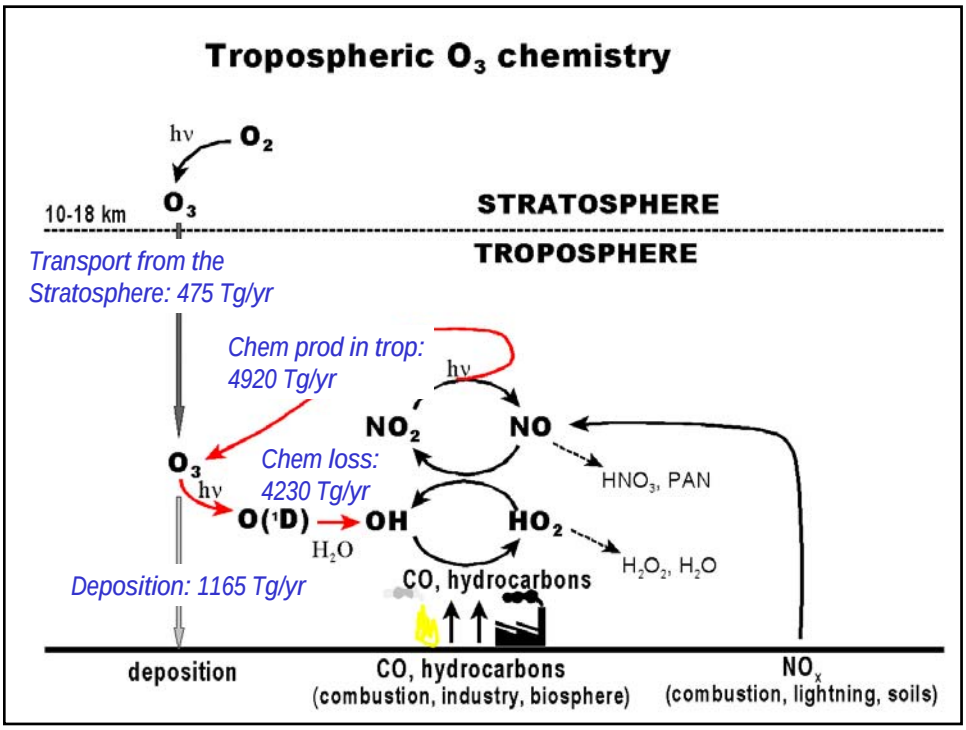
Tropospheric ozone and nitrogen oxides



Global budget of tropospheric ozone

- O_3 is supplied to the troposphere by transport from stratosphere
- Local production of O_3 by reactions of peroxy radicals with NO:

$$HO_2 + NO \rightarrow OH + NO_2 \quad [R1]$$
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad [R2]$$
$$RO_2 + NO \rightarrow RO + NO_2 \quad [R3]$$

followed by photolysis of NO_2

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$P(O_3) = (k_1 [HO_2] + k_2 [CH_3O_2] + k_3 [RO_2])[NO]$$

- Loss of O_3 by dry deposition (reaction with organic material at the earth's surface) and photochemical reactions:

$$[O_3 + h\nu \rightarrow O_2 + O(^1D)]$$
$$O(^1D) + H_2O \rightarrow OH + OH \quad [R4]$$
$$HO_2 + O_3 \rightarrow OH + 2\,O_2 \quad [R5]$$
$$OH + O_3 \rightarrow HO_2 + O_2 \quad [R6]$$
$$L(O_3) = k_4 [H_2O][O(^1D)] + k_5 [HO_2][O_3] + k_6 [OH][O_3] + L_{deposition}$$

Tropospheric O_3 Budget

Table 11-4 Present-Day Global Budget of Tropospheric Ozone

	$Tg\ O_3\ yr^{-1}$
Sources	3400–5700
Chemical production	3000–4600
$HO_2 + NO$	(70%)
$CH_3O_2 + NO$	(20%)
$RO_2 + NO$	(10%)
Transport from stratosphere	400–1100
Sinks	3400–5700
Chemical loss	3000–4200
$O(^1D) + H_2O$	(40%)
$HO_2 + O_3$	(40%)
$OH + O_3$	(10%)
others	(10%)
Dry deposition	500–1500

Jacob, Introduction to Atmospheric Chemistry

Role of NO_x in O_3 production

- **Too little NO_x:** O_3 loss (HO_2+O_3, $OH+O_3$) rather than radical cycling (e.g. HO_2+NO) leading to net O_3 chemical destruction.

  $P(O_3)<L(O_3)$ ($NO_x \approx$ a few pptv. Marine troposphere)

- **Intermediate NO_x**: efficient O_3 production via cycling of HO_x and NO_x radicals.

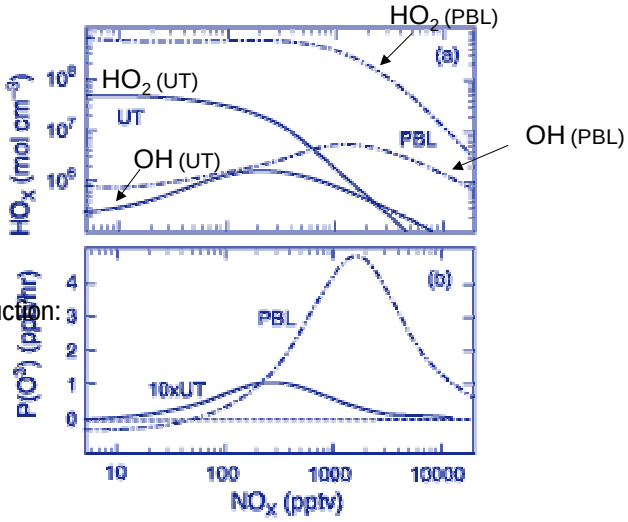
$P(O_3)>L(O_3)$ (Global free troposphere), $P(O_3)\uparrow$ as $NO_x\uparrow$

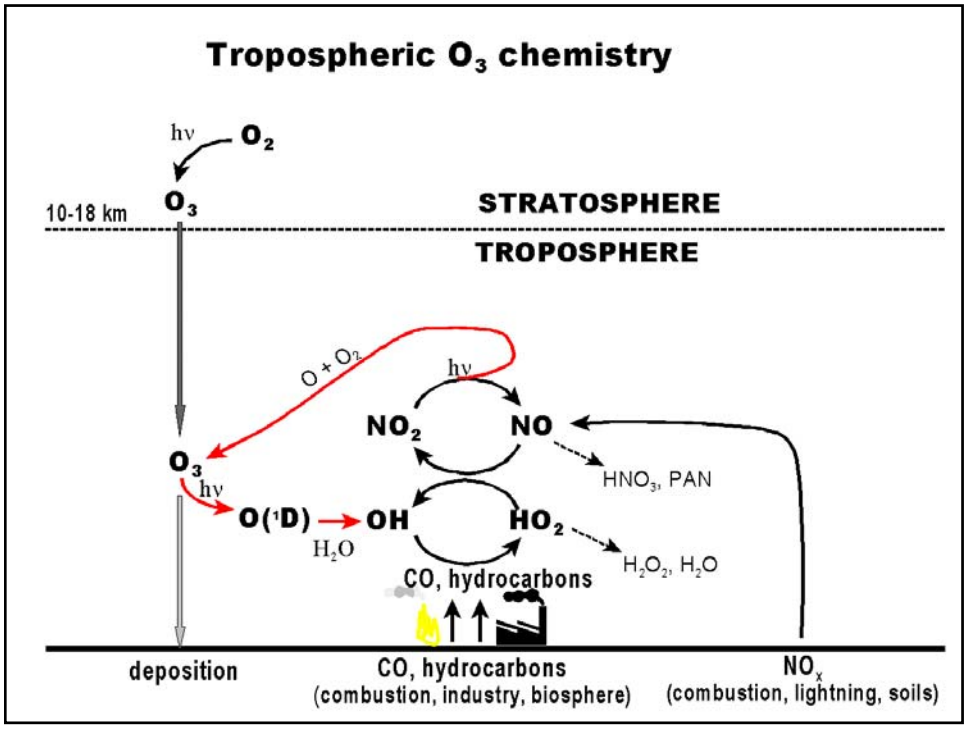
- **Too much NO_x**: Radical termination by alternate route (e.g. $OH+NO_2$).

$P(O_3)$ decreases with increases in NO_x
(NO_x> a few hundred pptv, urban and rural atmosphere)

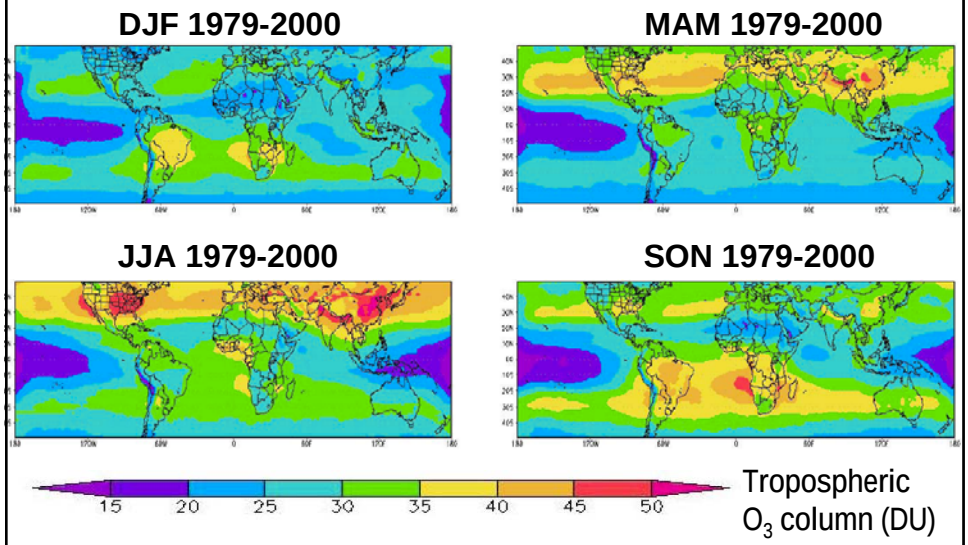
NO_x and O_3 production in the planetary boundary layer (PBL) and in the upper troposphere (UT)

Net ozone production: $P(O_3)-L(O_3)$



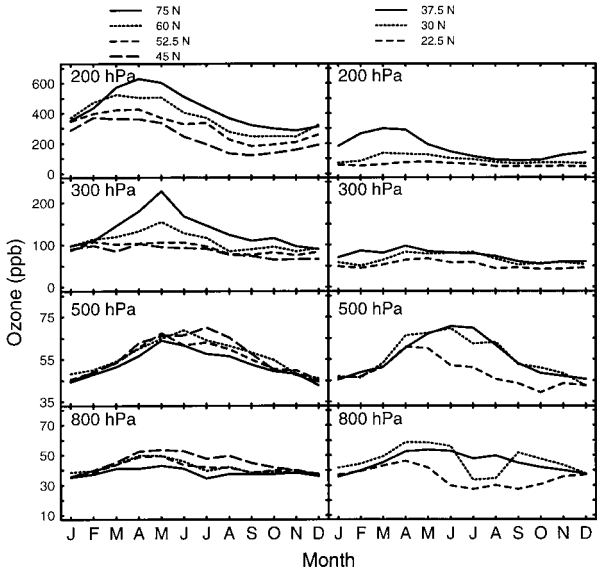


Seasonal climatology of tropospheric ozone seen by satellite



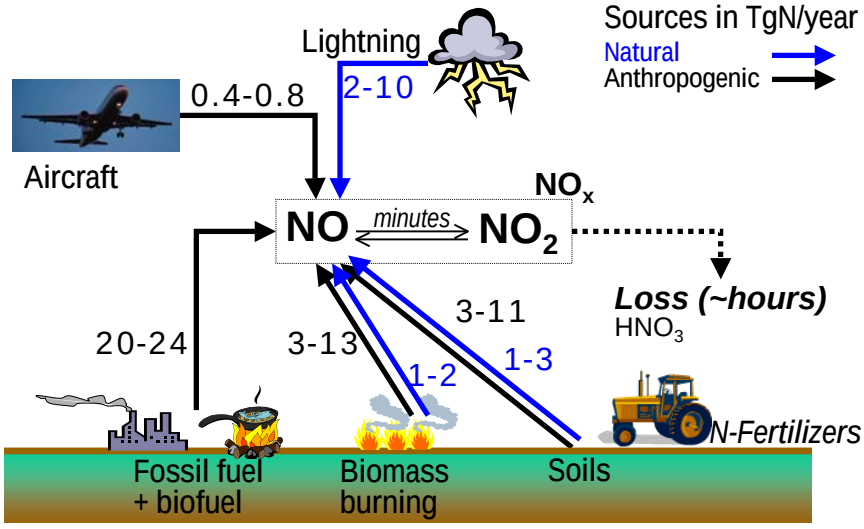
Fishman et al., Atmos. Chem. Phys., 3, 2003

Climatological annual cycle of O_3 for 22.5°N to 75°N



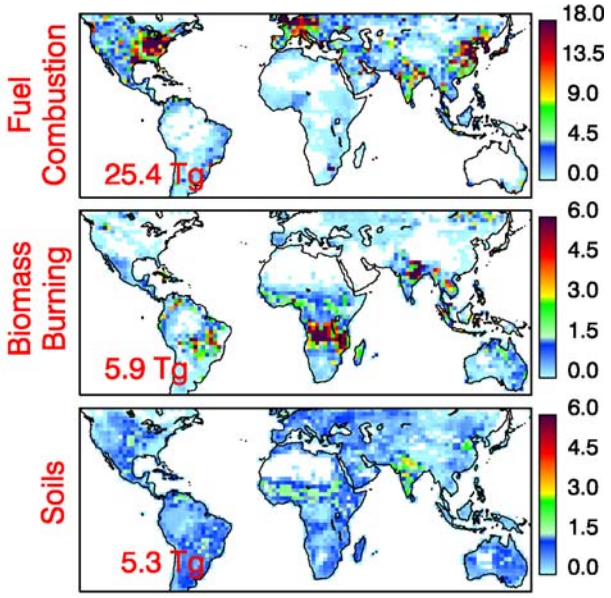
Logan, J. A., J. Geophys. Res., 104, 16115-16149, 1999

Global sources of nitrogen oxides (NO_x)

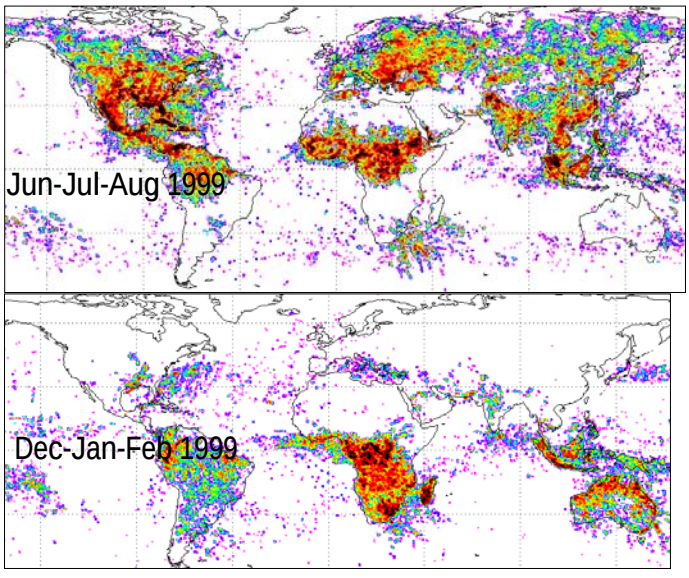


Anthropogenic activity → 3-6 fold increase in NO_x emissions

Distribution of surface NOx emissions



Lightning flashes seen from space



NOx source
~3-6 TgN/yr

http://thunder.nsstc.nasa.gov/data/otdbrowse.html

Chemistry of nitrogen oxides in the troposphere

- Sources from fossil fuel combustion, biomass burning, soils, lightning (emitted as NO)
- Rapid cycling between NO and NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + h\nu\ (+O_2) \rightarrow NO + O_3$$

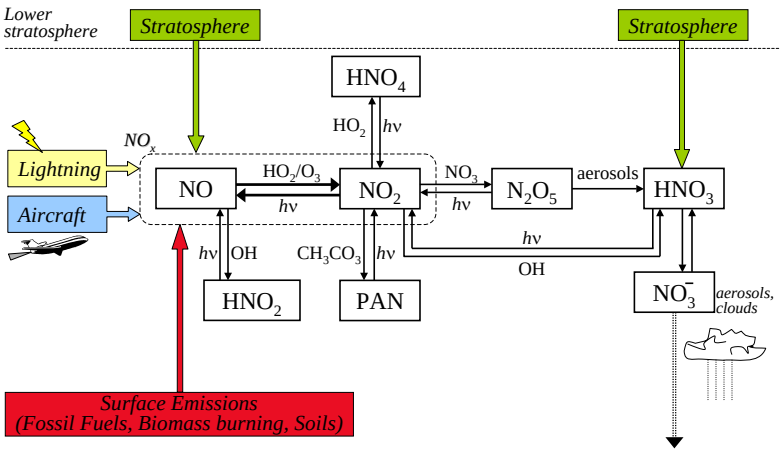
- Sink by formation of HNO_3, during daytime:

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

at night:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$
$$N_2O_5 + \text{aerosol}\ (+H_2O) \rightarrow 2\ HNO_3$$

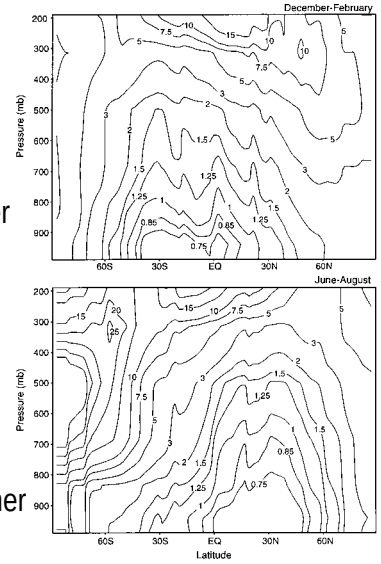
- HNO_3 scavenged by precipitation in the lower troposphere within a few days (wet deposition). NO, NO_2 and HNO_3 taken up by plants over continents (dry deposition). In the upper troposphere, HNO_3 is recycled back to NO_x by photolysis or reaction with OH.
- Lifetime of NO_x: ~hours near the surface, but 1-2 weeks in upper troposphere.



NO_x chemical lifetime (in days)

winter

summer



[1] $NO + O_3 \rightarrow NO_2 + O_2$
[2] $NO_2 + hv \rightarrow NO + O$
[3] $NO_2 + OH + M \rightarrow HNO_3 + M$

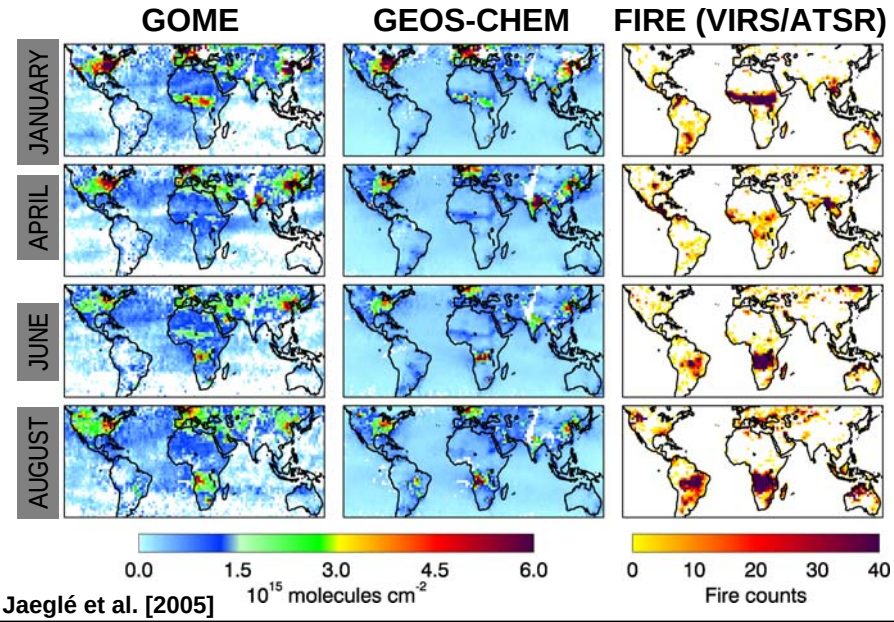
$\tau_{NOx} = [NO_x]/(k_3[NO_2][OH])$
$=(1 + [NO]/[NO_2])/k_3[OH]$
with $[NO]/[NO_2] = J_2/(k_1[O_3])$

In UT k_1 ~5 times smaller than in BL
[$k_1 = 2\ 10^{-12} \exp(-1400/T)$ molec/cm^3/s]
And OH much smaller in UT than in BL

➔longer lifetime of NO_x in the UT.

Levy II, H., et al., J. Geophys. Res., 104, 26279-26306, 1999

Mapping of Tropospheric NO_2 columns from space: 2000



Jaeglé et al. [2005]

Long range transport of anthropogenic NO_x: formation of PAN

- Peroxyacetyl nitrate (PAN, $CH_3C(O)OONO_2$) is produced by photooxidation of hydrocarbons in the presence of NO_x. Case of acetaldehyde (CH_3CHO):

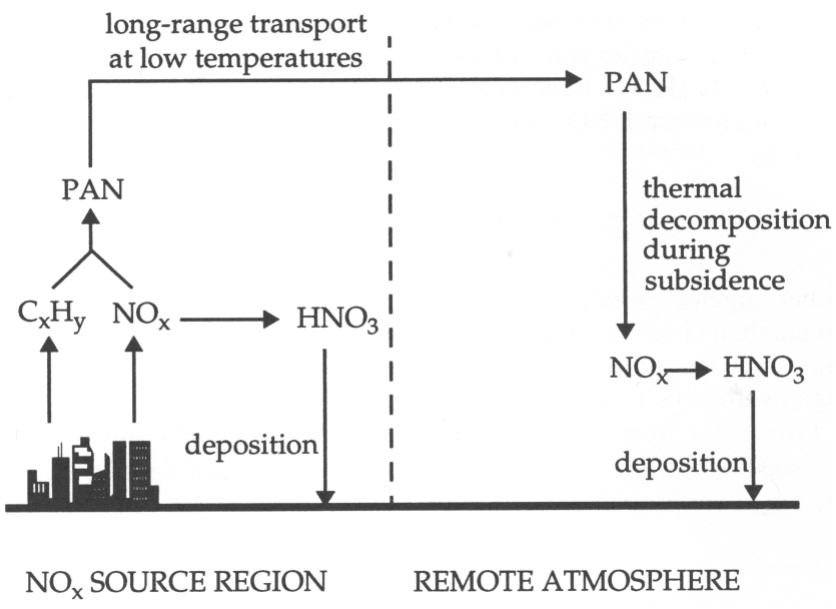
$$CH_3CHO+OH \rightarrow CH_3CO+H_2O$$
$$CH_3CO+O_2+M \rightarrow CH_3C(O)OO+M$$
$$CH_3C(O)OO+NO_2+M \rightarrow PAN+M$$

- PAN not soluble in water and is not removed by deposition. Main loss by thermal decomposition:

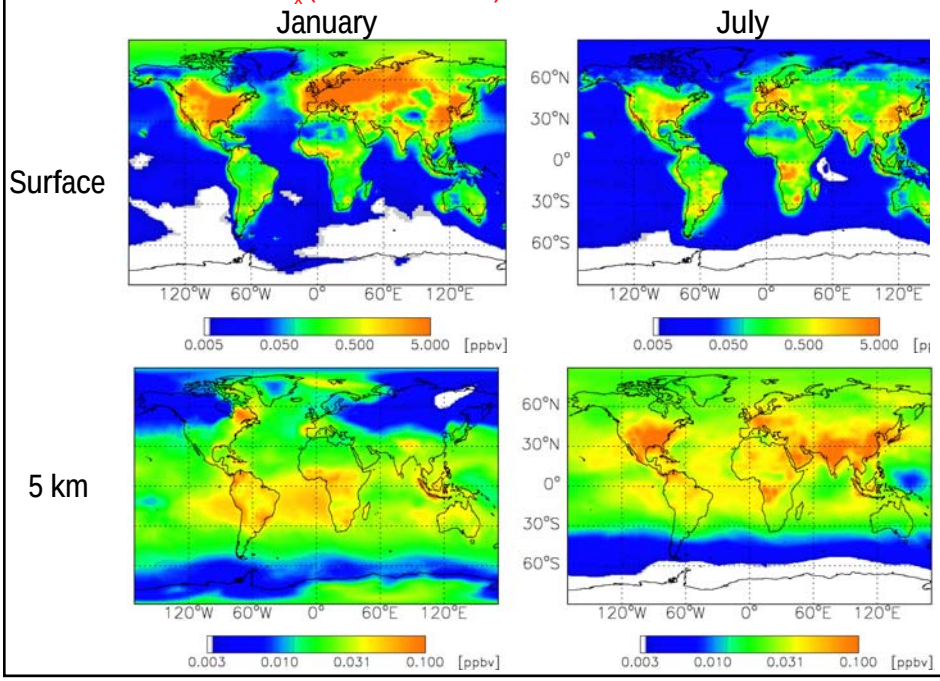
$$PAN\ (+heat) \rightarrow CH_3C(O)OO + NO_2$$

- Strong dependence of PAN decomposition on temperature: τ_{PAN}(295 K)~1 hour, τ_{PAN}(250 K)~1-2 months

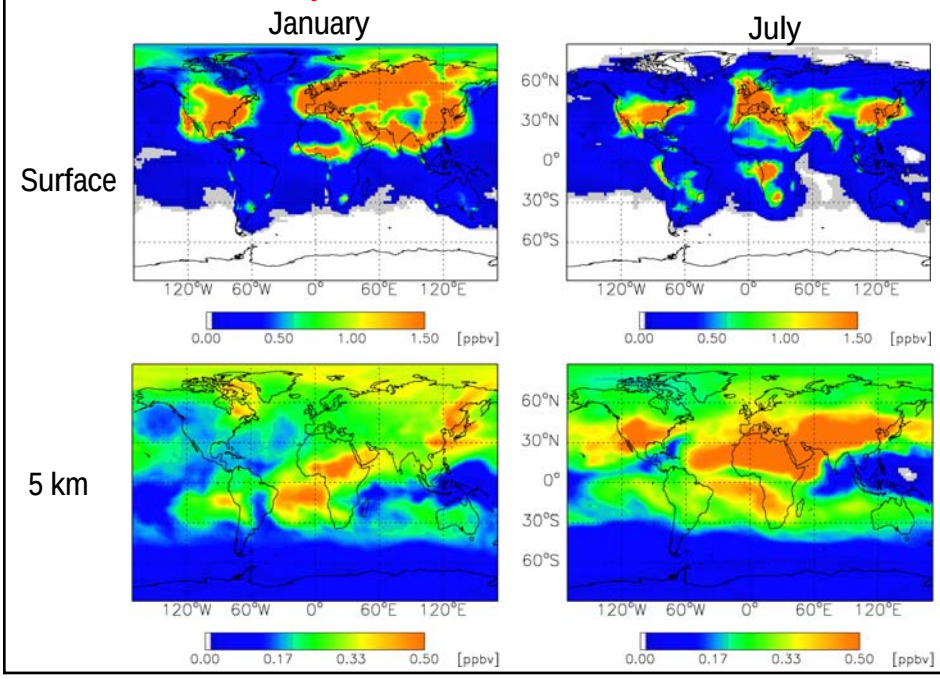
→ in the middle and upper troposphere PAN can be transported over long distances and decompose to release NO_x far from its source.



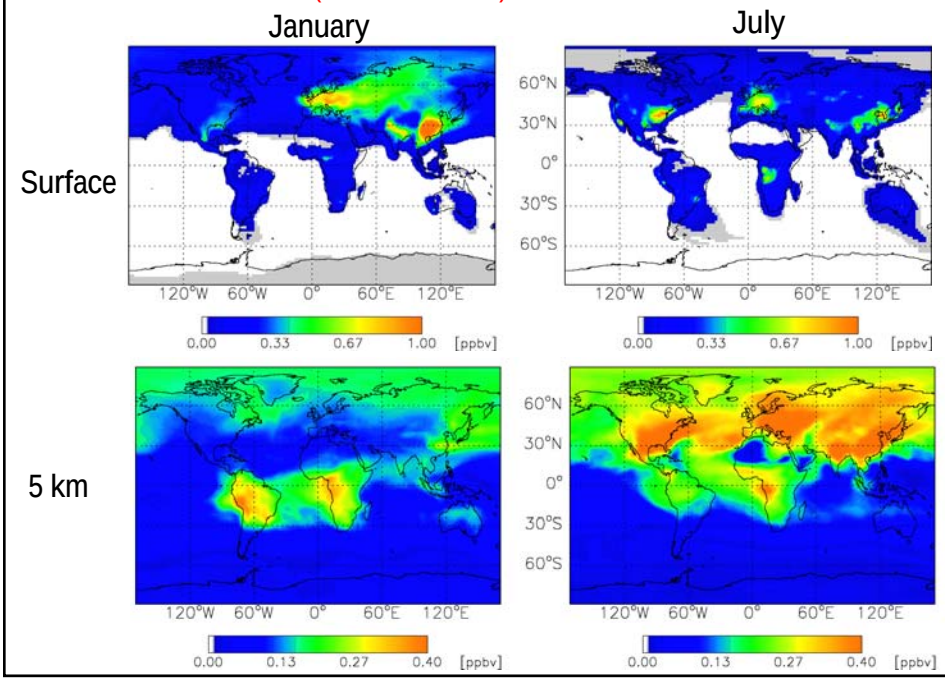
Global distribution of NO_x (model-calculated) at the surface and at 5 km altitude



Global distribution of HNO_3 (model-calculated) at the surface and at 5 km altitude



Global distribution of PAN (model-calculated) at the surface and at 5 km altitude



Sources of O_3 precursors

Sources	CH_4 (Tg/yr)	CO (Tg/yr)	NMHC (Tg C/yr)	NO_x (Tg N/yr)
⇨ Energy use	110 (65-155)	500 (300-900)	70 (60-100)	22 (20-24)
⇨ Aircraft				0.5 (0.2-1)
⇨ Biomass burning	40 (10-70)	500 (400-700)	40 (30-90)	8 (3-13)
Vegetation		100 (60-160)	400 (230-1150)	
Soils				7 (5-12)
Lightning				5 (2-20)
⇨ Ruminants	85 (60-105)			
⇨ Rice paddies	80 (30-120)			
⇨ Animal wastes	30 (15-45)			
⇨ Landfills	40 (20-60)			
NH_3 oxidation				0.9 (0-1.6)
N_2O breakdown*				0.6 (0.4-1)
⇨ Domestic sewage	25 (20-30)			
Wetlands	145 (115-175)			
Oceans	10 (5-15)	50 (20-200)	50 (20-150)	
Freshwaters	5 (1-10)			
CH_4 hydrates	10 (5-15)			
Termites	20 (1-40)			
Total	**600** (520-680)	**1150** (780-1960)	**560** (340-1490)	**44** (30-73)

* NO_y produced in the stratosphere and transported to the troposphere.

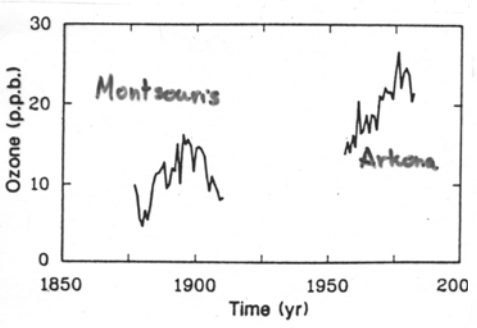
Contribution from anthropogenic sources: ~ 70% | ~ 85% | ~ 20% | ~ 70%

WMO, Scientific Assessment of Ozone Depletion, 1998

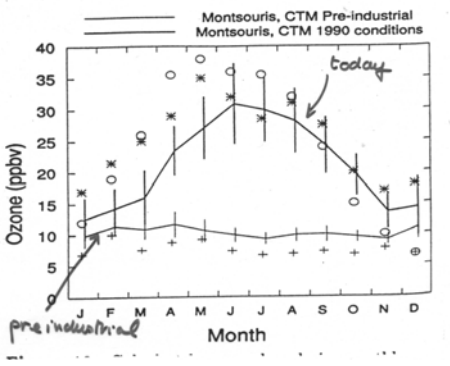
Change in tropospheric ozone since pre-industrial era

- O_3 is reactive: no ice core record.
- Surface measurements in 19th and early 20th century in Europe: much lower O_3 (10-20 ppbv) than today (40-50 ppbv), and different seasonal cycle. But relationship to Northern Hemisphere concentrations not obvious.
- Global chemical transport models imply a 50% increase in Northern Hemisphere O_3 since pre-industrial era due to increases in emissions of NO_x, CO, CH_4 and hydrocarbons.

Ozone observations at the Montsouris Observatory (outside Paris)



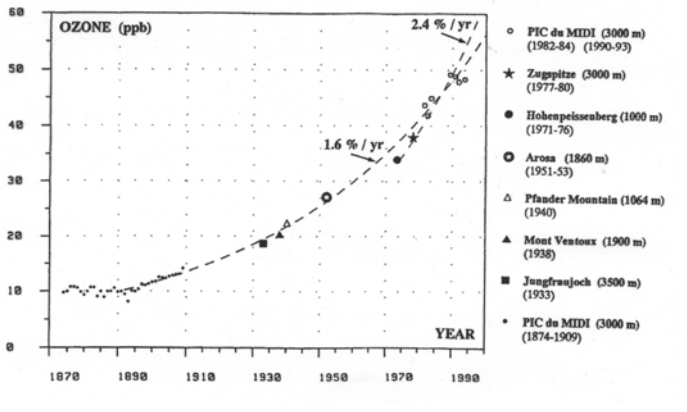
Voltz and Kley, 1988.



Anfossi et al., 1991.

Ozone observations at the Pic du Midi

(3000 m altitude, France)



Marenco et al., JGR, 16617-16632, 1994.

→ *Increase is important from pollution and climate perspectives*