Atmospheric chemistry
Ground-level ozone
Photochemical smog

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Damage cost of air pollution in Europe (2010) and policy response

Source: " EC, 2013: Impact assessment for new policy package to clean up Europe's air"

- Damage cost of mortality – at least EUR 330 billion

- Direct economic damage - EUR 15 billion from workdays lost
- Direct economic damage - EUR 4 billion in healthcare cost

- Direct economic damage - EUR 3 billion crop yield loss

European Environment Agency

Health Effects of Air Pollution in Europe (EU-28)

Source: EEA, "Air Quality in Europe - 2016 Report"

The EEA recently estimated (EEA, 2016) that

the health impacts attributable to exposure to fine particulate matter (**PM2.5**) in the EU-28 were responsible for around

PM2.5 → **436 000 premature deaths annually**

The health impact of exposure to **NO_2** and **O_3** concentrations on the EU-population was estimated to be about

NO_2 → **68 000 premature deaths per year**
O_3 → **16 000 premature deaths per year**

European Environment Agency

http://www.eea.europa.eu/publications/air-quality-in-europe-2016

Health Effects of Air Pollution in Sweden

Sweden:

The total number of premature deaths can be estimated to approximately

5 500 per year **(EEA: 3 180)**

when taking into account differences in exposure-response for different PM sources.

Using the division between PM sources and NO_2 as an indicator of traffic combustion the total socio-economic cost (2010) would be

approximately 42 billion SEK

Source: Quantification of population exposure to NO2, PM2.5 and PM10 and estimated health impacts in Sweden 2010, Gustafsson, mfl, IVL Report B 2197, Dec 2014

Evolution of WHO air quality guidelines: past, present and future (2017)

http://www.euro.who.int/en/publications/abstracts/evolution-of-who-air-quality-guidelines-past,-present-and-future-2017

Ground-level ozone

Tropospheric ozone is both good and bad.

Ozone is needed to produce *OH* radicals via

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

OH is essential for the **oxidizing capacity of the troposphere** and the **lifetime of trace gases**.

High levels of ozone are dangerous to humans, plants and and materials.

Preindustrial ozone levels in the lower troposphere were ~ 10-15 ppb. Increased emissions of hydrocarbons and nitrogen oxides have caused an increase in ozone background levels to ~30 ppb.

Background levels of ground-level ozone have increased 2-3 times.

Ground-level ozone – Photochemical smog

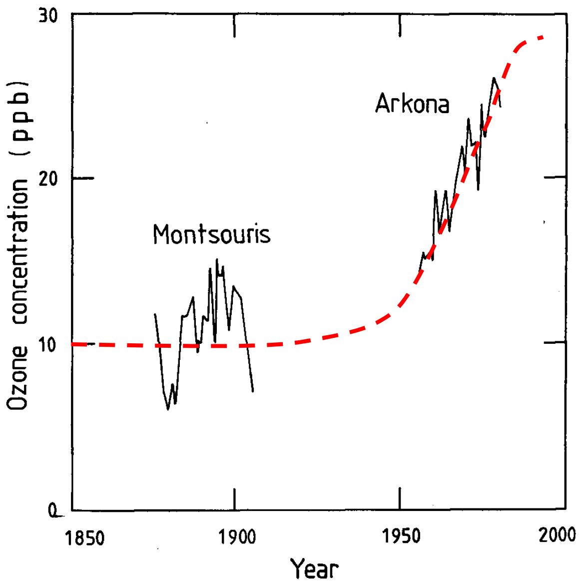
Background levels of ozone in the lower troposphere have increased from

10-15 ppb to

~30 ppb.

Ozone is a secondary pollutant.

Ozone is formed through chemical processes in the atmosphere and is not emitted from any source.



Ground-level ozone

High levels of ozone is dangerous to

humans
Irritation of airways and eyes

plants
destroy leaf stomata (*klyvöppningar*), wax layers, cell membranes and enzymes

and materials
Breaking down organic materials (rubber, plastics, paints)

Several air quality limit values and guidelines are in force in order to protect human health, plants and materials.

Damages to plants occur from [O_3] ~25-40 ppb.
Damages to human health occur from [O_3] ~40-60 ppb.

Ground-level ozone and crop damage

http://icpvegetation.ceh.ac.uk/publications/documents/EvidenceReportFINALPRINTEDVERSIONlow-res.pdf

Ozone exposure experiments, UK.

Ozone-sensitive (left) and ozone-resistant (right) white clover after exposure to ambient ozone for four weeks in Greece. Source: C. Saitanis

Ground-level ozone and crop damage

http://icpvegetation.ceh.ac.uk/publications/documents/EvidenceReportFINALPRINTEDVERSIONlow-res.pdf

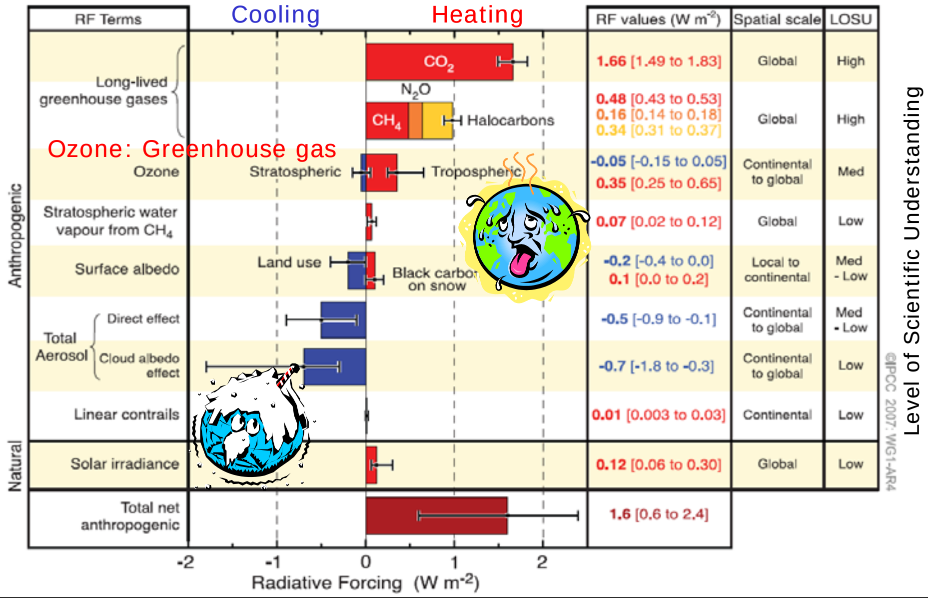
Ozone damage on tobacco bioindicator plants in Sweden (left leaf) and uninjured leaf from a filtered-air greenhouse *(right leaf). Håkan Pleijel*

Ozone injury on Trifolium subterraneum *in Sweden. Håkan Pleijel*

Intergovernmental Panel on Climate Change

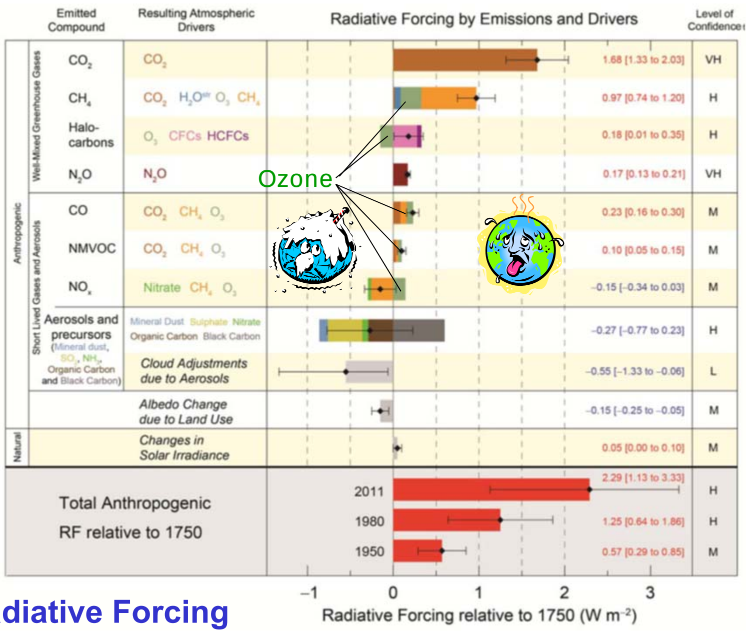
4th Assessment Report 2007

Radiative Forcing (W/m^2)



Intergovernmental Panel on Climate Change

5th Assessment Report 2013



Radiative Forcing

Photostationary equlibrium for ozone

In a **sunlit atmosphere with** NO **and** NO_2 **but without hydrocarbons:**

(11.11) $NO_2 + h\nu \rightarrow NO + O$ (λ< 420 nm)
(10.2) $O + O_2 + M \rightarrow O_3 + M$ (only way to produce O_3)
(11.14) $NO + O_3 \rightarrow NO_2 + O_2$

Net reaction:

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

A **photostationary equilibrium** exists.

More sun light (λ< 420 nm) gives more ozone O_3.

NO consumes ozone. In the vicinity of strong sources of NO, then O_3 is titrated out and can be entirely depleted (e.g. close to a smoke stack or the tail pipe of a car.)

Photostationary equilibrium for ozone

In a sunlit atmosphere with NO and NO_2 but without hydrocarbons:

(11.11) $NO_2 + h\nu \rightarrow NO + O$ (λ< 420 nm)
(10.2) $O + O_2 + M \rightarrow O_3 + M$ (only way to produce O_3)
(11.14) $NO + O_3 \rightarrow NO_2 + O_2$

Assuming ”steady state” conditions for O and O_3 →

$$0 = \frac{d}{dt}[O] = k_{11}[NO_2] - k_2[O][O_2][M] \quad \Rightarrow [O] = \frac{k_{11}[NO_2]}{k_2[O_2][M]}$$

$$0 = \frac{d}{dt}[O_3] = k_2[O][O_2][M] - k_{14}[NO][O_3] \quad \Rightarrow [O_3] = \frac{k_{11}[NO_2]}{k_{14}[NO]}$$

Expression for a photostationary equilibrium for ozone.

Photostationary equilibrium for ozone

We can use the photostationary equlibrium for ozone in a sunlit atmosphere with *NO* and NO_2 but without hydrocarbons

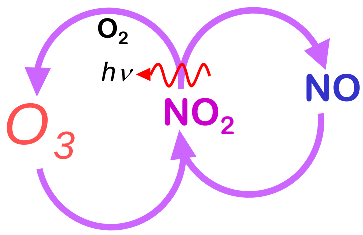
$$[O_3] = \frac{k_{11}[NO_2]}{k_{14}[NO]}$$

to calculate $[O_3]$.

For initial concentrations of $[NO_2]$ = $[NO]$ = 1 ppb (noon-time at 50°N) the ozone levels reach a stationary state within ~100 s and with $[O_3]$ = 23 ppb.

This is less than the ozone levels that are typically observed in tropospheric polluted air ➔

More reactions for ground-level ozone production are needed!

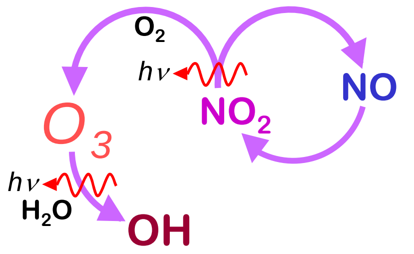


Photostationary equilibrium

In the absence of hydrocarbons (*RH* or VOC)

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

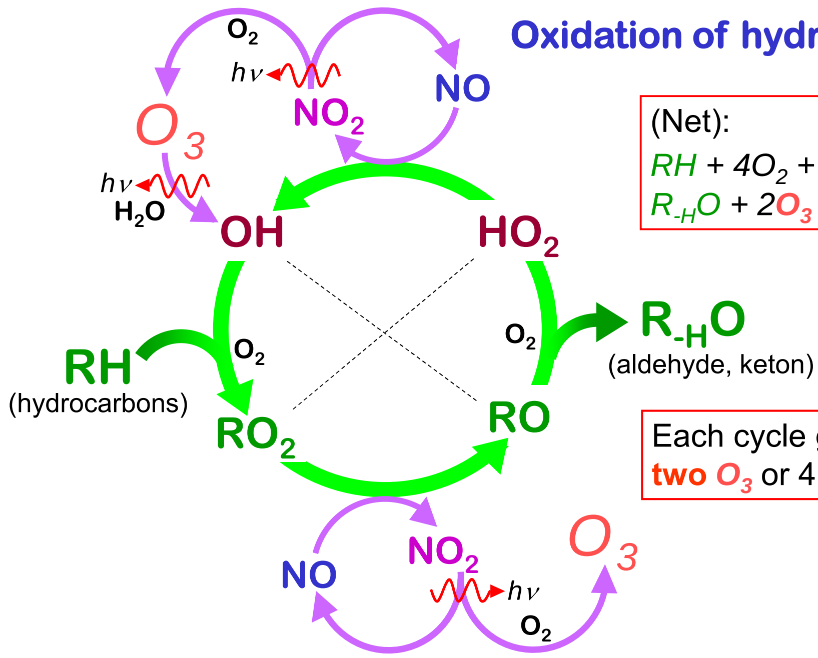
Oxidation of hydrocarbons



Production of the hydroxyl radical *OH*

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

Oxidation of hydrocarbons



(Net):
$RH + 4O_2 + 2h\nu \rightarrow$
$R_{-H}O + 2O_3 + H_2O$

Each cycle gives net **two** O_3 or 4 *OH*.

Oxidation of hydrocarbons in a photochemical smog

Example: Alkanes RH

(4)	$RH + OH$	$\rightarrow$	$R + H_2O$
	$R + O_2\,(+M)$	$\rightarrow$	$RO_2\,(+M)$
(5)	$RO_2 + NO$	$\rightarrow$	$RO + NO_2$
(6)	$RO + O_2$	$\rightarrow$	$R_{-H}O + HO_2$
(7)	$HO_2 + NO$	$\rightarrow$	$OH + NO_2$

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

2x ($NO_2 + h\nu \rightarrow NO + O$ and $O + O_2 \rightarrow O_3$)

(Net) $RH + 4O_2 + 2h\nu \rightarrow R_{-H}O + 2O_3 + H_2O$

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

Each cycle produces net $2O_3$ or $4OH$.

Shifting the equilibrium towards more ozone

Hydrocarbons are needed to shift the equilibrium to the right, that is towards a **higher ozone production**.

Hydrocarbons consume NO (by producing peroxyl radicals HO_2 and RO_2, which in turn react with NO).

More sun light (λ< 420 nm) **gives more ozone** O_3.

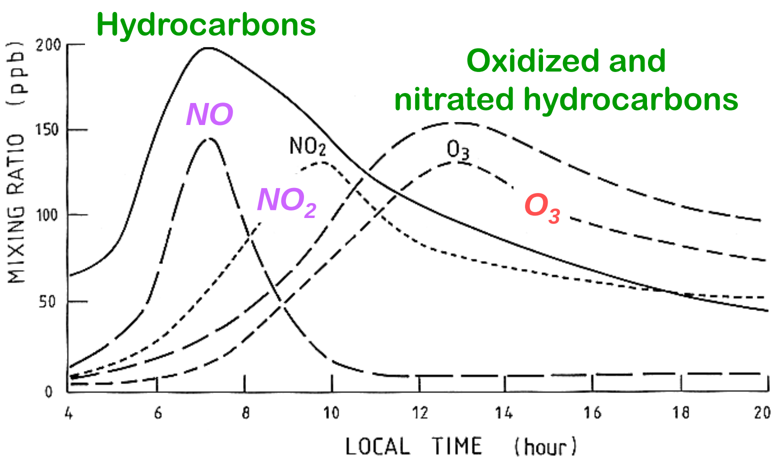
$$NO_2 + O_2 \overset{h\nu}{\Leftrightarrow} NO + O_3$$

Prerequisites for high ozone levels:

- **Sun light** (λ< 420 nm)
- **Hydrocarbons**
- **Nitrogen oxides** (NO_X)

Ground-level ozone – Photochemical smog

Levels of ozone, hydrocarbons and nitrogen oxides often follow a diurnal pattern in polluted environments (e.g. big cities).

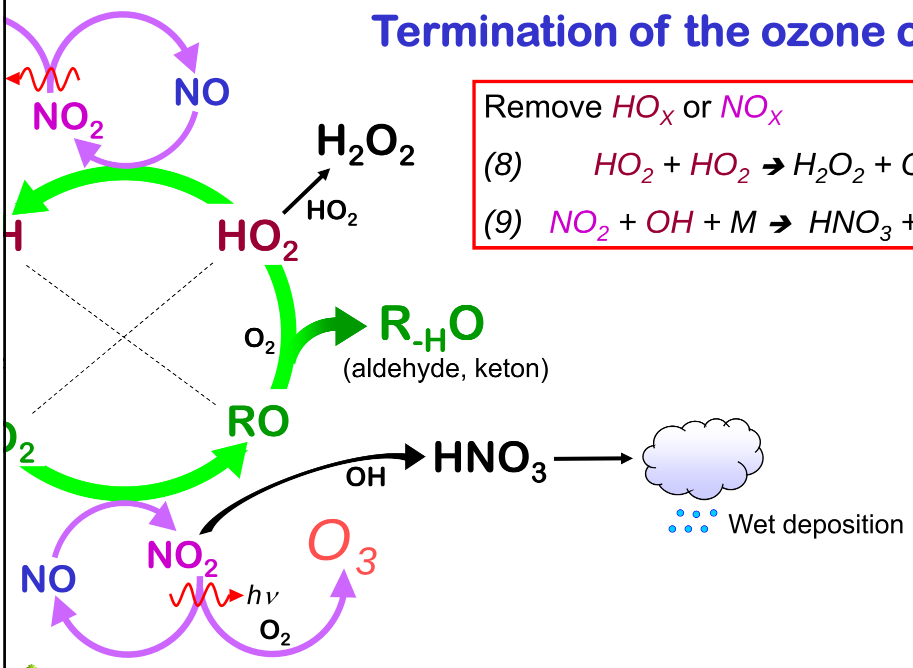


Termination of the ozone cycle

Remove HO_X or NO_X

(8) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

(9) $NO_2 + OH + M \rightarrow HNO_3 + M$



Ozone cycle

Production of O_3 is limited by reactions with NO

$$P_{O3} = k_5[RO_2][NO] + k_7[HO_2][NO] \approx 2k_7[HO_2][NO]$$

We can also assume a stationary state for OH

$$P_{OH} = L_{OH} \Rightarrow k_7[HO_2][NO] = k_4[RH][OH]$$

$$\Rightarrow [OH] = \frac{k_7[HO_2][NO]}{k_4[RH]}$$

Also assume a stationary state for the entire HO_X family

"low NO_X" "high NO_X"

$$P_{HOx} = L_{HOx} = k_8[HO_2]^2 + k_9[NO_2][OH][M]$$

NO_X -limited ozone production

Low NO_X

$$P_{HOx} \approx k_8[HO_2]^2 \quad \text{and} \quad P_{O3} \approx 2k_7[HO_2][NO] \quad \Rightarrow$$

$$\Rightarrow P_{O3} = 2k_7[NO] \cdot \sqrt{\frac{P_{HOx}}{k_8}}$$

At low $[NO_X]$ conditions, the **production of O_3 is proportional to** $[NO]$, **but independent of the hydrocarbon concentration** $[RH]$.

"NO_X - limited regime"

At low NO_X it is useless to try to decrease the ozone levels by limiting emissions of hydrocarbons.

Ozone production is often NO_X – limited in an air mass which has been transported some distance away from the source (τ_{NOx} = ~1 day).

VOC -limited ozone production

High NO_X

$$P_{HOx} \approx k_9[NO_2][OH][M] \;\Rightarrow\; \ldots\ldots \;\Rightarrow \ldots\ldots$$

$$\Rightarrow P_{O3} = \frac{2k_4 P_{HOx}[RH]}{k_9[NO_2][M]}$$

RH is often denoted VOC (Volatile Organic Compounds).

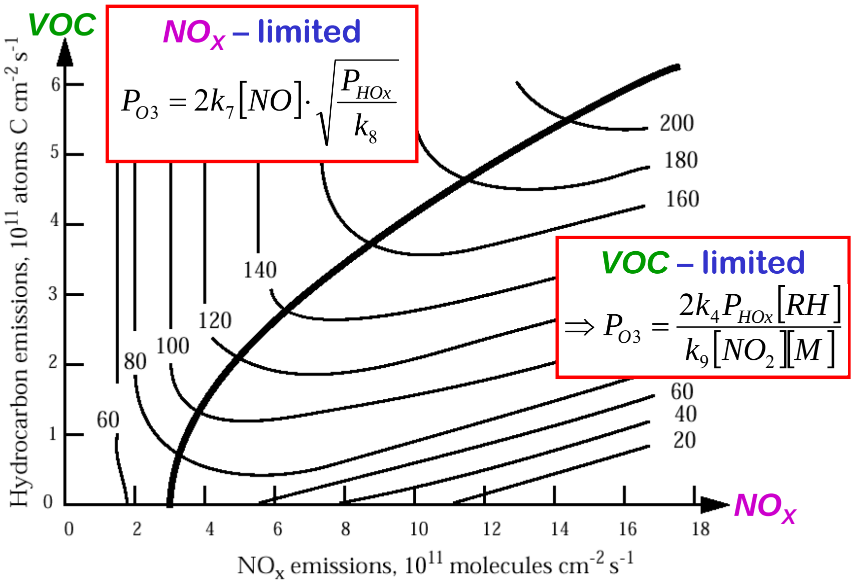
At high [NO_X] the production of O_3 is proportional to [*RH*] and inversely proportional to [NO_2],

"*VOC* - limited regime"

At high NO_X it is useless to try to decrease the ozone levels by limiting emissions of NO_X.

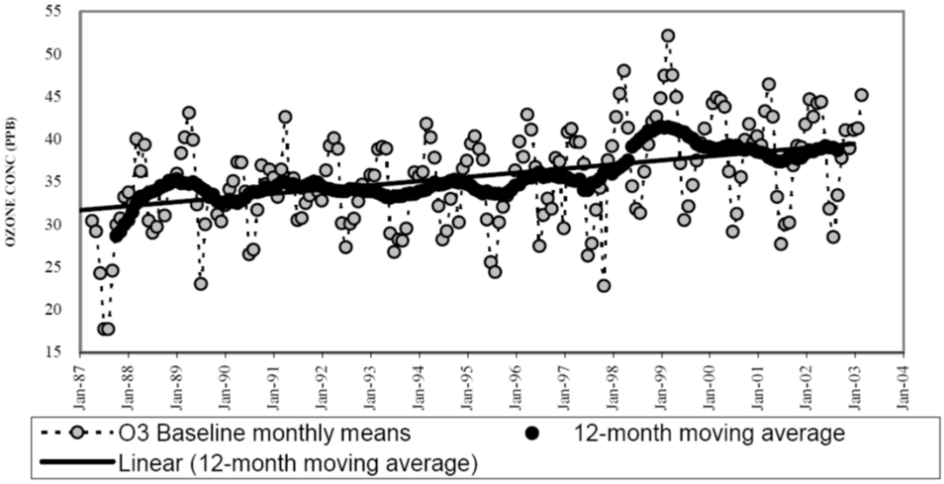
Ozone production is often *VOC* – limited close to the source.

Regimes for ozone production

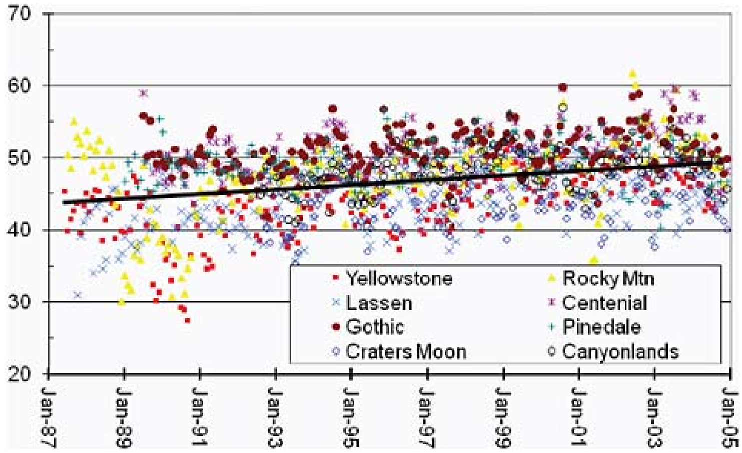


Hemispheric background levels of ground-level ozone have increased by ~5 ppb per decade the last 20-30 years.

Data from the station Mace Head on the west coast of Ireland.



US background sites show a ground-level ozone trend ~3.4 ppb per decade the last 20 years

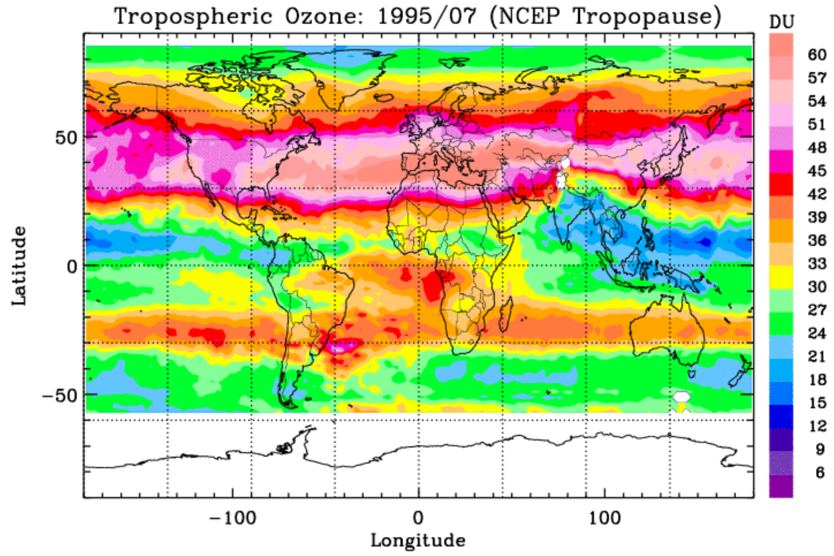


Monthly mean O_3 abundances (ppb) from 1987 to 2005 from eight rural CASTNET sites in the western U.S. The average seasonal pattern at each site has been removed and a linear regression fit to the data: +0.34 ppb/yr.

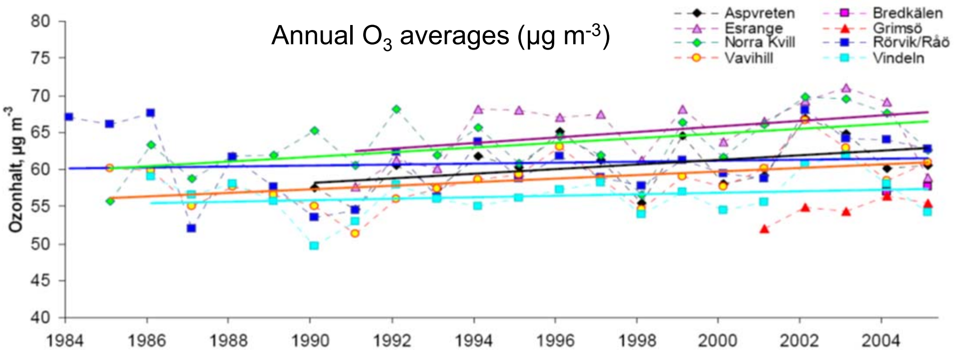
D. Jaffe and J. Ray, Increase in surface ozone at rural sites in the western U.S., Atmospheric Environment Vol. 41, 2007.

Example of satellite measurements of O_3

GOME tropospheric ozone columns (Dobson units) for July 1995

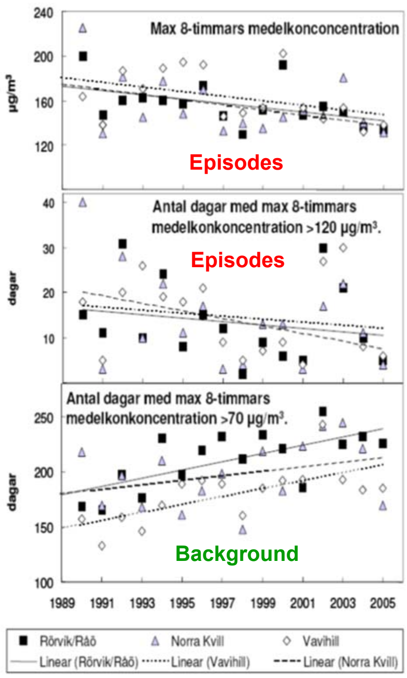


Trends in ground-level ozone in Swedish background air



In Europe, there is a trend that the **background concentrations of ground-level ozone are increasing**, while the number of **ozone episodes is decreasing**.
Episodes are short periods with highly elevated ozone concentrations, typically reaching above 120 µg m^{-3}.
The figure shows annual averages for Swedish EMEP stations since the start of the measurements.

Trends in ground-level ozone in Swedish background air



Air quality threshold values for Sweden and EU for ground-level ozone (*tröskelvärden*)

http://www.aces.su.se/reflab/gransvarden/norm_ozon.html

Levels not to be exceeded due to risk of damage on ***vegetation***	AOT40 (over 5 years) 18000 (μg/m³)·h	Exceeded during summer in whole Sweden
	200 μg/m³ hourly average	Exceeded at rare occasions in southern Sweden
Levels not to be exceeded due to risk of effects on ***human health***	120 μg/m³ (2010) 8 hour average	Exceeded several times every year in southern and middle Sweden
Level when the public should be *informed*	180 μg/m³ hourly average	Exceeded only a few times in southern Sweden
Level when the public should be *warned*	240 μg/m³ hourly average	Never exceeded in Sweden

1 ppb ozone = 2 μg/m³

Updated 2007

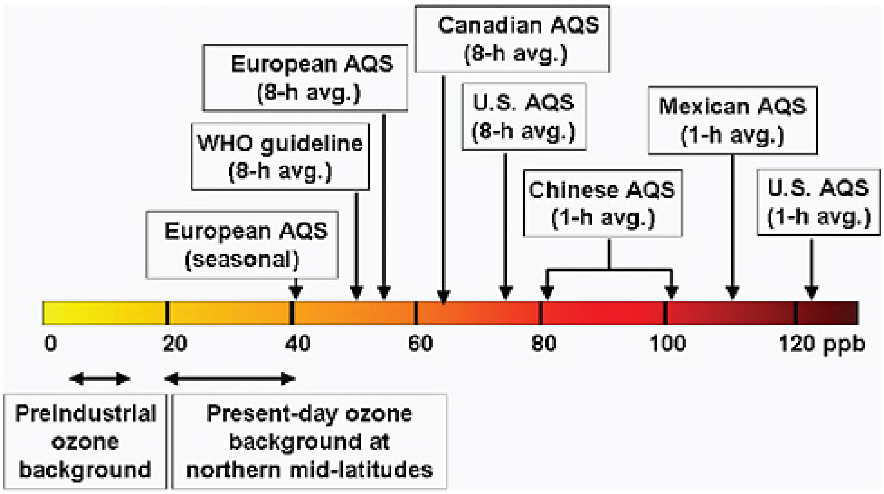
Air quality threshold values for Sweden and EU for ground-level ozone (*tröskelvärden*)

http://www.aces.su.se/reflab/gransvarden/norm_ozon.html

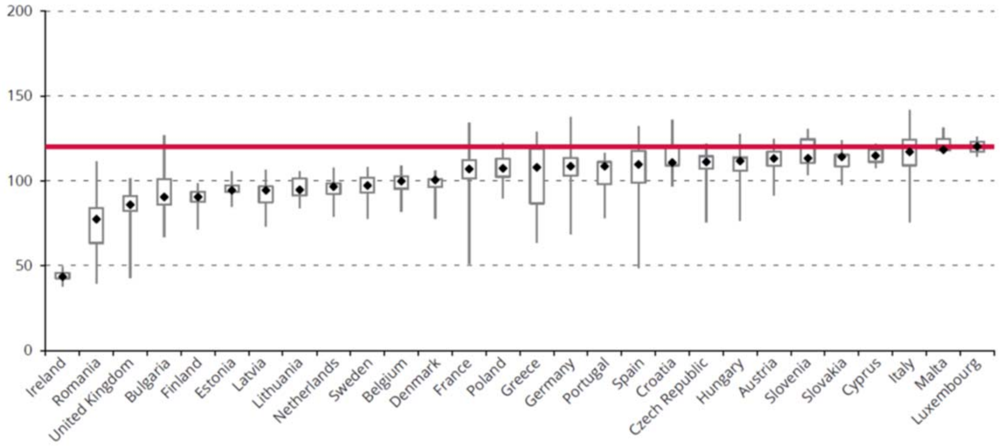
Table 5.1 Air-quality standards for O_3 as defined in the EU Ambient Air Quality Directive and WHO air quality guidelines

Averaging period	EU Air Quality Directive		WHO AQG	UNECE CLRTAP critical level
	Objective and legal nature	Concentration		
Maximum daily 8-hour mean	Human health long-term objective	120 µg/m³	100 µg/m³	
	Human health target value	120 µg/m³, not to be exceeded on more than 25 days per year averaged over 3 years		
AOT40 accumulated over May to July	Vegetation long-term objective	6 000 (µg/m³).h		10 000 (µg/m³).h (protection of forests)
	Vegetation target value	18 000 (µg/m³).h averaged over 5 years		
1 hour	Information threshold	180 µg/m³		
	Alert threshold	240 µg/m³		

Various Air Quality Standards for ground-level ozone



O3 concentrations in relation to the target value in 2014 in the EU-28

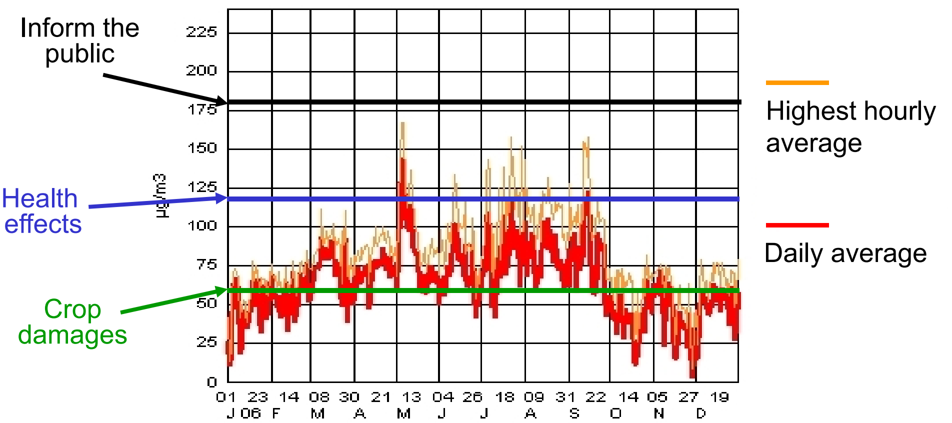


Notes: The graph is based, for each Member State, on the 93.2 percentile of maximum daily 8-hour mean concentration values, corresponding to the 26th highest daily maximum of the running 8-hour mean. For each country, the lowest, highest and median values (in µg/m3) at the stations are given. The rectangles mark the 25th and 75th percentiles. At 25 % of the stations, levels are below the lower percentile; at 25 % of the stations, concentrations are above the upper percentile. The target value threshold set by the EU legislation is marked by the red line.

Ground-level ozone background levels in Skåne

http://www.ivl.se/miljo/projekt/ozon/
http://www.eea.europa.eu/maps/ozone/map

Daily averages and highest hourly averages in southern Sweden
Station Vavihill (Söderåsen) 2006



Ozone damage to growing crops

Crop yields decrease with increasing accumulated exposure to ozone above the threshold level 40 ppb (AOT40). AOT40 should be < 3000 ppb·h during the growing season (5% loss in crop yield).

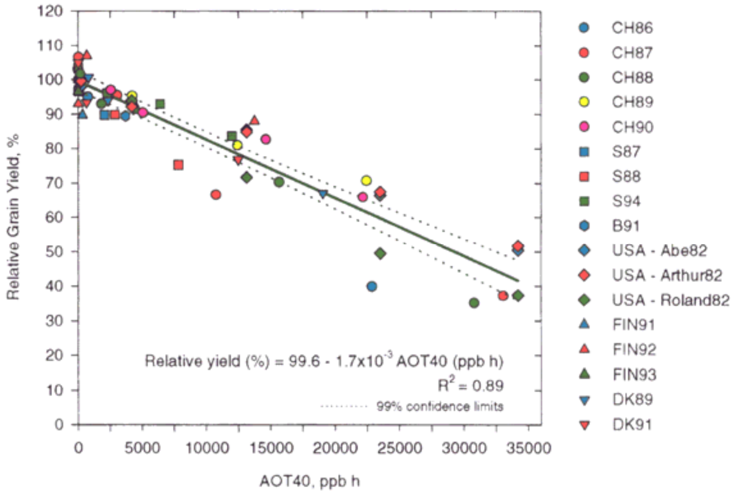
AOT40 is the accumulated amount of ozone over the threshold value of 40 ppb, that is:

AOT40 = $\int \max(O_3 - 40\ \text{ppb}, 0.0)\,dt$

where the max function ensures that only ozone values exceeding 40 ppb are included.

The integral is taken over time, namely the relevant growing season for the vegetation concerned, and for daytime only.

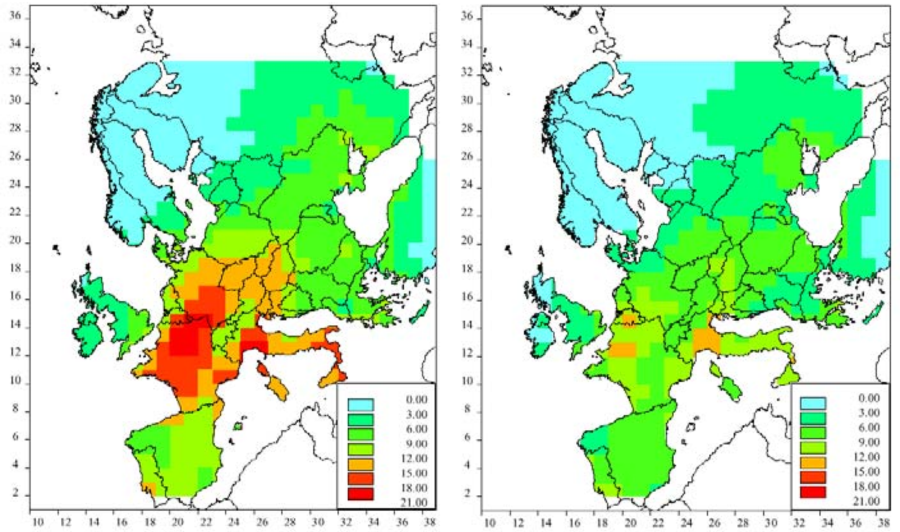
The corresponding unit are ppb·hours (abbreviated to ppb·h).



AOT40 based on the RAINS model

AOT40 (ppm·h)

for 1990 emissions — Emissions according to the protocol

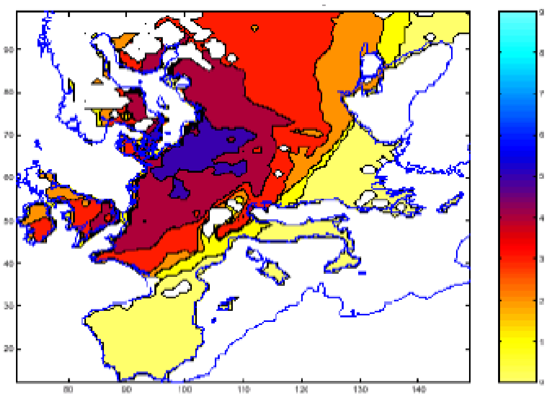


Growing crops take up ozone through their stomata (*klyvöppningar*)

AOT40 quantifies ozone exposure, not ozone uptake.

Southern Europe:
High ozone levels but dry climate

➔ Stomata closed
(klyvöppningarna stängda)
➔ Less ozone uptake



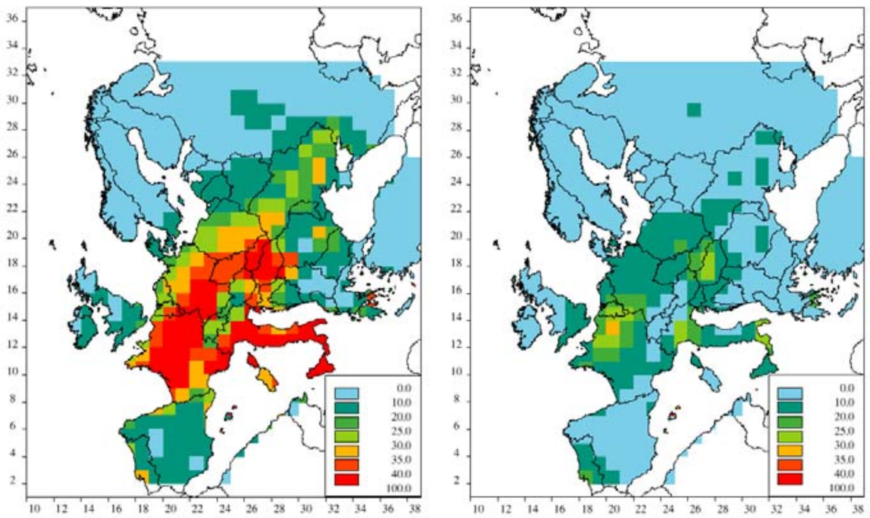
Estimated ozone uptake by growing crops through the stomata, June (nmol m-2 s-1)

Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe, EMEP Report 1&2 2002, http:/ /www.emep.int

Ground-level ozone levels based on the RAINS model

Number of days with ozone levels above 60 ppb

for 1990 emissions | Emissions according to the protocol



Exposure of agricultural area (left) and exposure of forest area (right) to ozone (AOT40 in µg/m3.h) in the EEA-32 member countries (2003/2004–2011)