Atmospheric Chemistry
Oxidizing capacity of the troposphere

Erik Swietlicki
Avd. för Kärnfysik
Fysiska institutionen
Lunds universitet

Tropospheric chemistry

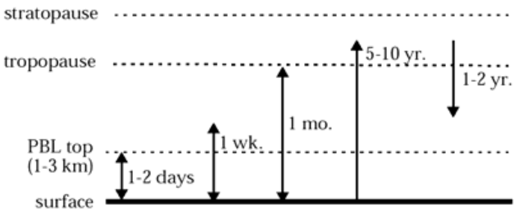
The troposphere is a chemical reservoir that is fairly well separated from the stratosphere.

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.

$$CO + OH \rightarrow H + CO_2$$

$$\ldots\ldots\ldots \rightarrow O_3$$

(Net, oxidation): $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$

Movie:

Example of how important oxidants are for life on Earth.

Concentrations of CO soon rise to toxic levels when left in the atmosphere.

Oxidants in the troposphere

The atmosphere is an **oxidizing** medium.

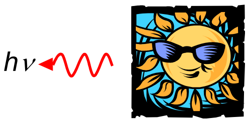
Examples			(oxidation numbers)
Hydrocarbons:	$CH_4 \rightarrow CO_2$	i.e.	C(-IV) → C(+IV)
Sulphur species:	$H_2S \rightarrow H_2SO_4$	i.e.	S(-II) → S(+VI)
Nitrogen species:	$NO \rightarrow HNO_3$	i.e.	N(+II) → N(+V)

The most abundant oxidants (O_2 and O_3) are relatively unreactive and therefore contribute very little to the oxidation of trace gases.

Oxidation of non-radicals involves **radical** species, not O_2 och O_3.

Tropospheric chemistry

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



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. CH_4 and CO that are both oxidized to 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. CO, SO_2).

Oxidants in the troposphere

The most important tropospheric oxidants are OH and other radicals in the HO_x family (OH, HO_2, RO, RO_2).

OH: Hydroxyl radical,	HO_2: Hydroperoxyl radical
RO: Organic oxyl radical	RO_2: Organic peroxyl radical

These radicals are formed in the troposphere in reactions that start with photolysis of ozone (**radical initiation**).

Initiation of the radical chain:

non-radical + $h\nu$ → radical + radical´ (two unpaired electrons in total)

Propagation:

radical + non-radical → radical´ + non-radical´

Termination:

radical **+** radical´ → non-radical + non-radical´

radical **+** radical´ + *M* → non-radical + *M*

Tropospheric ozone

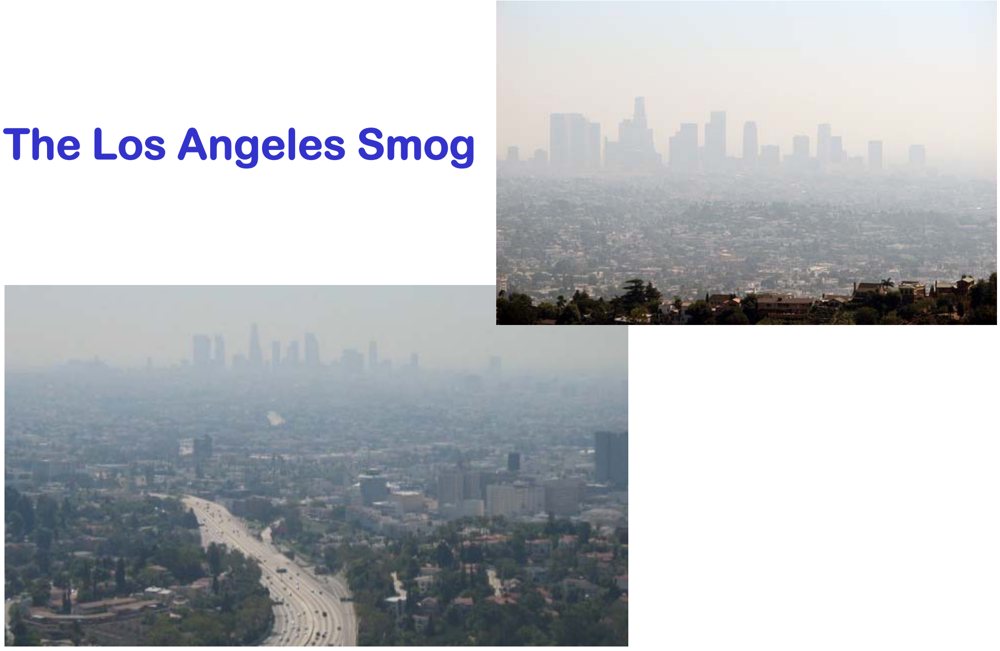
Ozone is needed to initiate the radical production and thus also to maintain an oxidizing atmosphere.

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



Ozone production in the troposphere

The only way to produce ozone is via

$$O + O_2 + M \rightarrow O_3 + M$$

with molecular oxygen O_2 and atomic oxygen O in its ground state $O(^3P)$,

This means that O has to be produced first.

Photolysis of O_2 does not occur in the troposphere (no UVc).

$$O_2 + h\nu \rightarrow O + O \qquad (\lambda < 240\ nm,\ UV)$$

There must therefore be other sources of O in the troposphere.

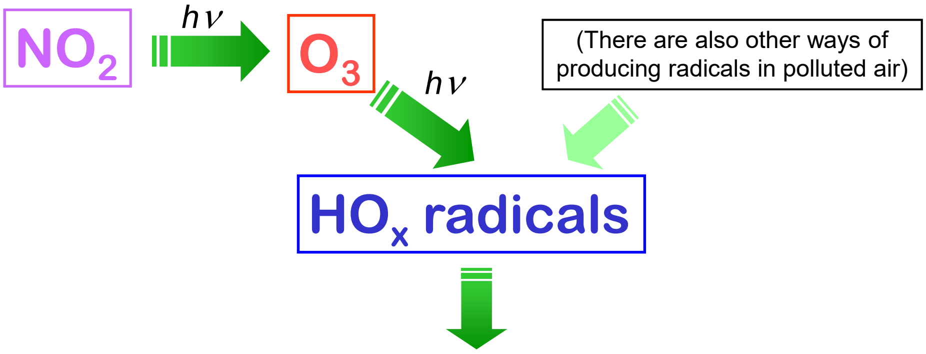
Main source of O in the troposphere is via photolysis of NO_2

$$NO_2 + h\nu \rightarrow NO + O \qquad (\lambda < 420\ nm)$$

This reaction is very important for the tropopheric chemistry!

Oxidants in the troposphere

NO_2 and solar radiation controls the production of O_3 , which in turn controls the production of HO_x radicals, which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.



NO_2 $\xrightarrow{h\nu}$ O_3 $\xrightarrow{h\nu}$ HO_x radicals

(There are also other ways of producing radicals in polluted air)

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 (N_2, O_2, CO_2, H_2O).

It reacts with most atmospheric trace gases.

The ”detergent” of the atmosphere.

Short lifetime (~1 s).

Exists in very low concentrations (10^5-10^7 molecules/cm^3).

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

Hydroxyl radical OH

Production of hydroxyl radicals OH via O_3

(1) $O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

(2) $O(^1D) + M \rightarrow O(^3P) + M$ (90%) or
(3) $O(^1D) + H_2O \rightarrow 2OH$ (10%, one O_3 gives two OH)

Prerequisite: Production of excited atomic oxygen O^1D

Hydroxyl radical OH

Production of hydroxyl radicals OH proceeds via three reactions:

(a) $O_3 + h\nu \xrightarrow{H_2O} 2OH + \ldots$
(b) $HO_2 + NO \rightarrow OH + \ldots$
(c) $HONO + h\nu \rightarrow OH + \ldots$

Reaction (a) dominates in background air (”low” NO_x , high RH).

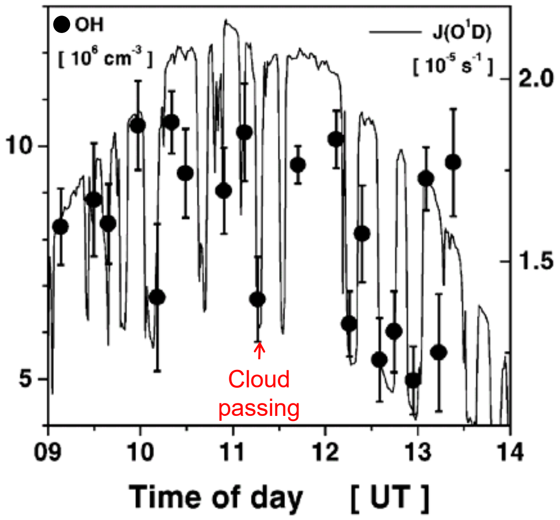
Reaction (b) dominates in polluted air (high NO_x).

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

Hydroxyl radical OH responds quickly to UV

$O_3 + h\nu \xrightarrow{H_2O} 2OH + \ldots$

OH has short lifetime (~1 s).



Cloud passing

J(O^{1}D) = Measured O_3 photolysis rate (λ < 320 nm)

● Measured *OH* concentrations

Production of the hydroxyl radical OH

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

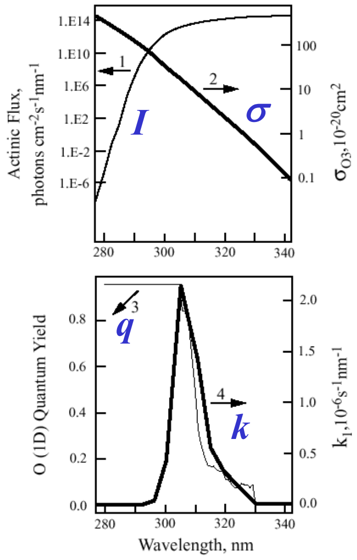
Actinic Flux (Ljusflöde) : I
Number of photons crossing the unit horizontal area per unit time (photons · m^{-2} · s^{-1})

Cross Section (Absorptionstvärsnitt) : σ
"Target area" per molecule within which the photon is absorbed (m^2 · molecule $^{-1}$)

Kvantutbyte (Quantum Yield) : q
Probability that absorption of a photon will cause photolysis (molecules · photon $^{-1}$)

Photolysis rate constant k :

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



Ozone photolysis in the troposphere

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

Exercise:

Calculate the photolysis rate constant k

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

Perform calculations in intervals centerred around 295, 305, 315 and 325 nm.

Photolysis

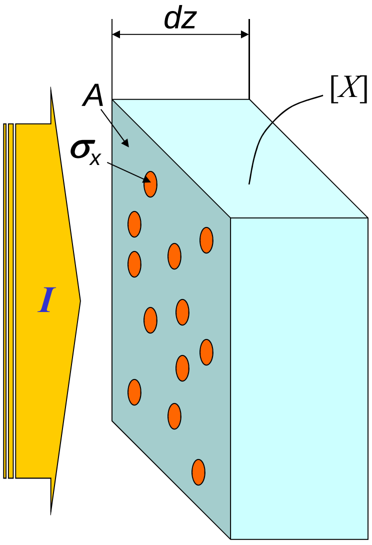
Absorption cross section: σ_x ($m^2 \cdot molecule^{-1}$)

Actinic Flux (Ljusflöde) : I
Number of photons crossing the unit horizontal area per unit time (photons · $m^{-2} \cdot s^{-1}$)

Quantum Yield (Kvantutbyte) : q_x
Probabality that absorption of a photon will cause photolysis of X (molecules · photon $^{-1}$)

Photolysis rate constant k :

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



Ozone photolysis in the troposphere

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

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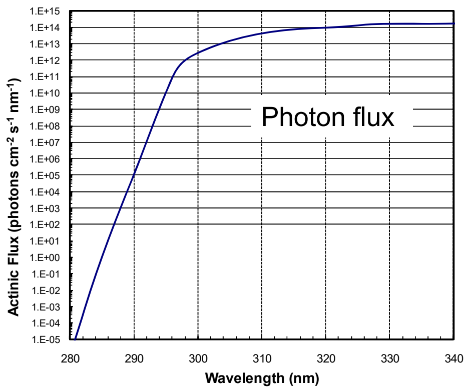
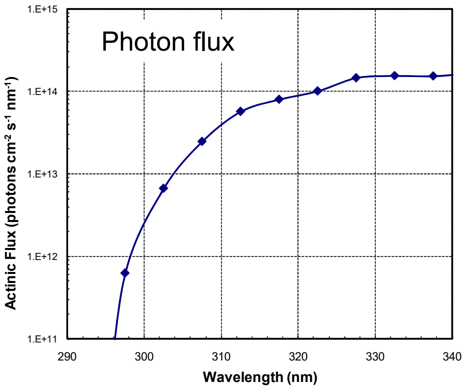
Actinic Flux I



Actinic Flux I

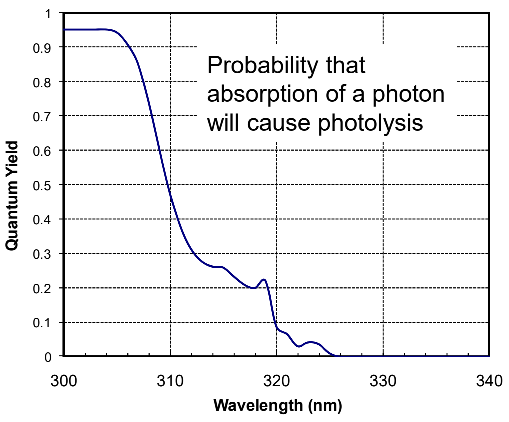


Ozone photolysis in the troposphere

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

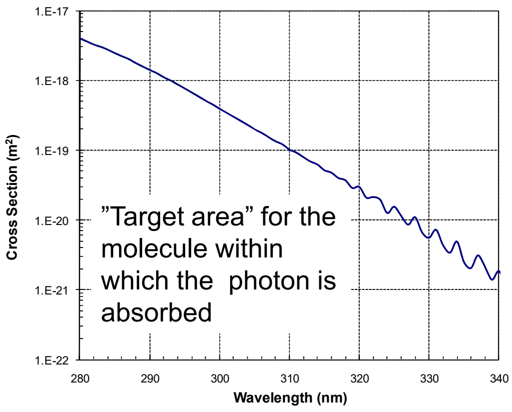
$k = q_x \cdot \sigma_x \cdot I$ (s^{-1}, wavelength dependent)

Ozone Photolysis Quantum Yield



Probability that absorption of a photon will cause photolysis

O_3 UV Absorption Cross Sections



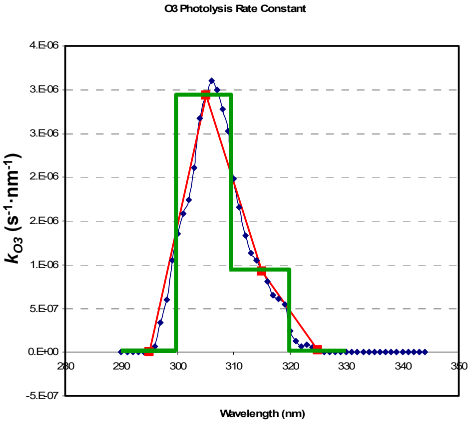
"Target area" for the molecule within which the photon is absorbed

Ozone photolysis in the troposphere

Photolysis of O_3 in the troposphere

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

$k=q\sigma I$ where q, σ and I all vary with the wavelength of light.
295 nm: $q=0.95$, $\sigma=8\cdot10^{-19}$ $cm^2\cdot molecules^{-1}$, $I=1\cdot10^{10}$ $photons\cdot cm^{-2}\cdot s^{-1}\cdot nm^{-1}$
$k \approx 7.3\cdot10^{-9}$ $s^{-1}\cdot nm^{-1}$. Note that the unit is $s^{-1}\cdot nm^{-1}$ since this value only represents a small wavelength interval around 295 nm).
305 nm: $q=0.94$, $\sigma=2\cdot10^{-19}$ $cm^2\cdot molecules^{-1}$, $I=1.6\cdot10^{13}$ $photons\cdot cm^{-2}\cdot s^{-1}\cdot nm^{-1}$
$k \approx 2.9\cdot10^{-6}$ $s^{-1}\cdot nm^{-1}$.
315 nm: $q=0.25$, $\sigma=5\cdot10^{-20}$ $cm^2\cdot molecules^{-1}$, $I=6.9\cdot10^{13}$ $photons\cdot cm^{-2}\cdot s^{-1}\cdot nm^{-1}$
$k \approx 9.2\cdot10^{-7}$ $s^{-1}\cdot nm^{-1}$.
325 nm: $q=0$, $\sigma=1.6\cdot10^{-20}$ $cm^2\cdot molecules^{-1}$, $I= 1.2\cdot10^{14}$ $photons\cdot cm^{-2}\cdot s^{-1}\cdot nm^{-1}$
$k = 0$ $s^{-1}\cdot nm^{-1}$.



Integrate over all wavelenghts, that is $k=\int q(l)s(l)I(l)dl$. The unit is then s^{-1}. Multiply the values values of the wavelength-dependent photolysis rate constants with the interval width (10 nm) and sum up. This **yields $k_{O3} = 3.9\cdot10^{-5}$ s^{-1}**. If one integrates (sums) only for 305 and 315 nm, you get almost the same result; $k_{O3} = 3.86\cdot10^{-5}$ s^{-1}.

Hydroxyl radical OH

Production of hydroxyl radicals OH via O_3

(1) $O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

(2) $O(^1D) + M \rightarrow O(^3P) + M$ (90%) or
(3) $O(^1D) + H_2O \rightarrow 2OH$ (10%, one O_3 gives two OH)

Prerequisite: Production of excited atomic oxygen

O^1D short-lived → Assume "steady state" for $O(^1D)$ →

$$0 = \frac{d}{dt}\left[O(^1D)\right] = k_1[O_3] - k_2\left[O(^1D)\right][M] - k_3\left[O(^1D)\right][H_2O] \Rightarrow$$

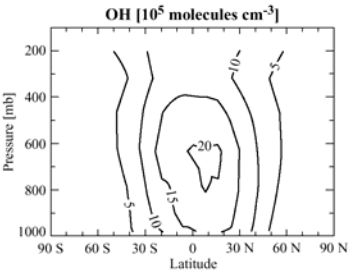
$$\left[O(^1D)\right] = \frac{k_1[O_3]}{k_2[M] + k_3[H_2O]}$$

Hydroxyl radical OH

Production of the hydroxyl radical *OH*

$$\frac{d}{dt}[OH] = 2k_3[O(^1D)][H_2O] = \frac{2k_1k_3[O_3][H_2O]}{k_2[M]+k_3[H_2O]} \approx$$

$$\approx \frac{2k_1k_3}{k_2[M]}[O_3][H_2O]$$ (*2*) Faster than (*3*), $[M]>[H_2O]$



Production of *OH* most efficient when

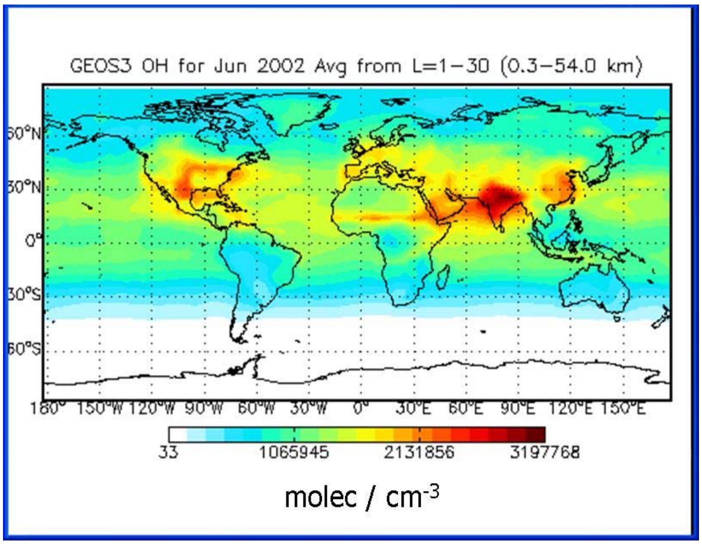
- plenty UVb radiation ($\lambda < 320$ nm, k_1)
- high ozone levels ($[O_3]$)
- high humidity ($[H_2O]$)
- low pressure ($[M]$)

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 τ_{OH} in the troposphere 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_4) are

(4) $CO + OH \rightarrow CO_2 + H$
(5) $CH_4 + OH \rightarrow CH_3 + H_2O$

τ_{OH} = seconds (τ_{CO} = 1-4 months, τ_{CH_4} = ~10 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_4 are strong enough to titrate out all tropospheric OH that originates from stratospheric ozone.

Levels of CO and CH_4 should rise to catastrophic levels!

Presence of NO_X (= NO + NO_2) gives a catalytic regeneration of OH (and O_3) in the troposphere.

Presence of NO_X 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_x

Catalytic ozone production:

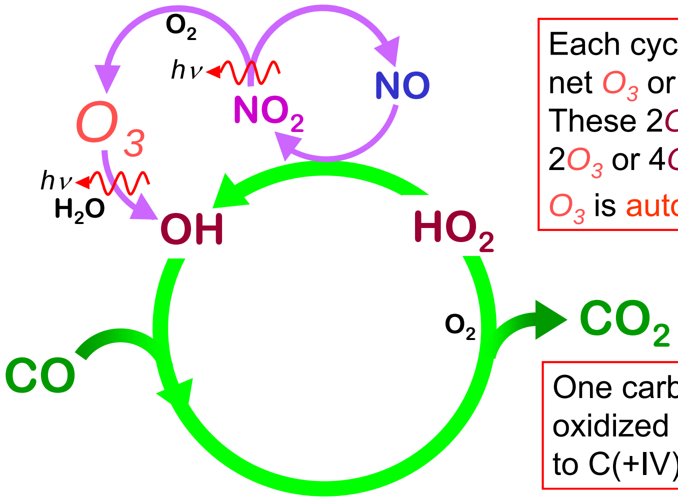
$CO + OH \rightarrow H + CO_2$
$H + O_2 (+M) \rightarrow HO_2 (+M)$
$HO_2 + NO \rightarrow OH + NO_2$
$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 (+M) \rightarrow O_3 (+M)$

(Net): $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ och $O(^1D) + H_2O \rightarrow 2OH$

Each cycle produces one net O_3 or $2OH$.

Oxidation of carbon monoxide – high NO_x



Each cycle produces one net O_3 or $2OH$.
These $2OH$ can in turn give $2O_3$ or $4OH$ and so on.
O_3 is autocatalytic.

One carbon atom is also oxidized from C(+II), CO, to C(+IV), CO_2.

(Net): $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$

Oxidation of carbon monoxide – low NO_x

Catalytic ozone loss:

$$CO + OH \rightarrow H + CO_2$$
$$H + O_2 (+M) \rightarrow HO_2 (+M)$$
$$HO_2 + O_3 \rightarrow OH + 2O_2$$

(Net): $CO + O_3 \rightarrow CO_2 + O_2$

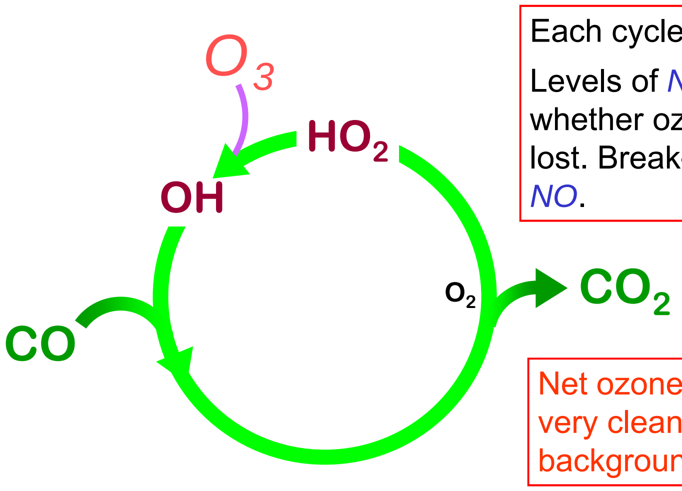
Each cycle consumes one net O_3.

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 NO_x



Each cycle consumes one O_3.

Levels of *NO* determine whether ozone is produced or lost. Break-even lies ~20 pptv *NO*.

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

(Net): $CO + O_3 \rightarrow CO_2 + O_2$

Oxidation of methane

Catalytic ozone production:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$
$$CH_3 + O_2\ (+M) \rightarrow CH_3O_2\ (+M)$$
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
$$CH_3O + O_2 \rightarrow HCHO + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$

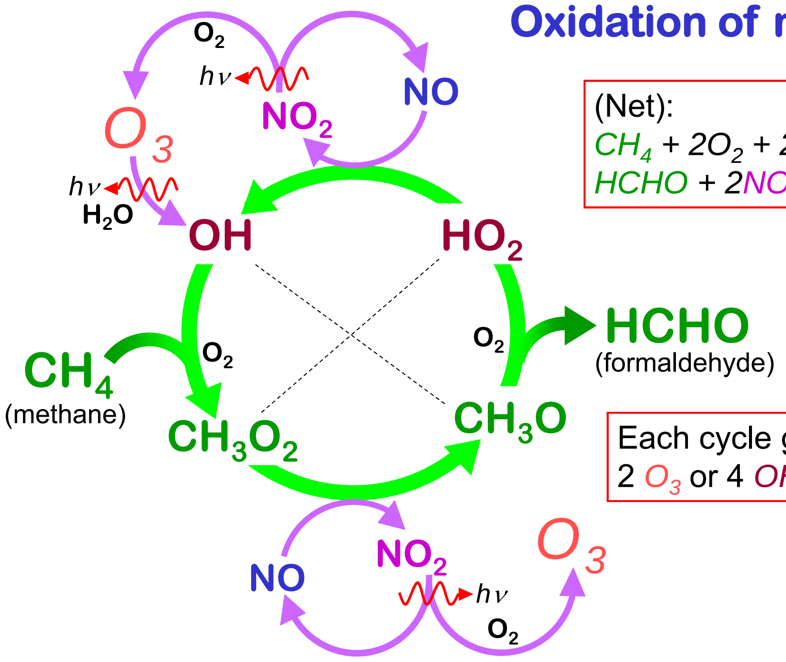
(Net): $CH_4 + 2O_2 + 2NO \rightarrow HCHO + 2NO_2 + H_2O$

$NO_2 + h\nu \rightarrow NO + O$ $\qquad$ $O + O_2 \rightarrow O_3$

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $\qquad$ $O(^1D) + H_2O \rightarrow 2OH$

Each cycle produces net 2O_3 or 4OH.

Oxidation of methane

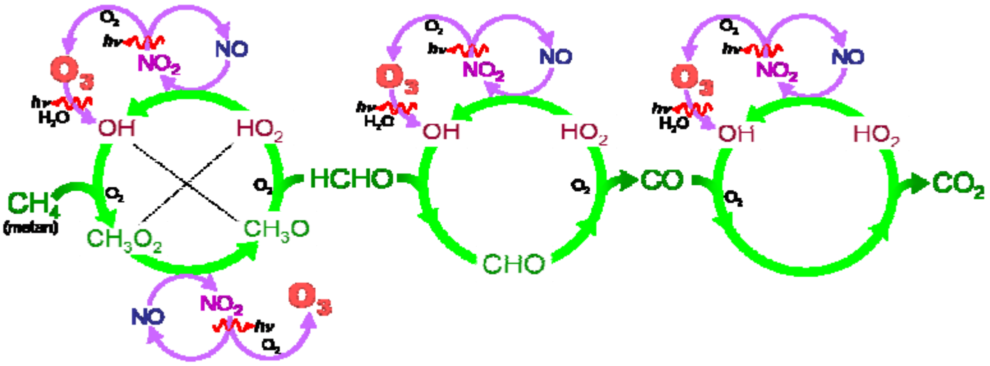


(Net):
$CH_4 + 2O_2 + 2NO \rightarrow$
$HCHO + 2NO_2 + H_2O$

Each cycle gives net 2 O_3 or 4 OH.

$CH_4 \rightarrow HCHO \rightarrow CO \rightarrow CO_2$

methane C(-IV) → formaldehyde C(0) → carbon monoxide C(II) → CO_2 C(IV)



Oxidation of hydrocarbons RH

Examples: Alkanes RH

$RH + OH \rightarrow R + H_2O$

$R + O_2 (+M) \rightarrow RO_2 (+M)$

$RO_2 + NO \rightarrow RO + NO_2$

$RO + O_2 \rightarrow R_{-H}O + HO_2$

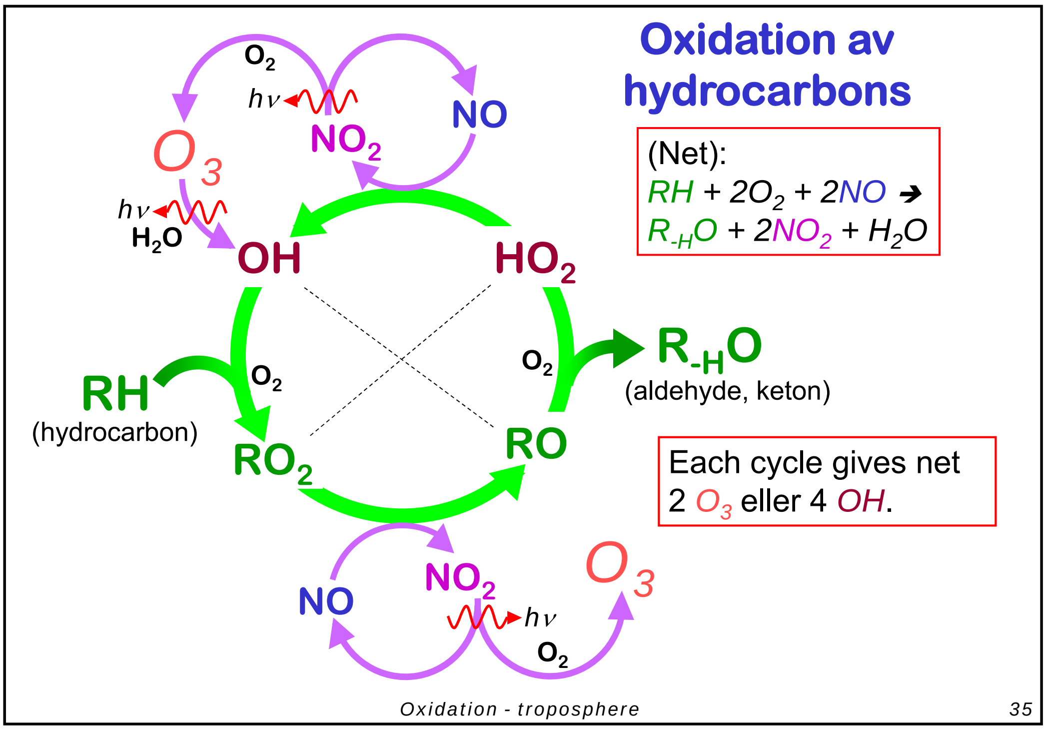
$HO_2 + NO \rightarrow OH + NO_2$

(Net) $RH + 2O_2 + 2NO \rightarrow R_{-H}O + 2NO_2 + H_2O$

$NO_2 + h\nu \rightarrow NO + O$ $O + O_2 \rightarrow O_3$

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2OH$

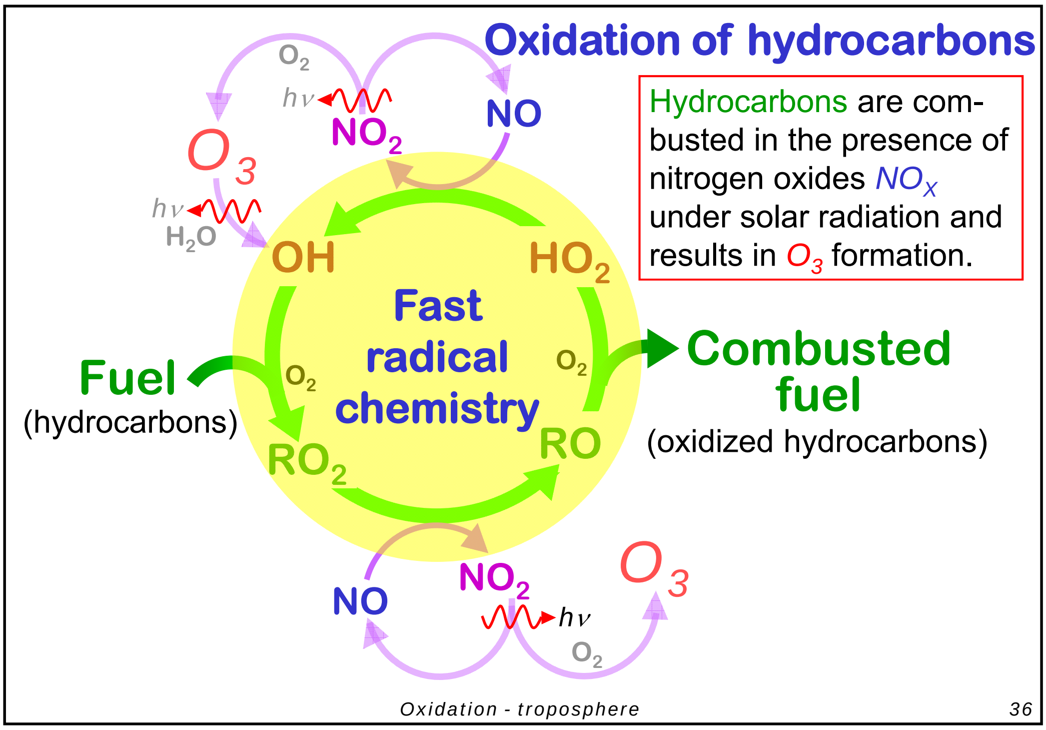
Each cycle produces net 2O_3 or 4OH.



Oxidation av hydrocarbons

(Net):
$RH + 2O_2 + 2NO \rightarrow$
$R_{-H}O + 2NO_2 + H_2O$

Each cycle gives net 2 O_3 eller 4 OH.



Oxidation of hydrocarbons

Hydrocarbons are combusted in the presence of nitrogen oxides NO_X under solar radiation and results in O_3 formation.

Oxidation of hydrocarbons

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

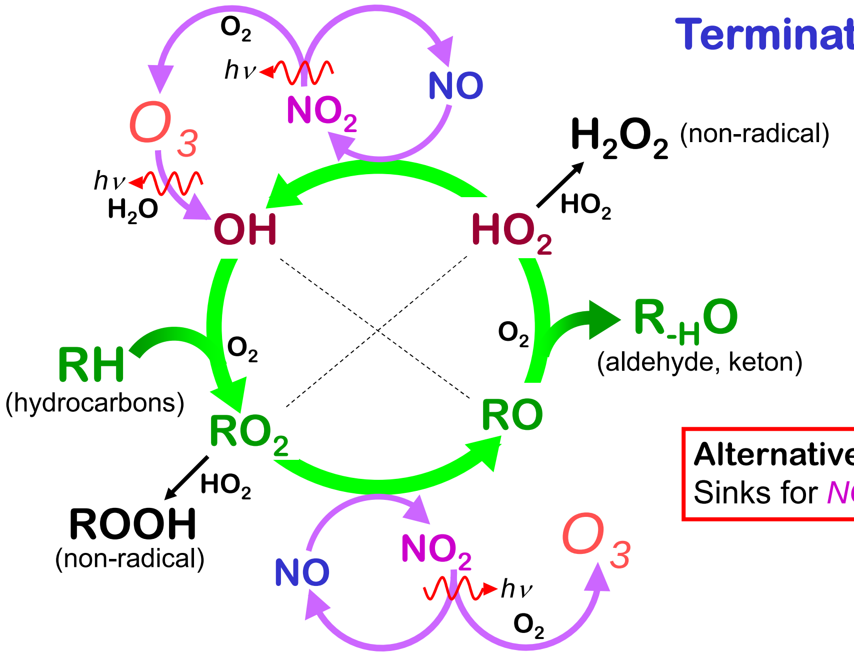
Hydrocarbon → aldehyde → organic acid → carbon monoxide → CO_2

$$RH \rightarrow R_{-H}O \rightarrow RCOOH \rightarrow CO \rightarrow CO_2$$

Oxidation number for carbon atom:

C(-IV) → C(0) → C(+II) → C(+II) → C(+IV)

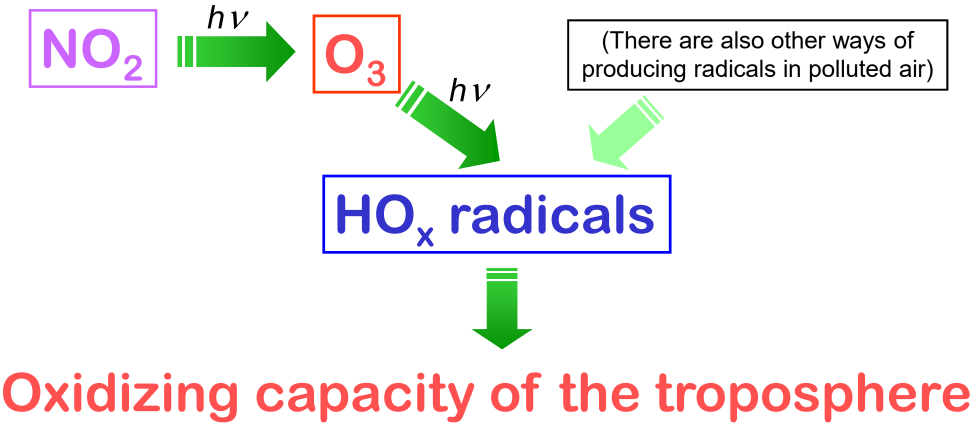
Termination



Alternative:
Sinks for NO_X.

Oxidants in the troposphere

NO_2 and solar radiation controls the production of O_3 , which in turn controls the production of HO_x radicals, which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.



NO_2 $\xrightarrow{h\nu}$ O_3 $\xrightarrow{h\nu}$ HO_x radicals

(There are also other ways of producing radicals in polluted air)

Oxidizing capacity of the troposphere

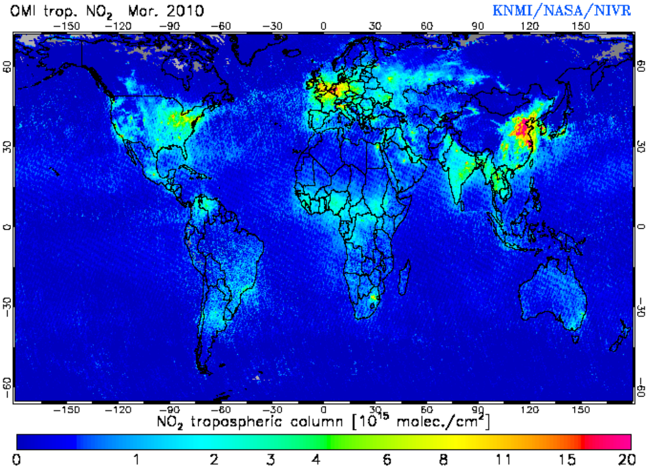
Sources of NO_x

	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
Total	**~46**

Sources of NO_x

Anthropogenic sources of NO_X (caused by human activities) dominate compared to the natural sources.

Levels of NO_2 measured from a satellite.



Sinks for NO_x

NO_X is mainly emitted as NO (at high temperatures).
NO_X is cycled between NO and NO_2 (~1 minute).

(11) $NO_2 + h\nu \rightarrow NO + O$ ($\lambda < 420$ nm)
(10.2) $O + O_2 + M \rightarrow O_3 + M$ (only way to produce O_3)
(14) $NO + O_3 \rightarrow NO_2 + O_2$

Net reaction:

$$\boxed{NO_2 + O_2 \overset{h\nu}{\Leftrightarrow} NO + O_3}$$

This however is no sink for NO_X .

Sinks for NO_x

Apart from removal of HO_X radicals, the catalytic ozone production cycle can also be broken by removing NO_X .

(30) $NO_2 + OH + M \rightarrow HNO_3 + M$ (daytime)

Nigthtime:

(31) $NO_2 + O_3 \rightarrow NO_3 + O_2$ (NO_3 rapidly photolyzed)

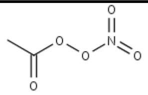
(32) $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$ (N_2O_5 water-soluble)

(33) $N_2O_5 + H_2O \rightarrow 2HNO_3$ (on an aerosol particle)

τ_{NOx} = ~1 day

HNO_3 is very water-soluble and is washed out by precipitation (wet deposition).

HNO_3 is not a long-term reservoir for NO_X (τ_{HNO3} = days).



PAN - Reservoir for NO_x

Peroxyacetylnitrate (PAN) is an efficient reservoir for NO_X .

PAN = $CH_3C(O)OONO_2$

PAN enables NO_X to be transported long distances and contribute to the levels of 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 NO_2 . Levels of PAN in polluted air can reach 1 ppb.

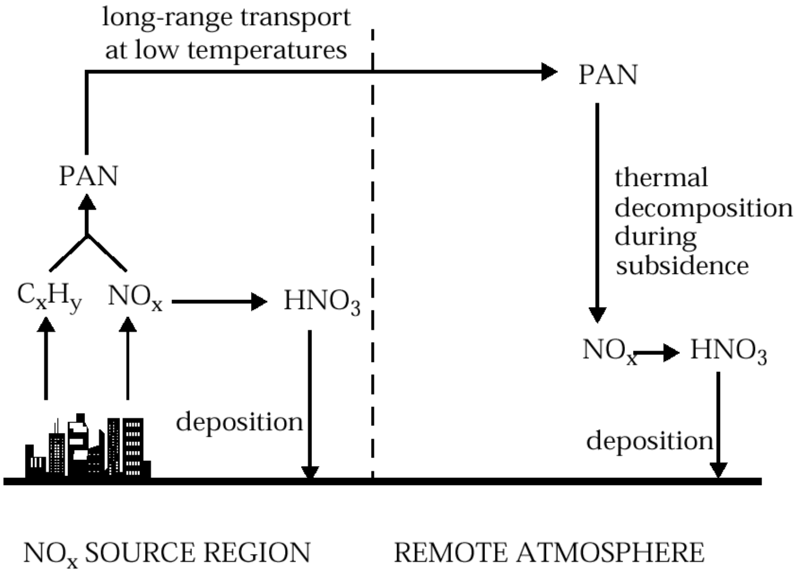
PAN is thermally unstable.

(37) $\text{PAN} \xrightarrow{\text{heat}} CH_3C(O)OO + NO_2$

τ_{PAN} = ~1 hour at 295 K (lower troposphere)

τ_{PAN} = months at 250 K (upper troposphere)

Long-range transport of NO_x via PAN



Global budget for tropospheric ozone

Ozone production in the troposphere is limited by the reactions

$HO_2 + NO \rightarrow OH + NO_2$ (70% globally)

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$ (20% globally)

$RO_2 + NO \rightarrow CH_3O + NO_2$ (10% globally)

followed by

$NO_2 + h\nu \rightarrow NO + O$ and $O + O_2 \rightarrow O_3$

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

Ozone loss in the troposphere is limited by the reactions

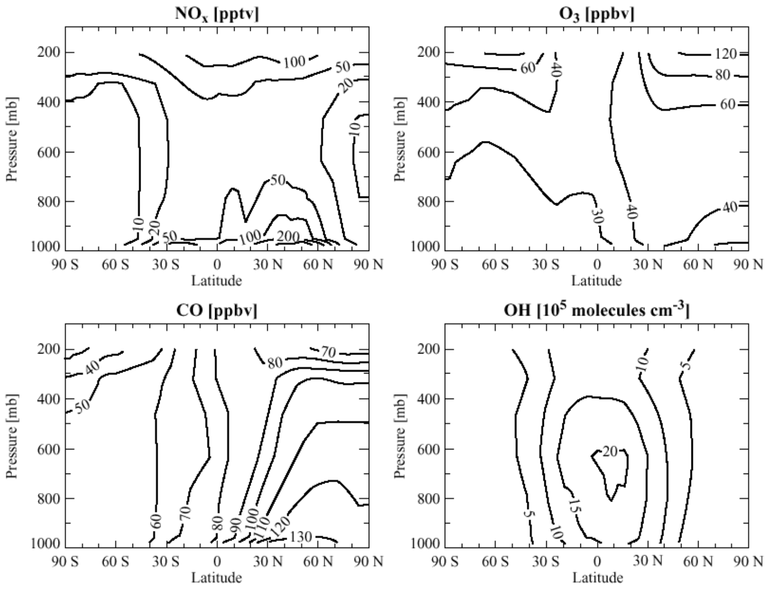
$O(^1D) + H_2O \rightarrow 2OH$ (40% globally, photolysis of O_3)

$HO_2 + O_3 \rightarrow OH + 2O_2$ (40% globally)

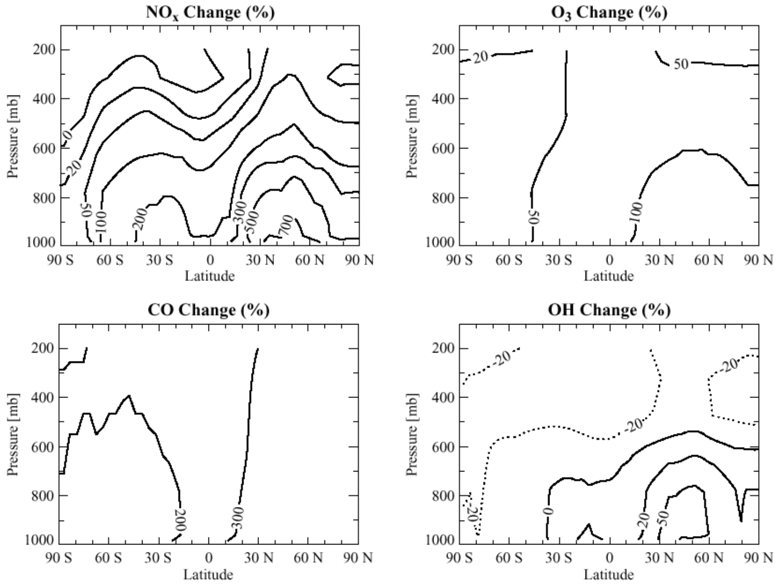
$OH + O_3 \rightarrow HO_2 + O_2$ (10% globally)

Dry deposition of ozone is also a significant sink.

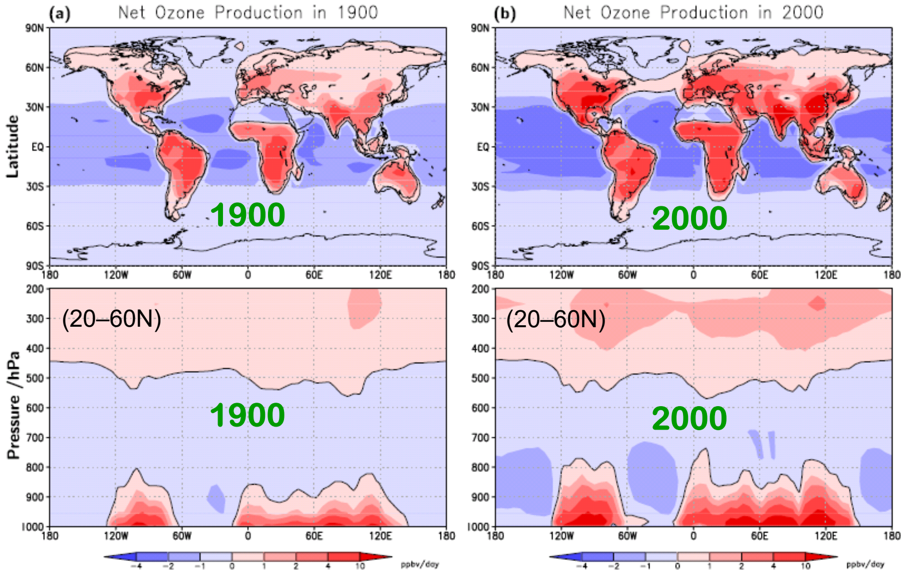
Global models of tropospheric ozone



Anthropogenic modifications of the troposphere



Modelled net O_3 production rates (ppbv/day)

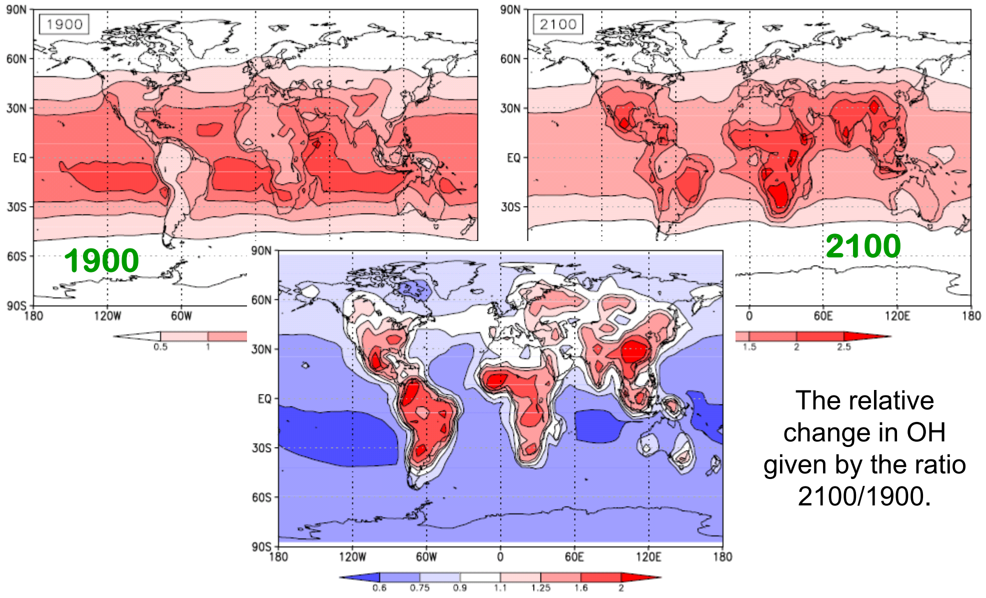


Annual mean distribution of net O3 production in ppbv/day in (top) the boundary layer and (bottom) at northern mid-latitudes (20–60N) in (a) 1900, and (b) 2000. The contour line marks zero net production.

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

Modelled OH concentrations 1900 - 2100

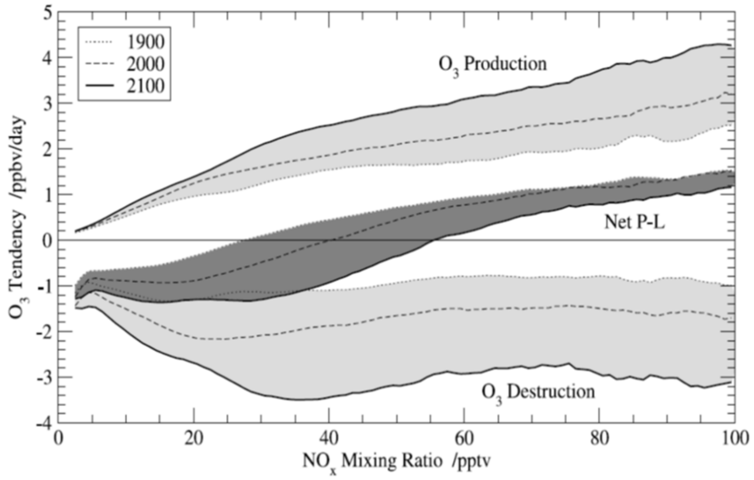
O. Wild, P.I. Palmer, How sensitive is tropospheric oxidation to anthropogenic emissions? GRL, VOL. 35, L22802, doi:10.1029/2008GL035718, 2008



The relative change in OH given by the ratio 2100/1900.

Annual mean distribution of OH (in units of 106 molecules cm−3) **in the boundary layer** in (left) 1900 and (right) 2100.

Modelled O_3 production and loss rates (ppbv/day)



Tropospheric O_3 production and loss rates (ppbv/day) below 250 hPa (10 km) as a function of NO*x* (pptv) for 1900, 2000, and 2100.
The critical NO*x* value for O_3 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

http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html

A searchable compilation of chemical reactions of atmospheric importance.

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

http://jpldataeval.jpl.nasa.gov/
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A compilation of kinetic and photochemical data prepared by the NASA Panel for Data Evaluation.