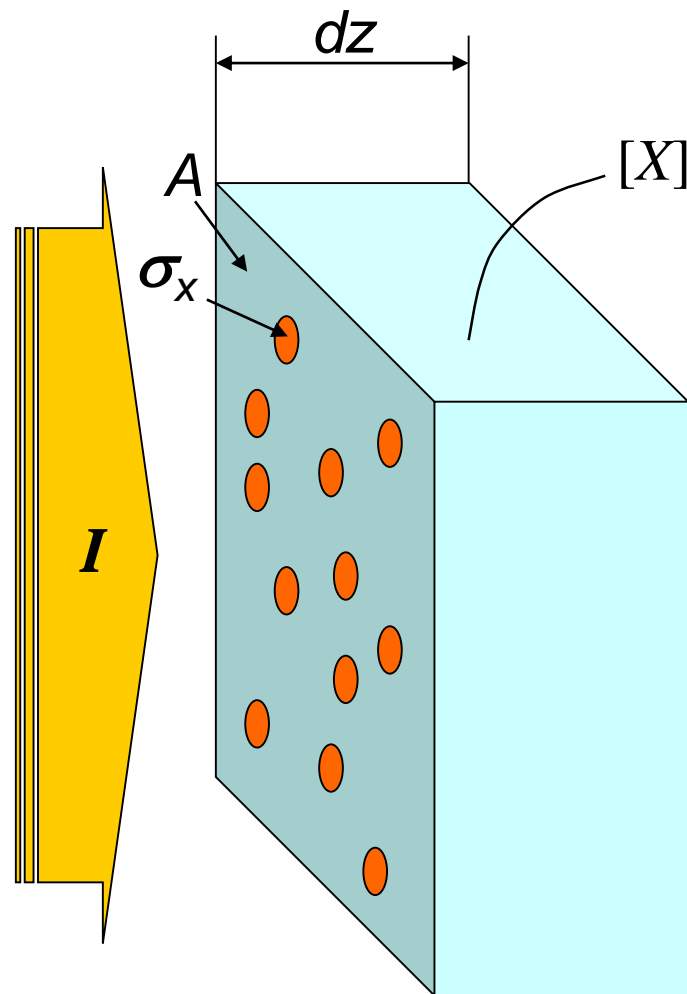
Number of photons crossing the unit horizontal area per unit time ( $\text{photons} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ )

Quantum Yield (Kvantutbyte) :  $q_x$

Probability that absorption of a photon will cause photolysis of  $X$  ( $\text{molecules} \cdot \text{photon}^{-1}$ )

Photolysis rate constant  $k$  :

$$k = q_x \cdot \sigma_x \cdot I \quad (\text{s}^{-1}, \text{wavelength dependent})$$



# Ozone photolysis in the troposphere

## Photolysis of O<sub>3</sub> in the troposphere



$k = q\sigma I$  where  $q$ ,  $\sigma$  and  $I$  all vary with the wavelength of light.

295 nm:  $q=0.95$ ,  $\sigma=8 \cdot 10^{-19} \text{ cm}^2 \cdot \text{molecules}^{-1}$ ,  $I=1 \cdot 10^{10} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$

$k \approx 7.3 \cdot 10^{-9} \text{ s}^{-1} \cdot \text{nm}^{-1}$ . Note that the unit is  $\text{s}^{-1} \cdot \text{nm}^{-1}$  since this value only represents a small wavelength interval around 295 nm).

305 nm:  $q=0.94$ ,  $\sigma=2 \cdot 10^{-19} \text{ cm}^2 \cdot \text{molecules}^{-1}$ ,  $I=1.6 \cdot 10^{13} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$

$k \approx 2.9 \cdot 10^{-6} \text{ s}^{-1} \cdot \text{nm}^{-1}$ .

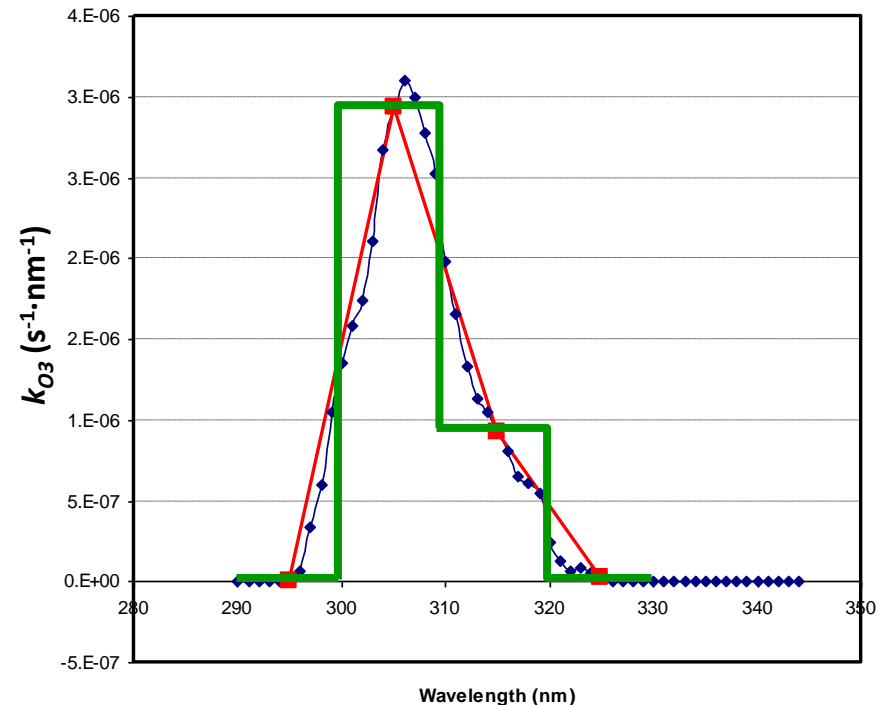
315 nm:  $q=0.25$ ,  $\sigma=5 \cdot 10^{-20} \text{ cm}^2 \cdot \text{molecules}^{-1}$ ,  $I=6.9 \cdot 10^{13} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$

$k \approx 9.2 \cdot 10^{-7} \text{ s}^{-1} \cdot \text{nm}^{-1}$ .

325 nm:  $q=0$ ,  $\sigma=1.6 \cdot 10^{-20} \text{ cm}^2 \cdot \text{molecules}^{-1}$ ,  $I=1.2 \cdot 10^{14} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$

$k = 0 \text{ s}^{-1} \cdot \text{nm}^{-1}$ .

O3 Photolysis Rate Constant



Integrate over all wavelengths, that is  $k = \int q(l)\sigma(l)I(l)dl$ . The unit is then  $\text{s}^{-1}$ . Multiply the values of the wavelength-dependent photolysis rate constants with the interval width (10 nm) and sum up. This yields  $k_{\text{O}_3} = 3.9 \cdot 10^{-5} \text{ s}^{-1}$ . If one integrates (sums) only for 305 and 315 nm, you get almost the same result;  $k_{\text{O}_3} = 3.86 \cdot 10^{-5} \text{ s}^{-1}$ .

# Hydroxyl radical OH

## Production of hydroxyl radicals OH via O<sub>3</sub>

(1) O<sub>3</sub> + hν → O<sub>2</sub> + O(<sup>1</sup>D) (excited atomic oxygen, λ < 320 nm)

(2) O(<sup>1</sup>D) + M → O(<sup>3</sup>P) + M (~90%) or

(3) O(<sup>1</sup>D) + H<sub>2</sub>O → 2OH (~10%, one O<sub>3</sub> gives two OH)

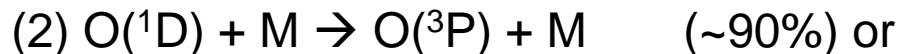
## Prerequisite: Production of excited atomic oxygen

O(<sup>1</sup>D) short-lived → Assume "steady state" for O(<sup>1</sup>D)

$$0 = \frac{d}{dt} [O(^1D)] = k_1 [O_3] - k_2 [O(^1D)] [M] - k_3 [O(^1D)] [H_2O] \Rightarrow [O(^1D)] = \frac{k_1 [O_3]}{k_2 [M] + k_3 [H_2O]} \quad \text{Eq. 1}$$

# Hydroxyl radical OH

## Production of hydroxyl radicals OH via O<sub>3</sub>



## Prerequisite: Production of excited atomic oxygen

O(<sup>1</sup>D) short-lived → Assume "steady state" for O(<sup>1</sup>D)

$$0 = \frac{d}{dt}[O(^1D)] = k_1[O_3] - k_2[O(^1D)][M] - k_3[O(^1D)][H_2O] \Rightarrow [O(^1D)] = \frac{k_1[O_3]}{k_2[M] + k_3[H_2O]} \quad \text{Eq. 1}$$

$$P_{OH} = \frac{d}{dt}[OH] = 2k_3[O(^1D)][H_2O] \quad \text{Eq. 2}$$

Insert Eq. 1 into Eq. 2 → 
$$P_{OH} = \frac{2k_1k_3[O_3][H_2O]}{k_2[M] + k_3[H_2O]} \approx$$

# Hydroxyl radical OH

## Production of hydroxyl radicals OH via O<sub>3</sub>



## Prerequisite: Production of excited atomic oxygen

O(<sup>1</sup>D) short-lived → Assume "steady state" for O(<sup>1</sup>D)

$$0 = \frac{d}{dt}[O(^1D)] = k_1[O_3] - k_2[O(^1D)][M] - k_3[O(^1D)][H_2O] \Rightarrow [O(^1D)] = \frac{k_1[O_3]}{k_2[M] + k_3[H_2O]} \quad \text{Eq. 1}$$

$$P_{OH} = \frac{d}{dt}[OH] = 2k_3[O(^1D)][H_2O] \quad \text{Eq. 2}$$

Insert Eq. 1 into Eq. 2 → 
$$P_{OH} = \frac{2k_1k_3[O_3][H_2O]}{k_2[M] + k_3[H_2O]} \approx$$

(2) Faster than (3),  $[M] \gg [H_2O] \rightarrow P_{OH} \approx \frac{2k_1k_3}{k_2[M]}[O_3][H_2O] \quad \text{Eq. 3}$

# Hydroxyl radical OH

## Production of the hydroxyl radical OH

$$P_{\text{OH}} \approx \frac{2k_1k_3}{k_2[M]} [O_3][H_2O] \quad \text{Eq. 3}$$

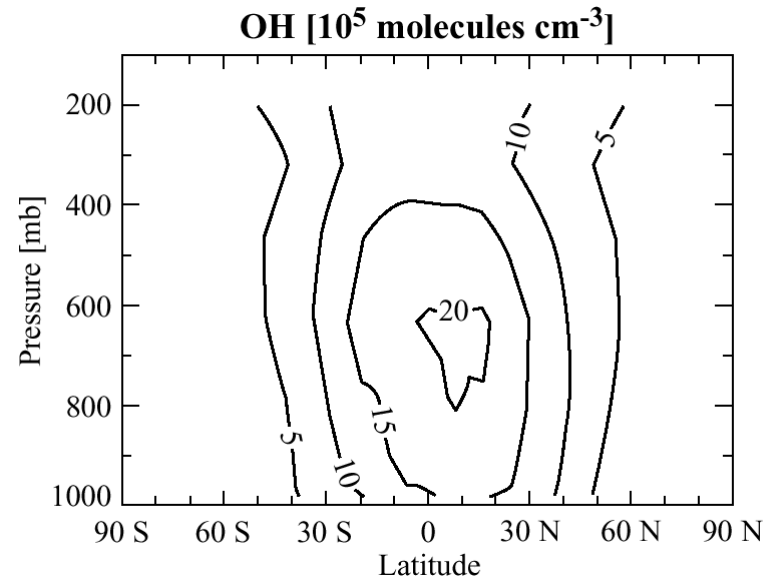
Production of OH most efficient when

- plenty UVb radiation ( $\lambda < 320 \text{ nm}$ ,  $k_1$ )
- high ozone levels ( $[O_3]$ )
- high humidity ( $[H_2O]$ )
- low pressure ( $[M]$ )

Production of OH largest in middle troposphere in the tropics.

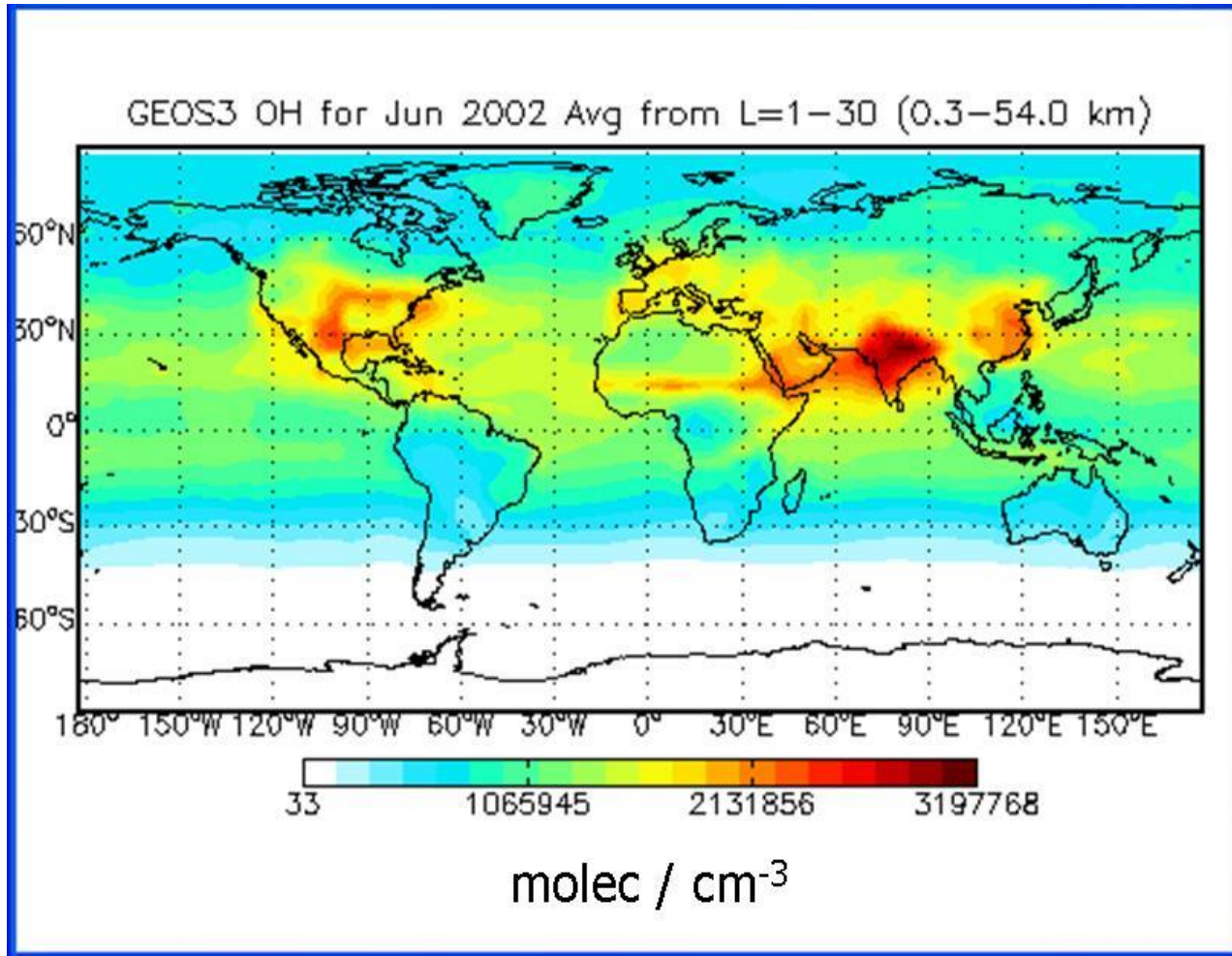
It takes 1-2 months for an air mass at our latitudes to disperse to the tropics.

Large fractions of our air pollutants are processed in tropics.



# Hydroxyl radical OH – Modelling

The 3-dimensional global chemistry transport model GEOS-CHEM



<http://www.chem.leeds.ac.uk/Atmospheric/Field/fage/modelling.html>



# Lifetime for the hydroxyl radical OH

OH lifetime  $\tau_{OH}$  can be estimated by knowing the most important sinks  $i$

$$\tau_{OH} = \frac{1}{\sum_i k_i n_i}$$

where  $n_i$  is the number concentration of molecule  $i$  and  $k_i$  is the corresponding rate constant.

The most important OH sinks (and for CO and CH<sub>4</sub>) are



$\tau_{OH} = \text{seconds}$  ( $\tau_{\text{CO}} = 1\text{-}4 \text{ months}$ ,  $\tau_{\text{CH}_4} = \sim 10 \text{ years}$ )

# Titration of hydroxyl radical OH

The stratosphere is not a sufficient source of tropospheric ozone to account for the levels of OH in the troposphere.

The global sources of CO and CH<sub>4</sub> are strong enough to titrate out all tropospheric OH that originates from stratospheric ozone.

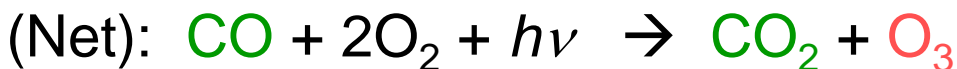
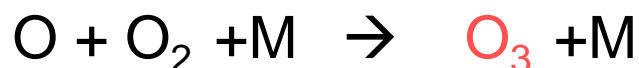
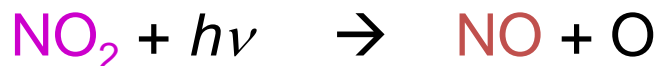
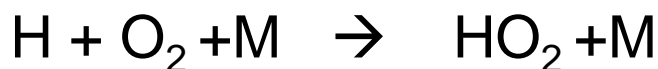
Levels of CO and CH<sub>4</sub> should rise to catastrophic levels!

Presence of NO<sub>x</sub> ( $\equiv$  NO + NO<sub>2</sub>) gives a catalytic regeneration of OH (and O<sub>3</sub>) in the troposphere.

Presence of NO<sub>x</sub> even at the low levels typically found in background air masses is very important for the oxidizing capacity of the troposphere and thereby life on Earth.

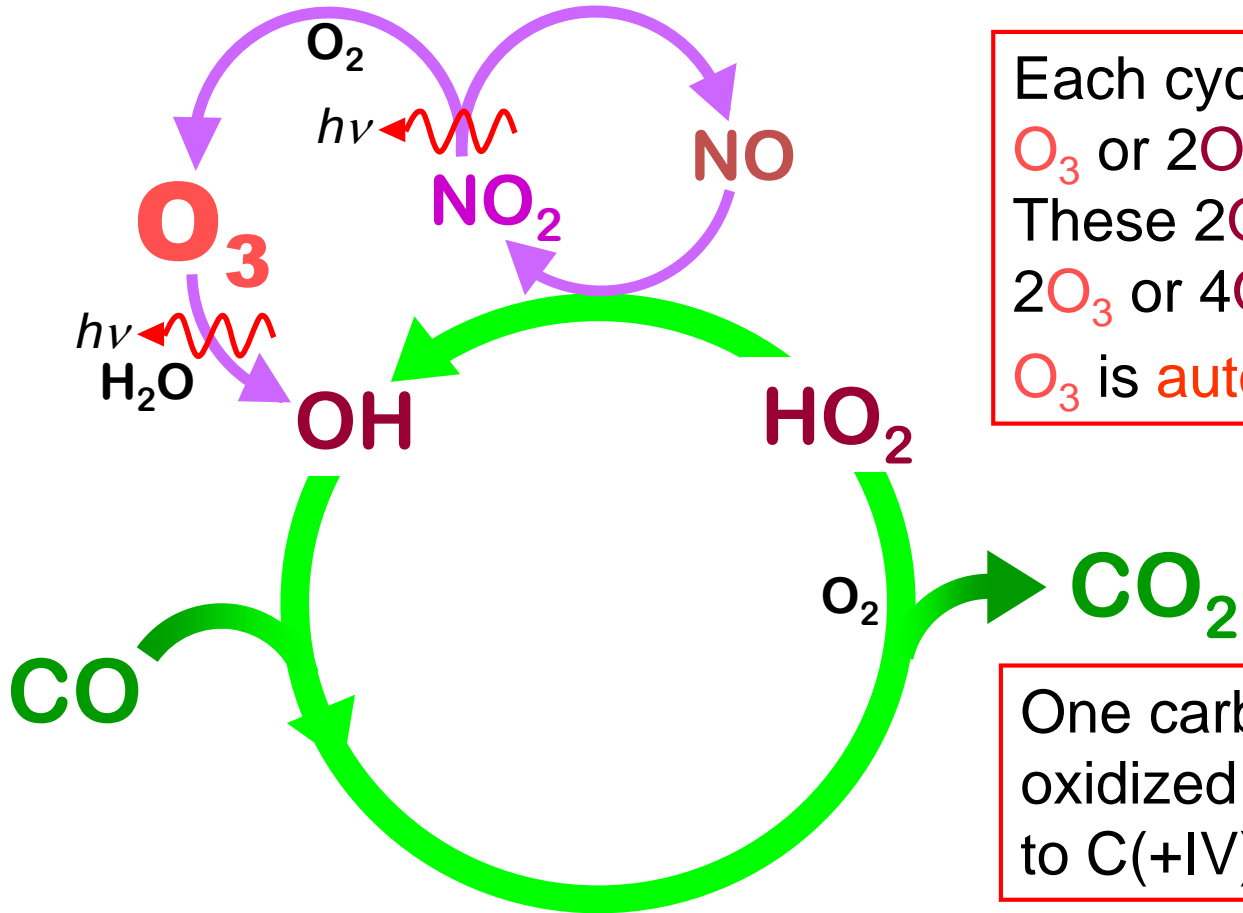
# Oxidation of carbon monoxide – high NO<sub>x</sub>

Catalytic ozone production:



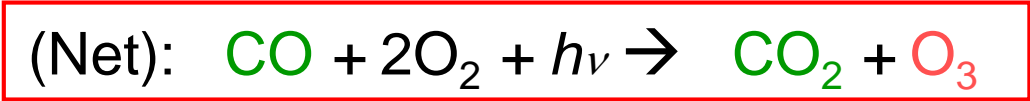
Each cycle produces one net O<sub>3</sub> or 2OH.

# Oxidation of carbon monoxide – high NO<sub>x</sub>



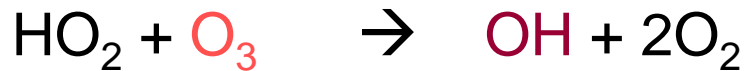
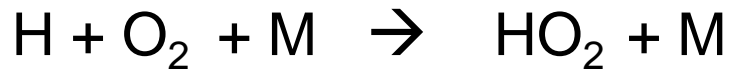
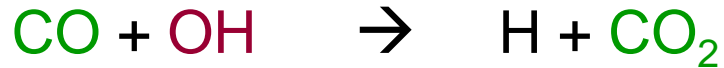
Each cycle produces one O<sub>3</sub> or 2OH. These 2OH can in turn give 2O<sub>3</sub> or 4OH and so on. O<sub>3</sub> is autocatalytic.

One carbon atom is also oxidized from C(+II), CO, to C(+IV), CO<sub>2</sub>.



# Oxidation of carbon monoxide – low NO<sub>x</sub>

Catalytic ozone loss:



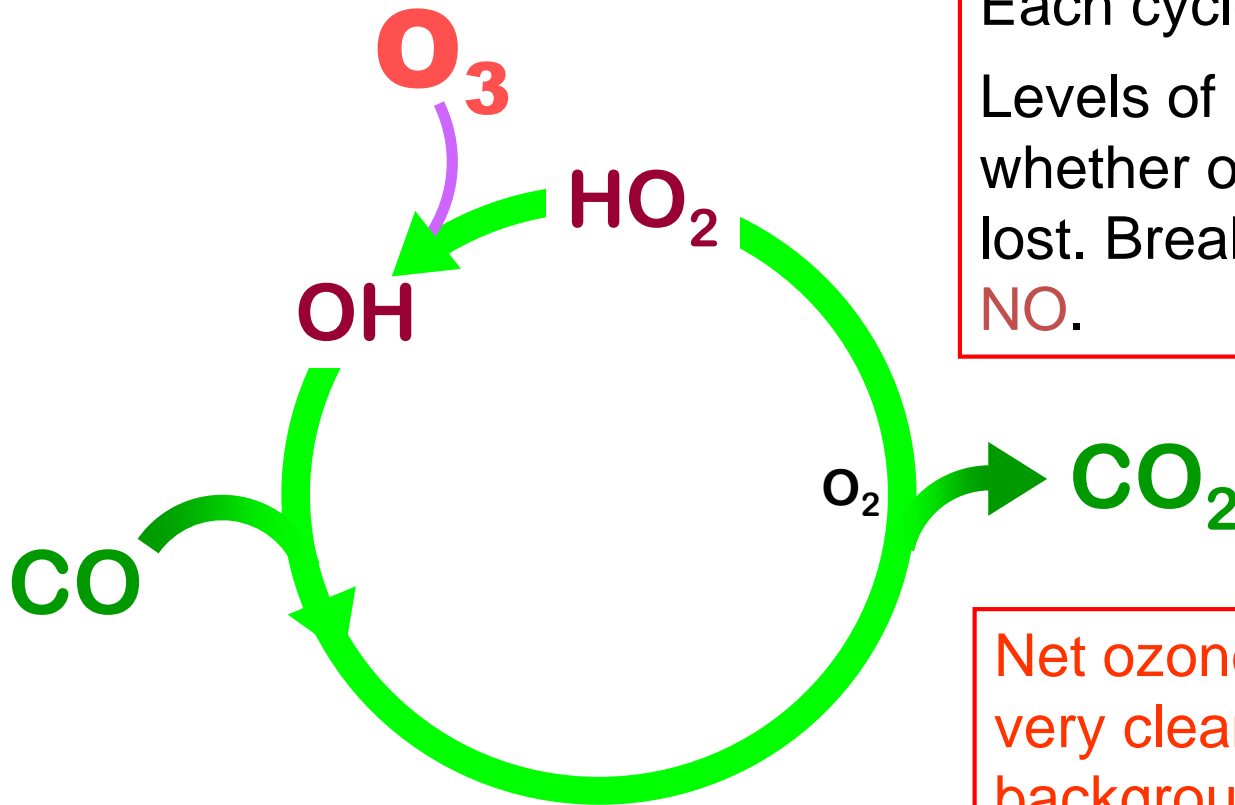
Each cycle consumes one O<sub>3</sub>.

Levels of NO are crucial to whether ozone is produced or consumed. Break-even lies at ~20 pptv NO (very low).

Ozone suffers a net loss only in very clean background air in the troposphere.

Such pristine air can still be found in large parts of the troposphere.

# Oxidation of carbon monoxide – low $\text{NO}_x$



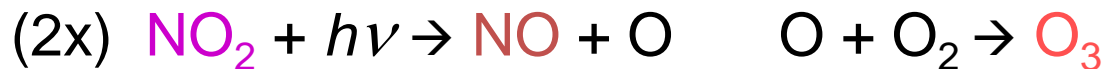
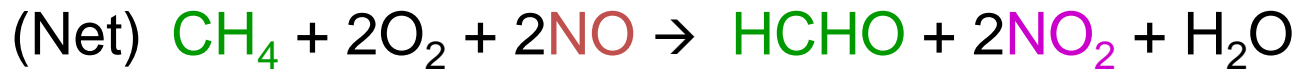
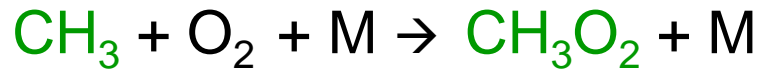
Each cycle **consumes** one  $\text{O}_3$ .  
Levels of **NO** determine whether ozone is produced or lost. Break-even lies  $\sim 20$  pptv **NO**.

Net ozone loss occurs only in very clean tropospheric background air.



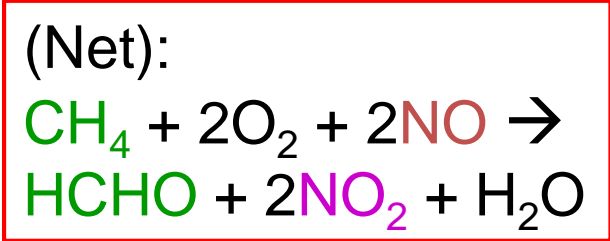
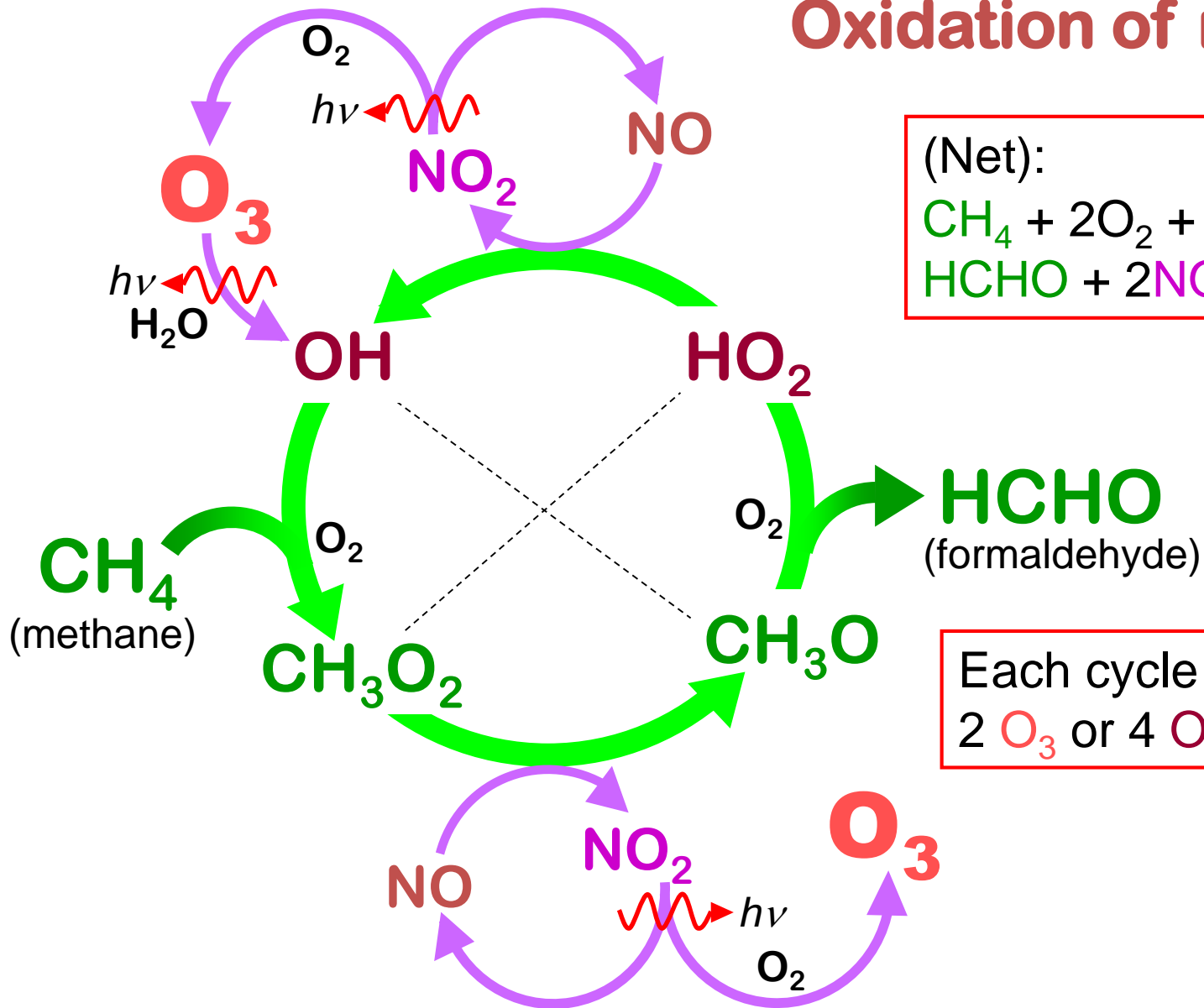
# Oxidation of methane

Catalytic ozone production:



Each cycle produces net  $2\text{O}_3$  or  $4\text{OH}$ .

# Oxidation of methane

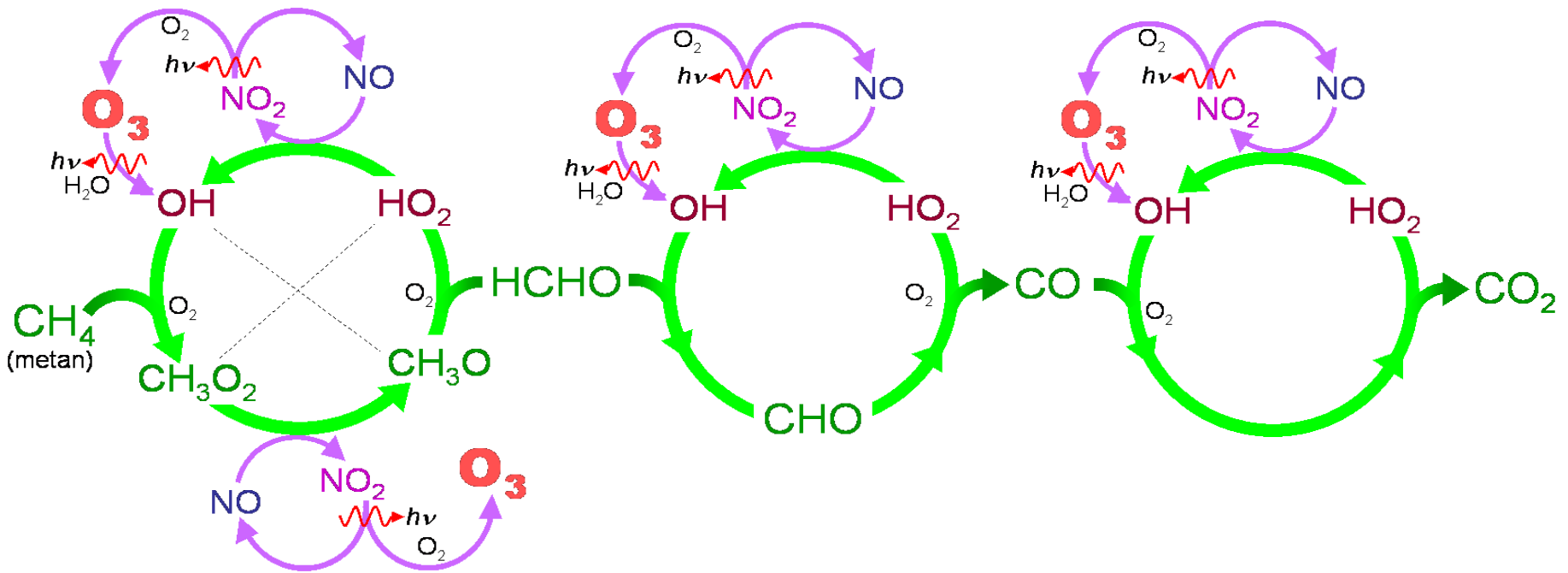


Each cycle gives net 2 O<sub>3</sub> or 4 OH.



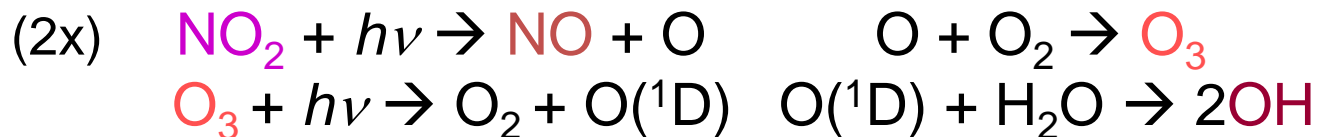
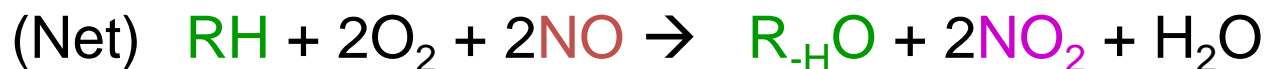


methane C(-IV) → formaldehyde C(0) → carbon monoxide C(II) → CO<sub>2</sub> C(IV)



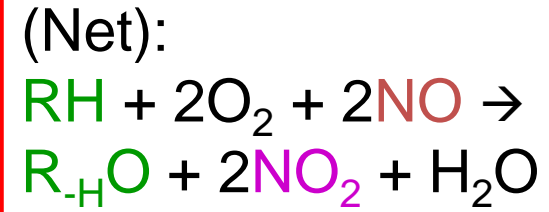
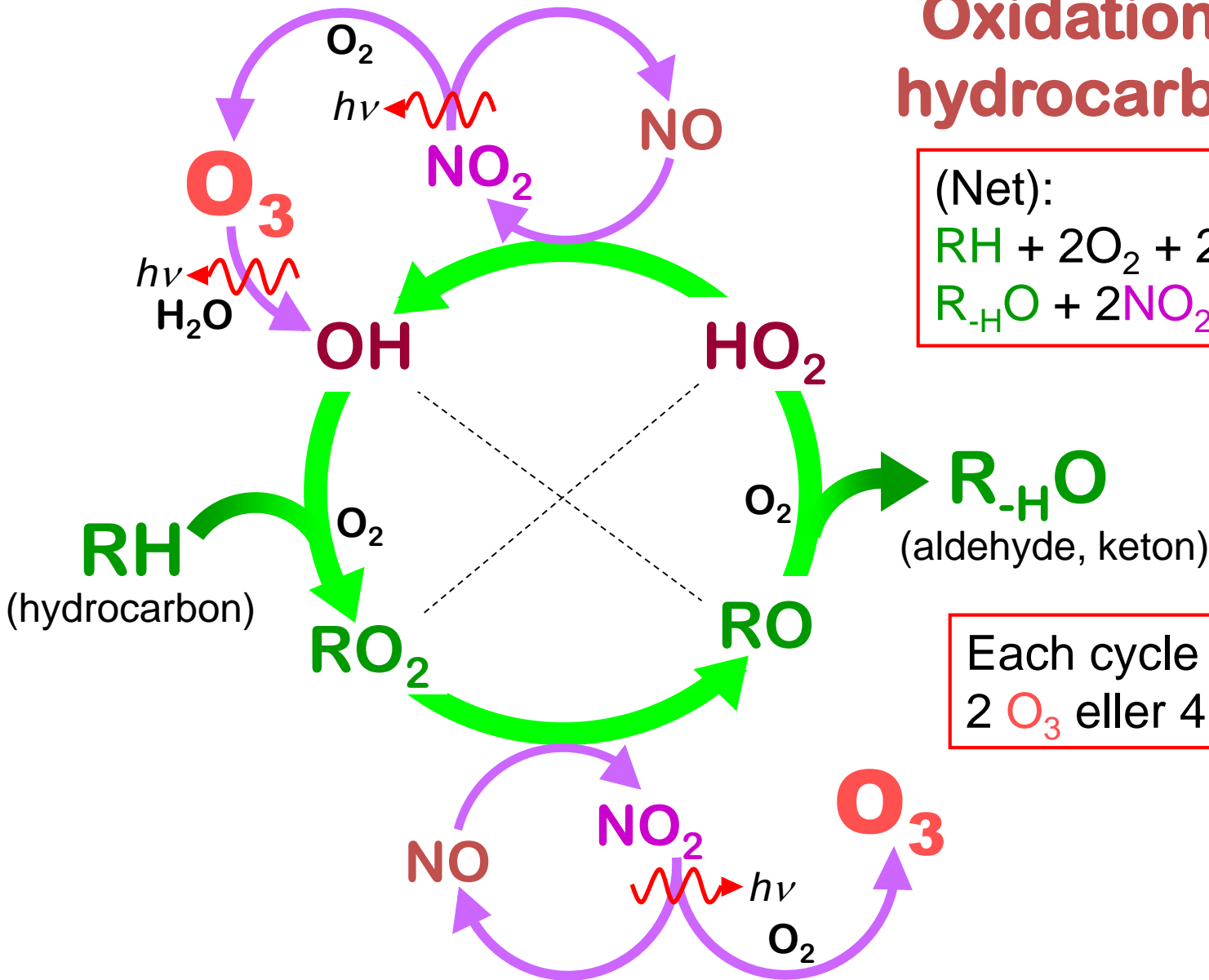
# Oxidation of hydrocarbons RH

## Examples: Alkanes RH



Each cycle produces net 2O<sub>3</sub> or 4OH.

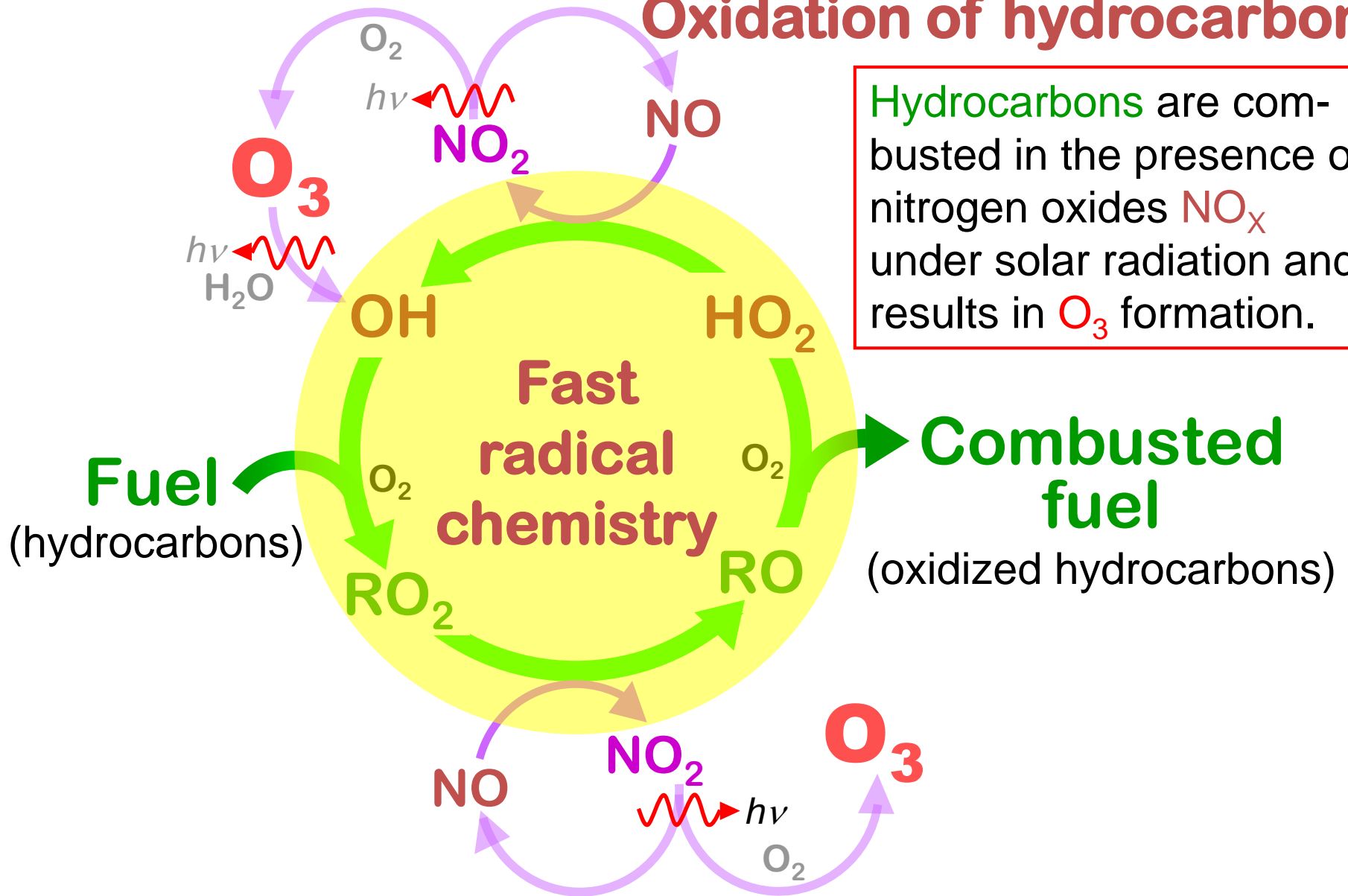
# Oxidation av hydrocarbons



Each cycle gives net 2 O<sub>3</sub> eller 4 OH.

# Oxidation of hydrocarbons

Hydrocarbons are combusted in the presence of nitrogen oxides  $\text{NO}_x$  under solar radiation and results in  $\text{O}_3$  formation.



# Oxidation of hydrocarbons

Hydrocarbons (the fuel) are oxidized in the troposphere in multiple steps.

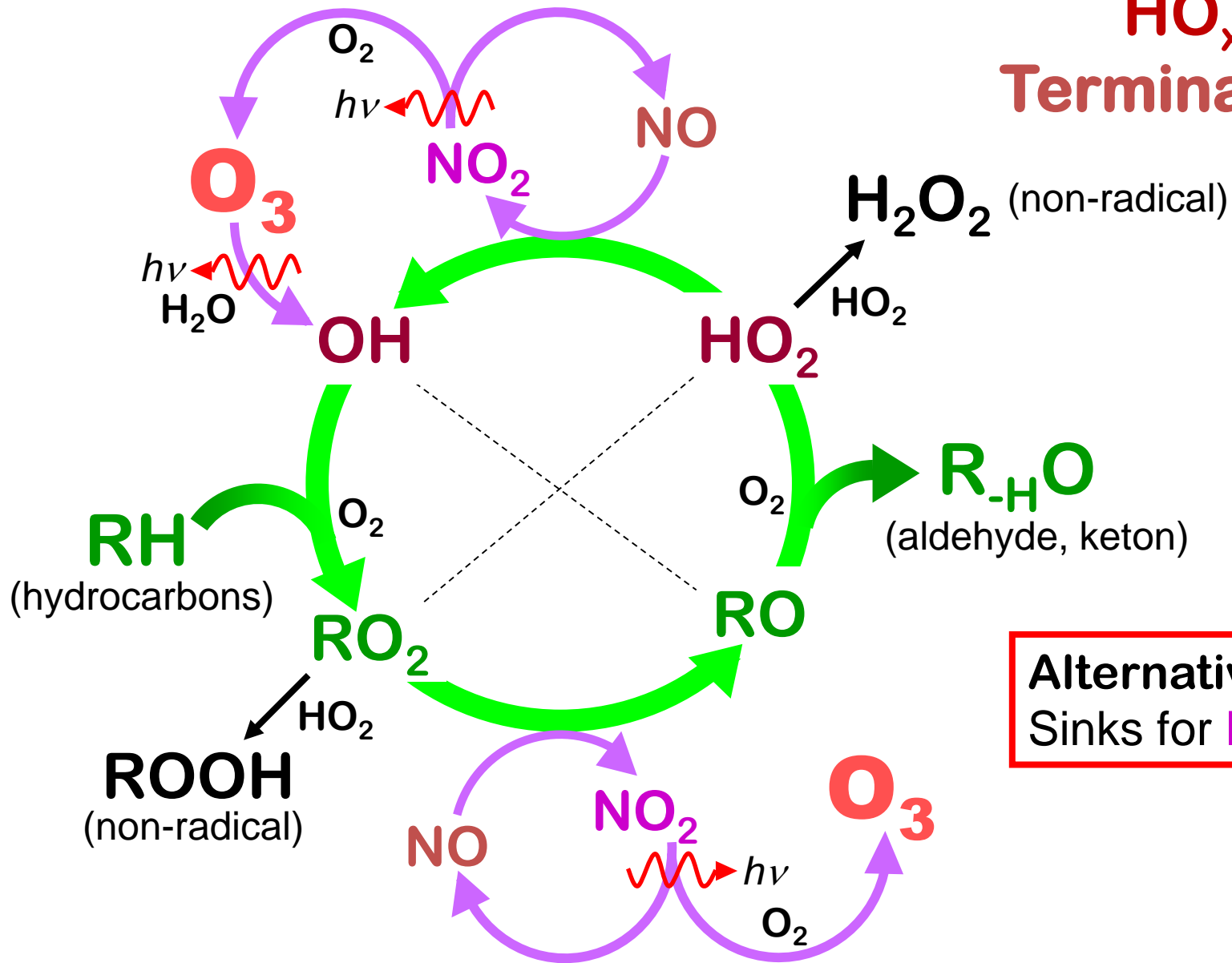
Hydrocarbon  $\rightarrow$  aldehyde  $\rightarrow$  organic acid  $\rightarrow$  carbon monoxide  $\rightarrow$   $\text{CO}_2$



Oxidation number for carbon atom:



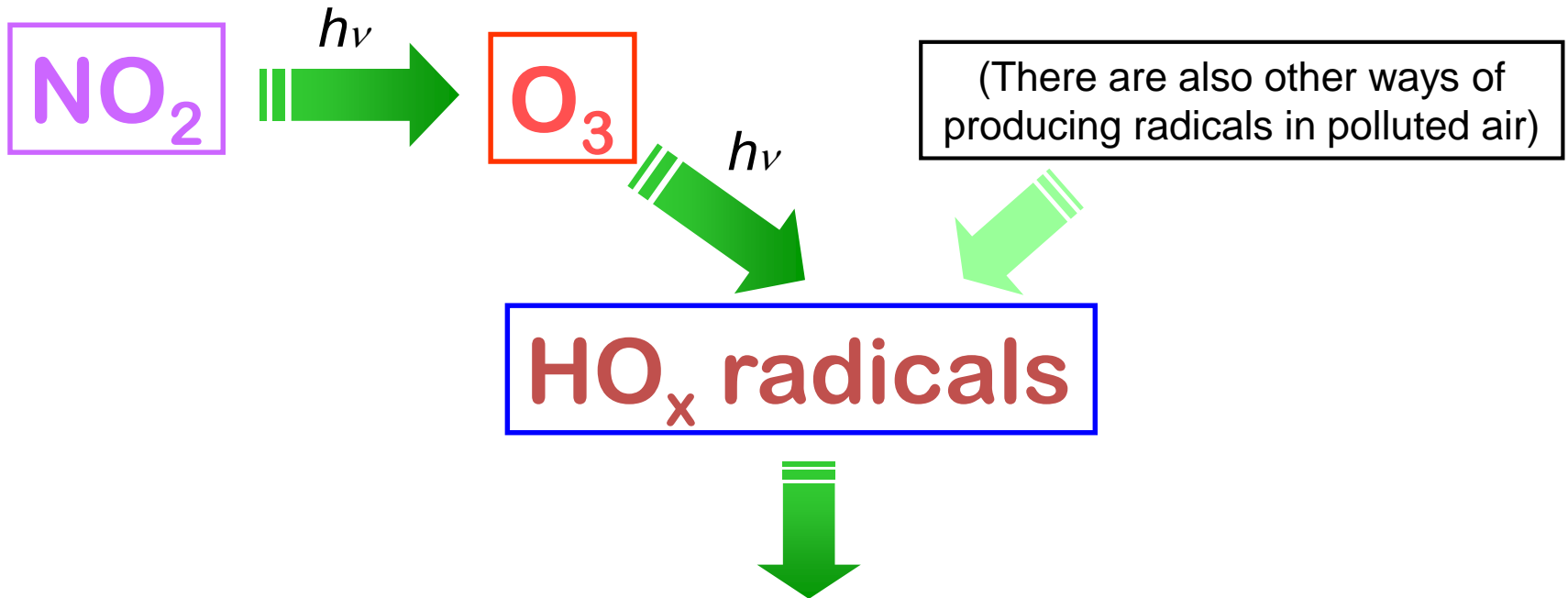
# HO<sub>x</sub> Termination



Alternative:  
Sinks for NO<sub>x</sub>.

# Oxidants in the troposphere

$\text{NO}_2$  and solar radiation controls the production of  $\text{O}_3$ , which in turn controls the production of  $\text{HO}_x$  radicals, which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.



Oxidizing capacity of the troposphere

## Sources of NO<sub>x</sub>

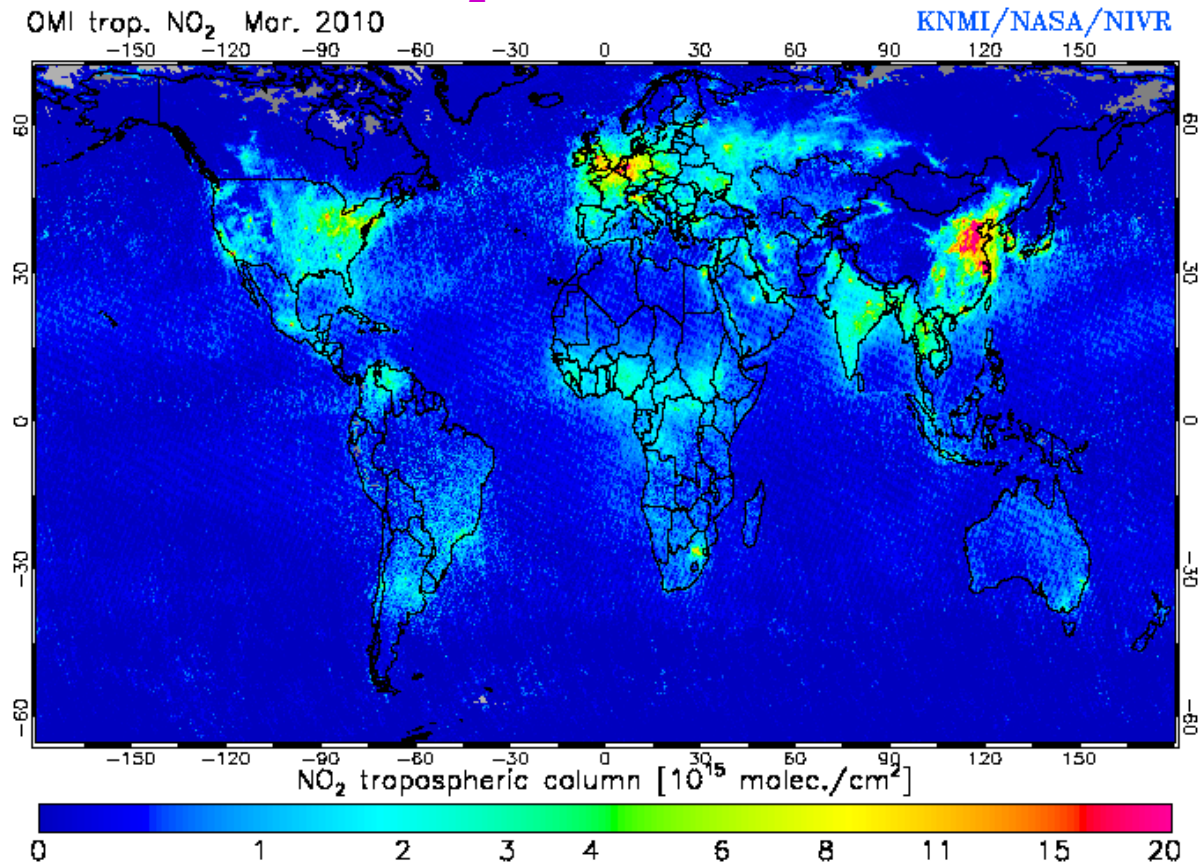
	Source (Tg N/yr)
Fossil fuel combustion	21 (45%)
Biomass combustion	12 (25%)
Soils	6 (13%)
Lightning	3 ( 7%)
Oxidation of $NH_3$	3 ( 7%)
Air traffic	0.5 ( 1%)
Transport from the stratosphere	0.1
<b>Total</b>	<b>~46</b>



# Sources of NO<sub>x</sub>

Anthropogenic sources of NO<sub>x</sub> (caused by human activities) dominate compared to the natural sources.

Levels of NO<sub>2</sub> measured from a satellite.



**Oxidation - troposphere**

## Sinks for NO<sub>x</sub>

NO<sub>x</sub> is mainly emitted as NO (at high temperatures).

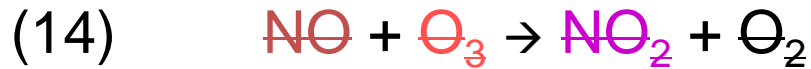
NO<sub>x</sub> is cycled between NO and NO<sub>2</sub> (~1 minute).



## Sinks for NO<sub>x</sub>

NO<sub>x</sub> is mainly emitted as NO (at high temperatures).

NO<sub>x</sub> is cycled between NO and NO<sub>2</sub> (~1 minute).



(Net) No net formation or loss of either NO<sub>x</sub> or O<sub>3</sub>

The above reactions represents a null-cycle for NO<sub>x</sub> and O<sub>3</sub>

## Sinks for NO<sub>x</sub>

Apart from removal of HO<sub>x</sub> radicals, the catalytic ozone production cycle can also be broken by removing NO<sub>x</sub>.



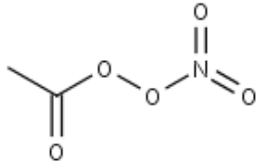
Nighttime:



$$\tau_{\text{NO}_x} = \sim 1 \text{ day}$$

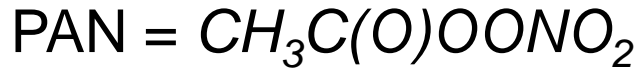
HNO<sub>3</sub> is very water-soluble and is washed out by precipitation (wet deposition).

HNO<sub>3</sub> is not a long-term reservoir for NO<sub>x</sub> ( $\tau_{\text{HNO}_3} = \text{days}$ ).



## PAN - Reservoir for $\text{NO}_x$

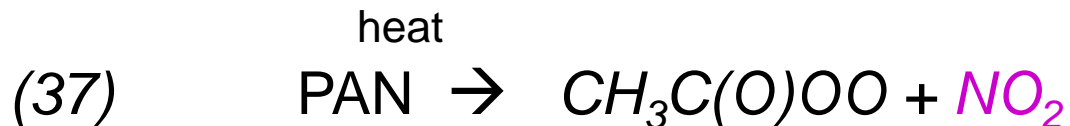
Peroxyacetyl Nitrate (PAN) is an efficient reservoir for  $\text{NO}_x$ .



PAN enables  $\text{NO}_x$  to be transported long distances and contribute to the levels of  $\text{NO}_x$  in background air, which in turn adds to the oxidizing capacity in remote environments.

PAN is formed for instance when acetaldehyde reacts with OH radicals and then further with  $\text{NO}_2$ . Levels of PAN in polluted air can reach 1 ppb.

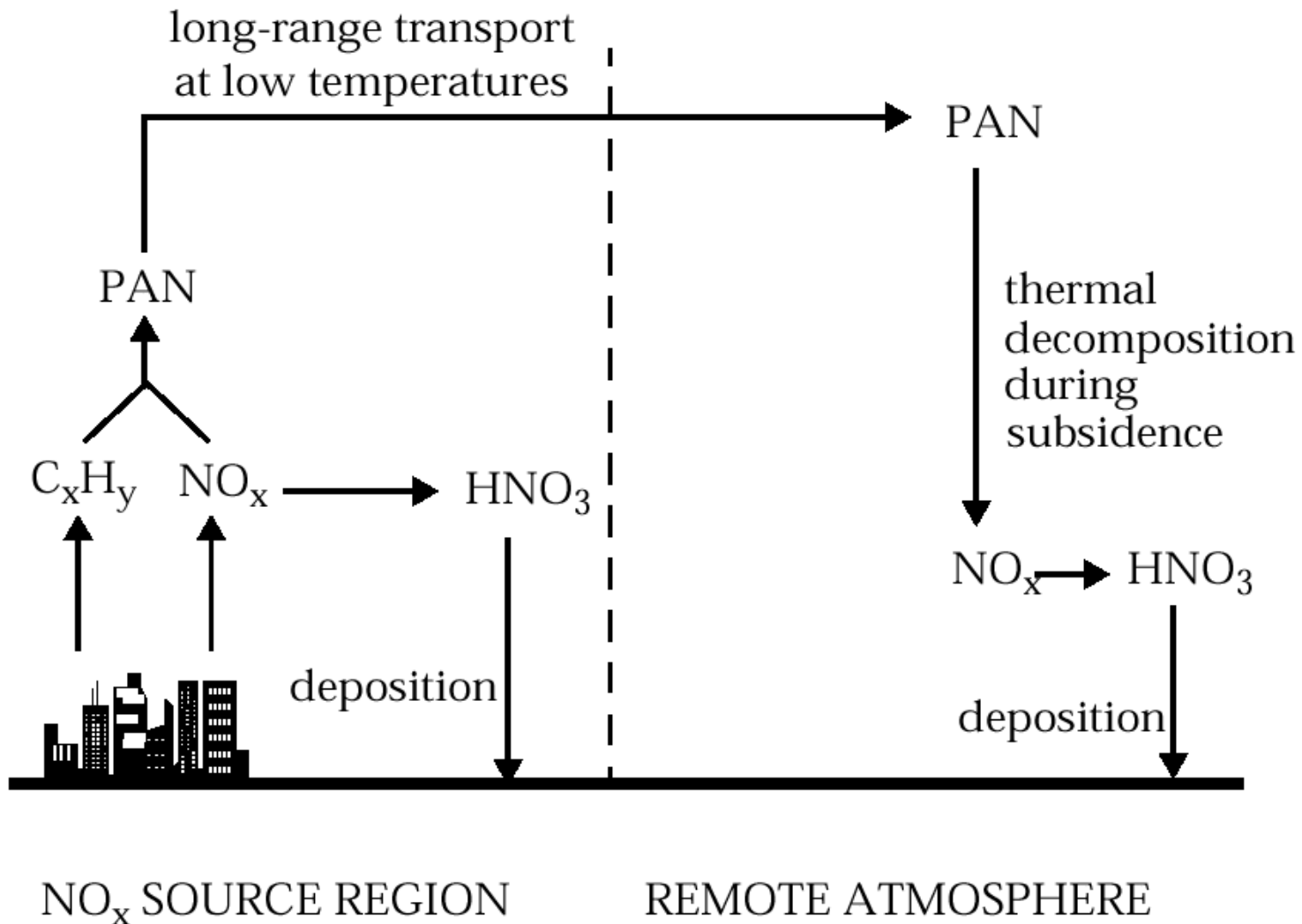
PAN is thermally unstable.



$\tau_{\text{PAN}} = \sim 1$  hour at 295 K (lower troposphere)

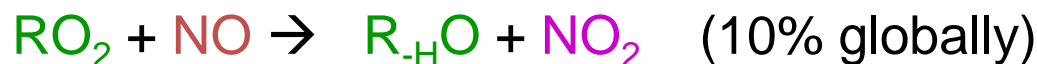
$\tau_{\text{PAN}} =$  months at 250 K (upper troposphere)

# Long-range transport of $\text{NO}_x$ via PAN



# Global budget for tropospheric ozone

Ozone production in the troposphere is limited by the reactions

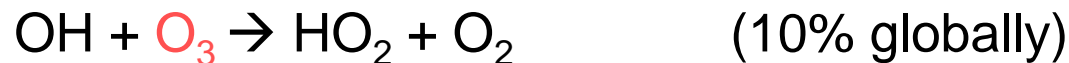
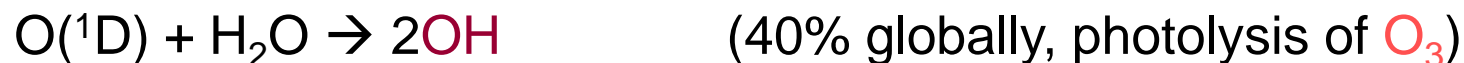


followed by



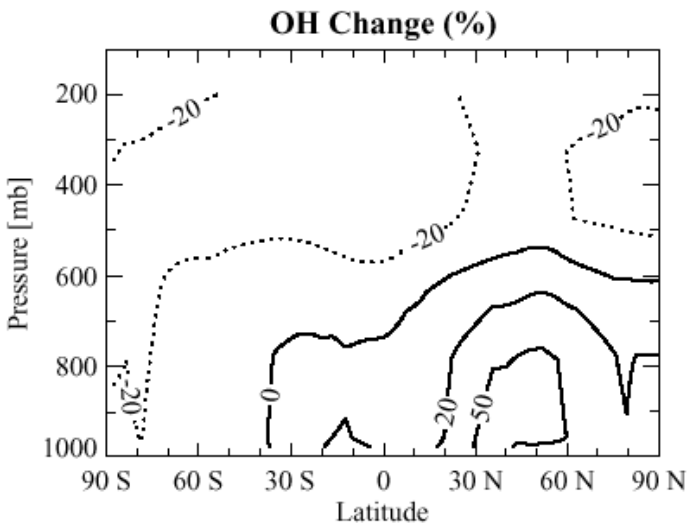
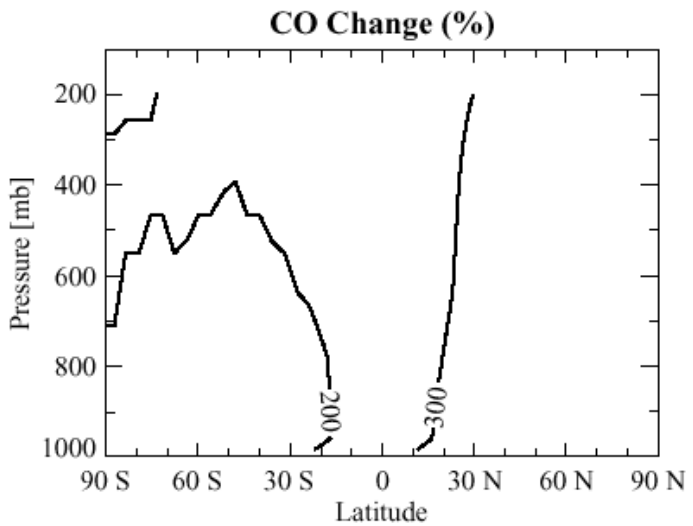
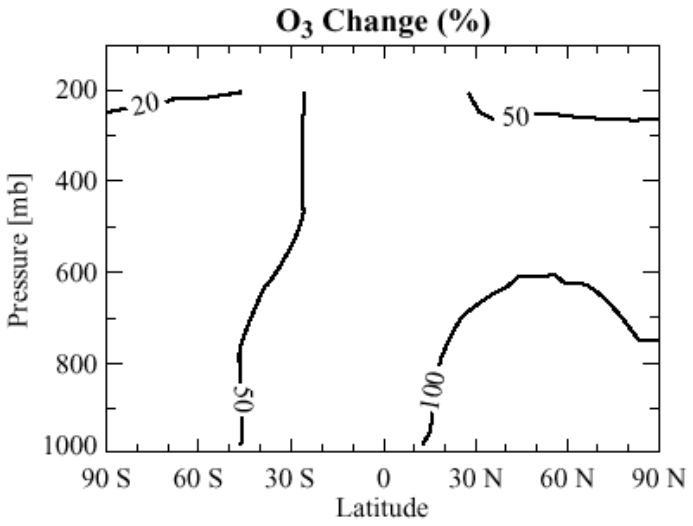
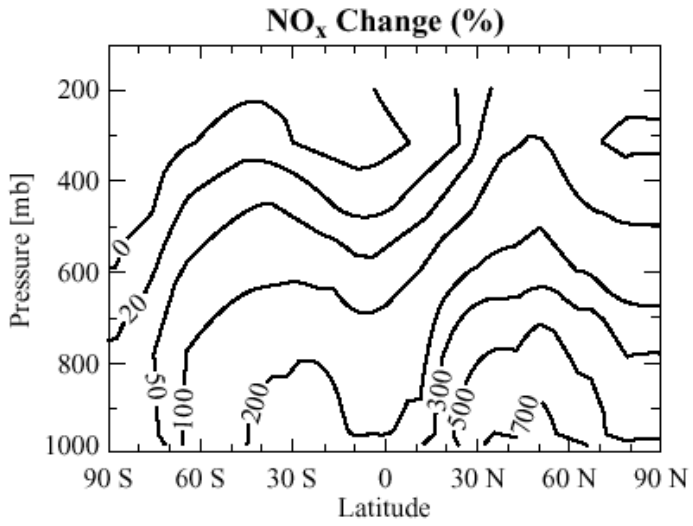
Down-mixing of stratospheric ozone is also a significant source.

Ozone loss in the troposphere is limited by the reactions



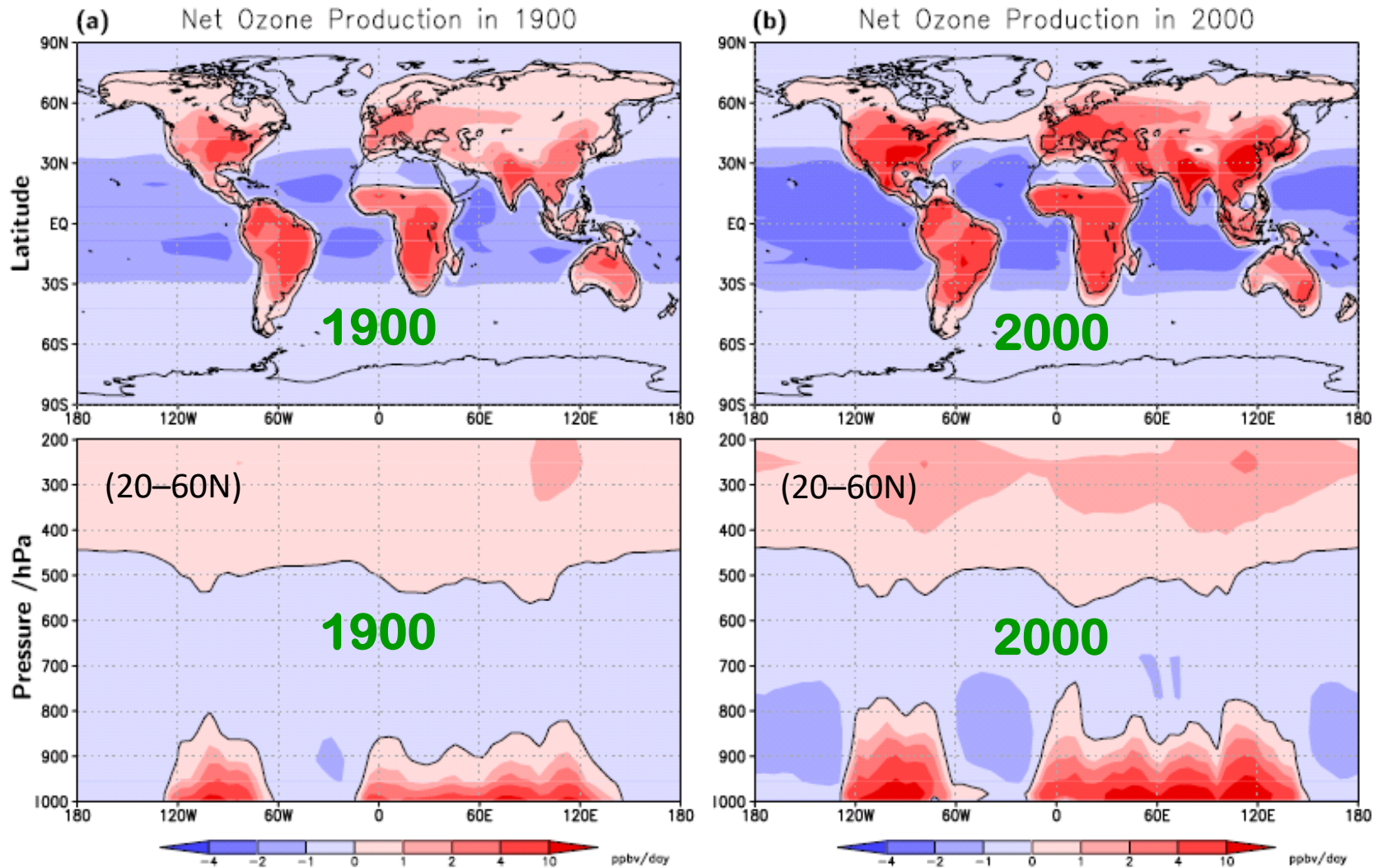
Dry deposition of ozone is also a significant sink.

# Anthropogenic modifications of the troposphere





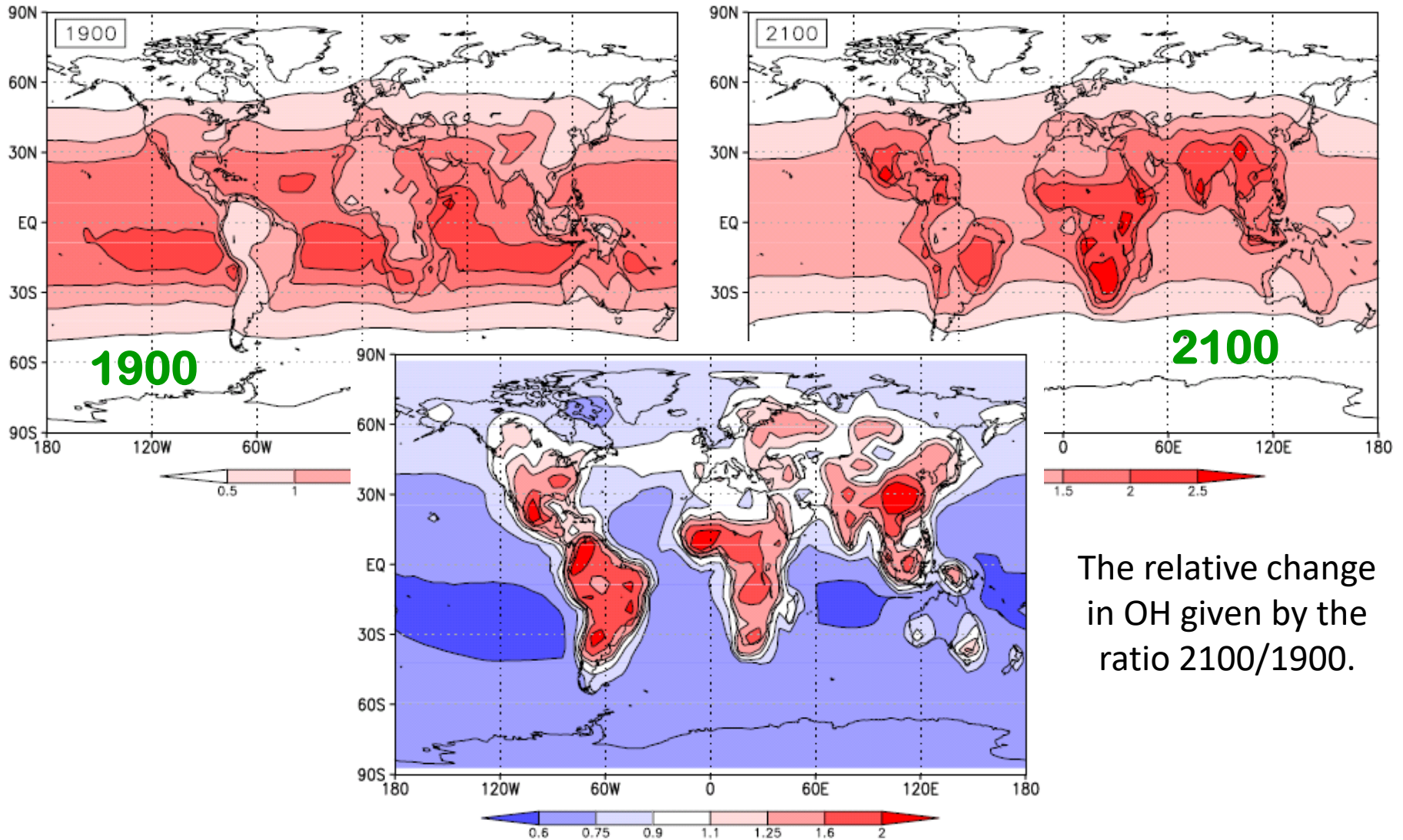
# Modelled net O<sub>3</sub> production rates (ppbv/day)



Annual mean distribution of net O<sub>3</sub> production in ppbv/day in (top) the boundary layer and (bottom) at northern mid-latitudes (20-60N) in (a) 1900, and (b) 2000. The contour line marks zero net production.

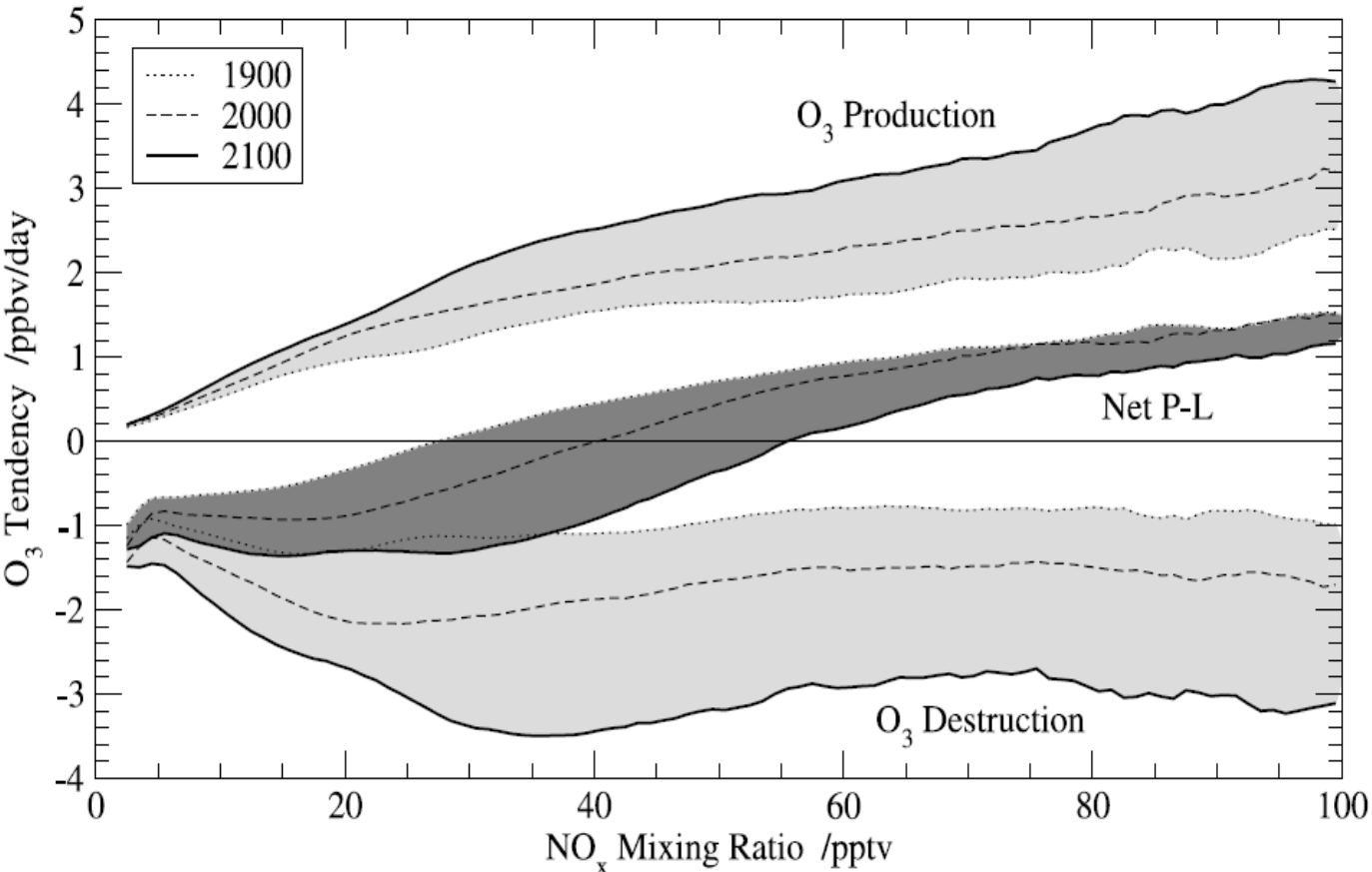
# Modelled OH concentrations 1900 - 2100

O. Wild, P.I. Palmer, How sensitive is tropospheric oxidation to anthropogenic emissions? GRL, VOL. 35, L22802, doi:10.1029/2008GL035718, 2008



Annual mean distribution of OH (in units of  $10^6$  molecules  $\text{cm}^{-3}$ ) in the boundary layer in (left) 1900 and (right) 2100.

# Modelled O<sub>3</sub> production and loss rates (ppbv/day)



Tropospheric O<sub>3</sub> production and loss rates (ppbv/day) below 250 hPa (10 km) as a function of NO<sub>x</sub> (pptv) for 1900, 2000, and 2100.

The critical NO<sub>x</sub> value for O<sub>3</sub> production occurs where net production (P-L) crosses zero, doubling between 1900 (28 pptv) and 2100 (55 pptv).

O. Wild, P.I. Palmer, How sensitive is tropospheric oxidation to anthropogenic emissions? GRL, VOL. 35, L22802, doi:10.1029/2008GL035718, 2008

## The Master Chemical Mechanism

[mcm.leeds.ac.uk/MCM/](http://mcm.leeds.ac.uk/MCM/)

A searchable compilation of chemical reactions of atmospheric importance.



UNIVERSITY OF LEEDS

## NASA JPL Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

<https://jpldataeval.jpl.nasa.gov/>

A compilation of kinetic and photochemical data prepared by the NASA Panel for Data Evaluation.

**Oxidation - troposphere**