# Atmospheric Chemistry

Lecture 18

# Excellent Tutorial Article on Tropospheric Gas-Phase Chemistry

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## Gas-phase radical chemistry in the troposphere

**Paul S. Monks**

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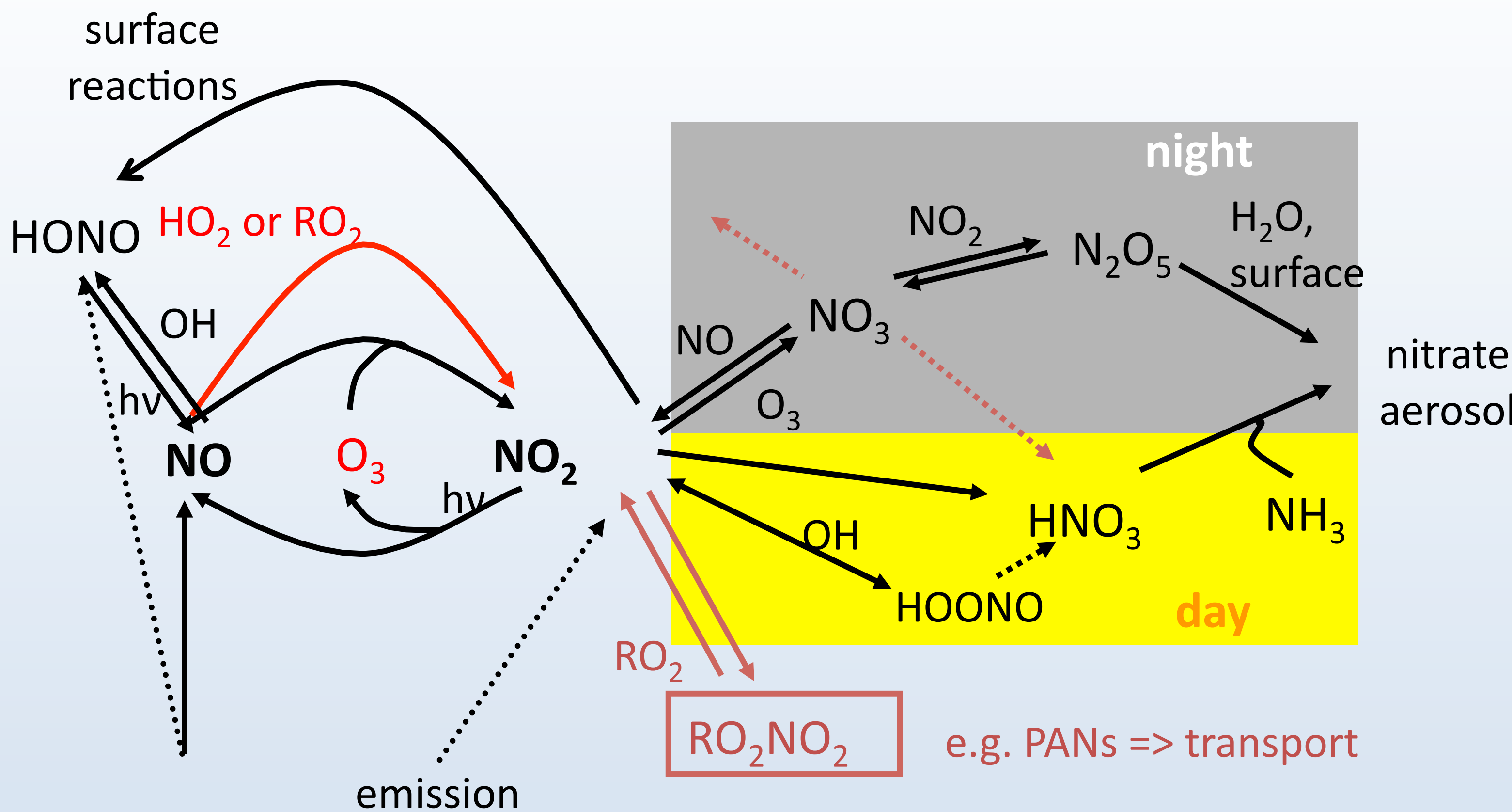
Atmospheric free radicals are low concentration, relatively fast reacting species whose influence is felt throughout the atmosphere. Reactive radicals have a key role in maintaining a balanced atmospheric composition through their central function in controlling the *oxidative capacity* of the atmosphere. In this *tutorial review*, the chemistry of three main groups of atmospheric radicals $HO_x$, $NO_x$ and $XO_x$ (X = Cl, Br, I) are examined in terms of their sources, interconversions and sinks. Key examples of the chemistry are given for each group of radicals in their atmospheric context.

# Simplified NOx Chemistry in the Troposphere



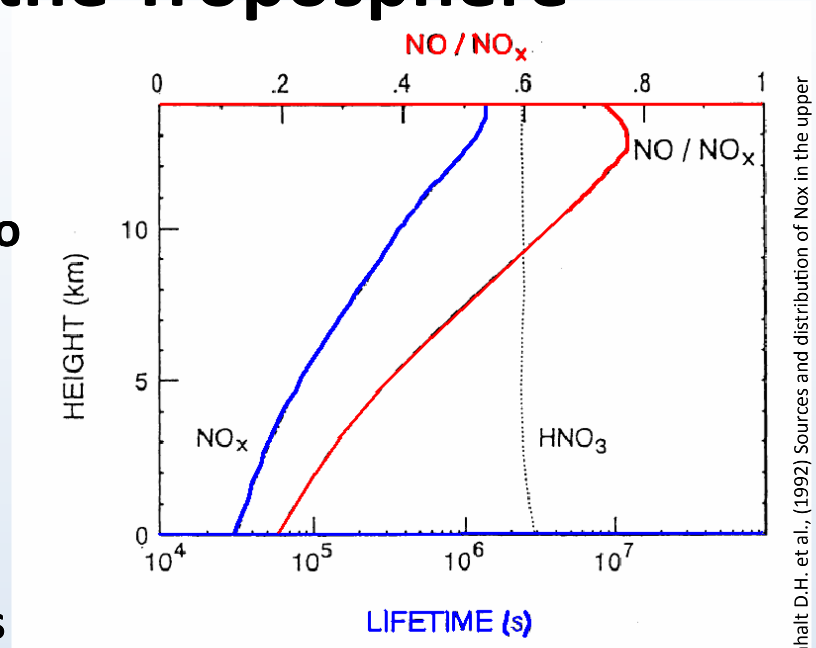

adapted from M. Jenkin

Nitrogen Oxides in the Troposphere, Andreas Richter, ERCA 2010

From an excellent review of the role of NOx in tropospheric chemistry by Andreas Richter obtained by googling “nox troposphere richter”

# Some facts on $NO_x$ in the Troposphere

- NO and $NO_2$ are rapidly converted into each other and are therefore combined to
  $NO_x = NO + NO_2$
- the ratio [NO] / [$NO_x$] is about 0.2 at the surface but increases towards higher altitudes (temperature dependence of $O_3$ + NO reaction)
- the atmospheric lifetime of $NO_x$ is short close to the surface (hours) and increases towards higher altitudes (days)
- lifetime is longer in winter than in summer (lower [OH])

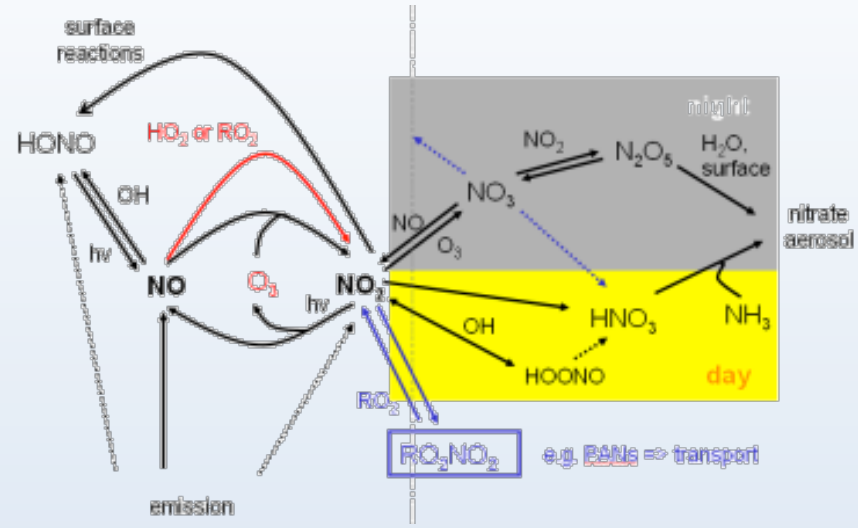



Ehhalt D.H. et al., (1992) Sources and distribution of Nox in the upper troposphere at northern mid-latitudes. J Geophys Res 97: 3725–3738

- the short lifetime results in little transport, both vertically and horizontally, at least in the form of $NO_x$
  => $NO_x$ is found close to its sources
- PAN has a long lifetime and can be transported and re-release $NO_x$ when temperature increases

From Andreas Richter

# The Role of $NO_x$ in Ozone Chemistry




## Background conditions

- photolysis of $NO_2$ is only known way to produce $O_3$ in the troposphere
- $O_3$, $NO_2$, and NO are in photostationary state (*Leighton relationship*):

  $$[O_3][NO_2] / [NO] = J_{NO2} / k_{O3 + NO}$$

- at very low [NO] / [$O_3$] ratio, destruction of $O_3$ by $HO_2$ dominates over $O_3$ production

## Polluted conditions

- if NO is oxidized to $NO_2$ by $HO_2$ or $RO_2$ instead of $O_3$, ozone is catalytically formed by NO
- how much $O_3$ can be formed in the presence of $NO_x$ is eventually limited by the amount of CO, $CH_4$, and other hydrocarbons available
- at high $NO_x$ concentrations, $O_3$ levels are reduced by reaction with NO and $NO_2$ in particular at night

From Andreas Richter

# Net result for CO oxidation

***Can Produce Ozone***

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + NO \rightarrow OH + NO_2$

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

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

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$CO + 2O_2 \rightarrow CO_2 + O_3$

***Can Consume Ozone***

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + O_3 \rightarrow OH + 2O_2$

----------------------------

$CO + O_3 \rightarrow CO_2 + O_2$

***Depending on the $NO_x$ Concentration***

# CO, NO, $NO_2$, OH, $HO_2$ and J($O^1D$) Measurements in Urban Summer Conditions

***Note different scale for $HO_2$ measurements compared to OH measurements.***

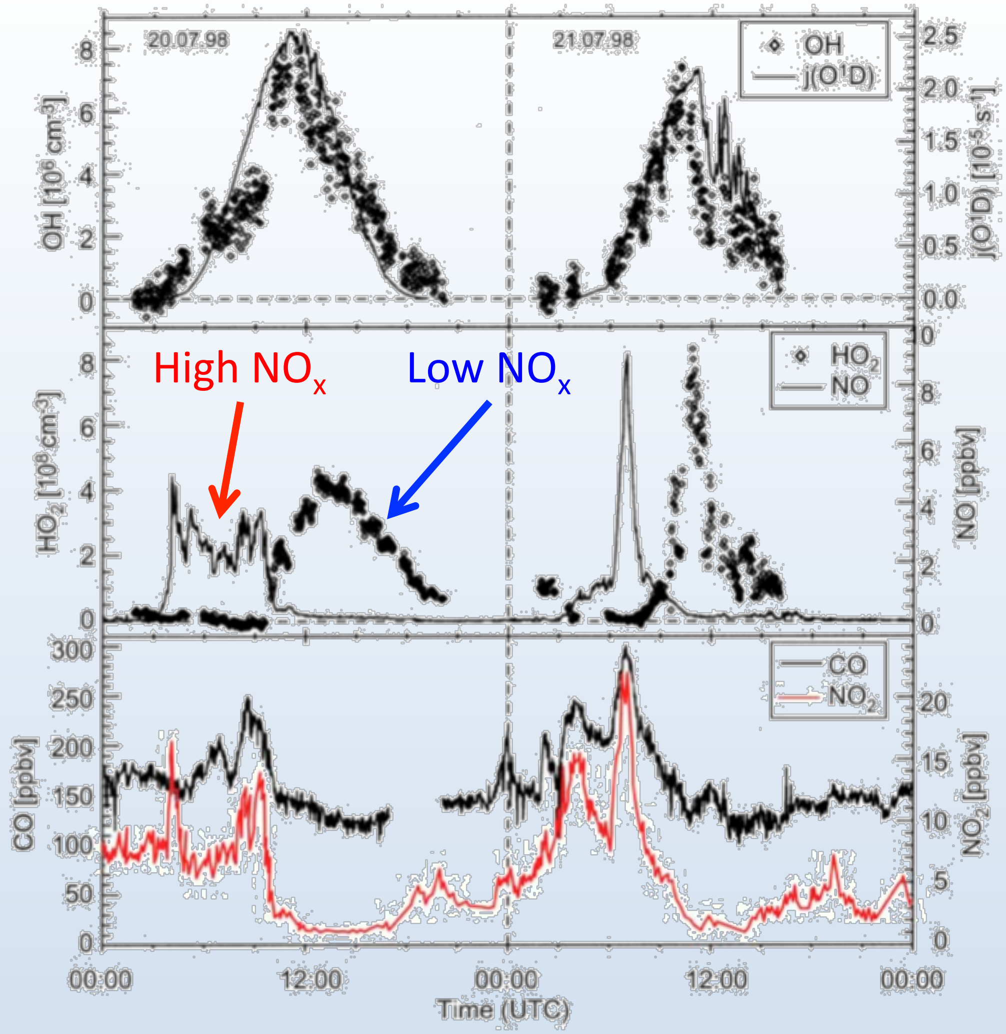



**Fig. 8** Measurements of OH, $HO_2$, $j(O^1D)$, NO, $NO_2$ and CO during a summer urban campaign.[13] The figure demonstrates the dramatic feedback of $NO_x$ on $HO_x$ radicals, the [$HO_2$] clearly suppressed at high $NO_x$ while the [OH] remains largely unaffected.

from Monks, 2005

# Net Ozone Production vs $NO_x$

- A: $NO_x$ concentrations very low; loss of ozone due to $OH + O_3$ and $HO_2 + O_3$ dominate
- B: $NO_x$ increasing leads to more efficient diversion of HC oxidation into ozone-producing reactions, e.g. converts NO to $NO_2$
- C: Peak as production saturates; decrease in efficiency as conversion to organic nitrates removes some HC products before ozone production

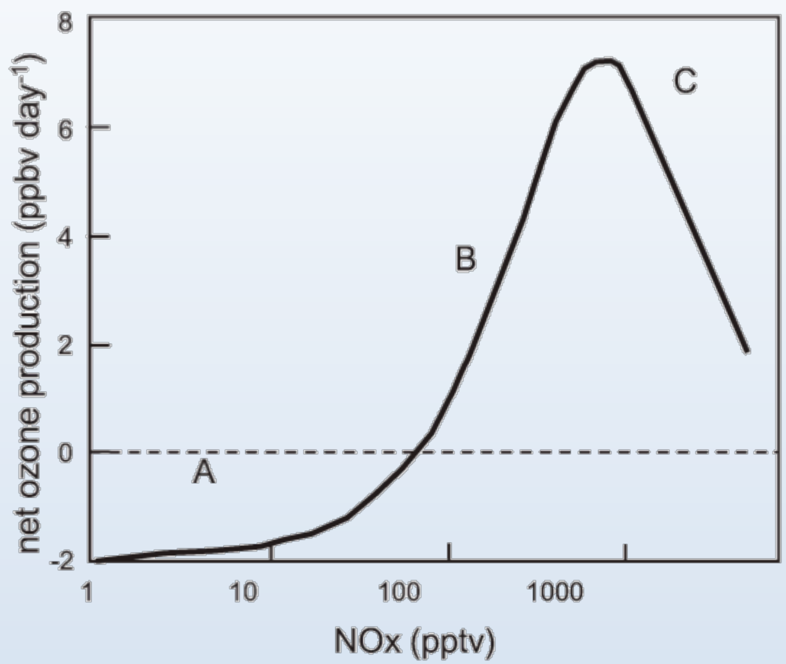



**Fig. 9** Schematic representation of the dependence of the net ozone ($N(O_3)$) production (or destruction) on the concentration of $NO_x$. The magnitudes reflect clean free tropospheric conditions.

from Monks, 2005

# Net Ozone Production vs NOx and VOCs

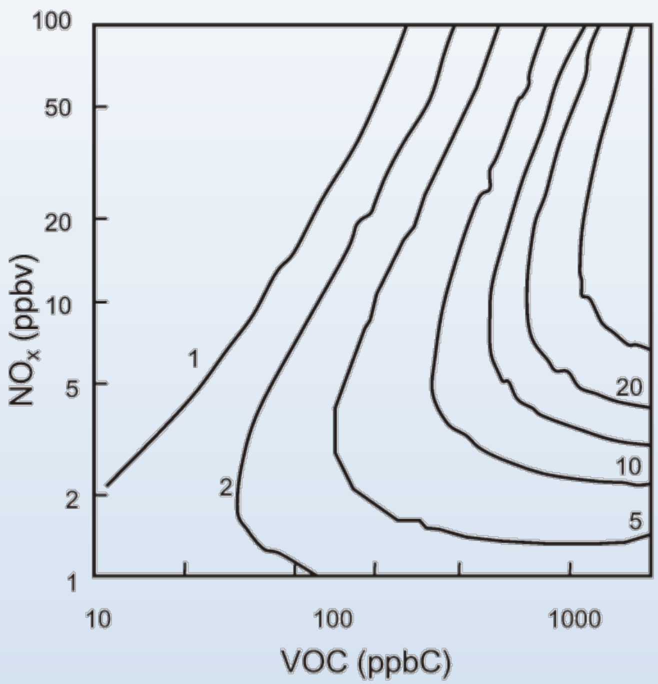



**Fig. 10** Isopleths giving net rate of ozone production (ppb $h^{-1}$) as a function of VOC (ppbC) and $NO_x$ (ppbv) for mean summer daytime meteorology and clear skies under urban conditions.[16]

- **Note that $NO_x$ begins at 1 ppbv (1000 pptv), i.e. urban conditions**
- **Turnover point (as a function of $NO_x$) increases as amount of VOCs increase**

from Monks, 2005

# Sources of $NO_x$ in the Troposphere

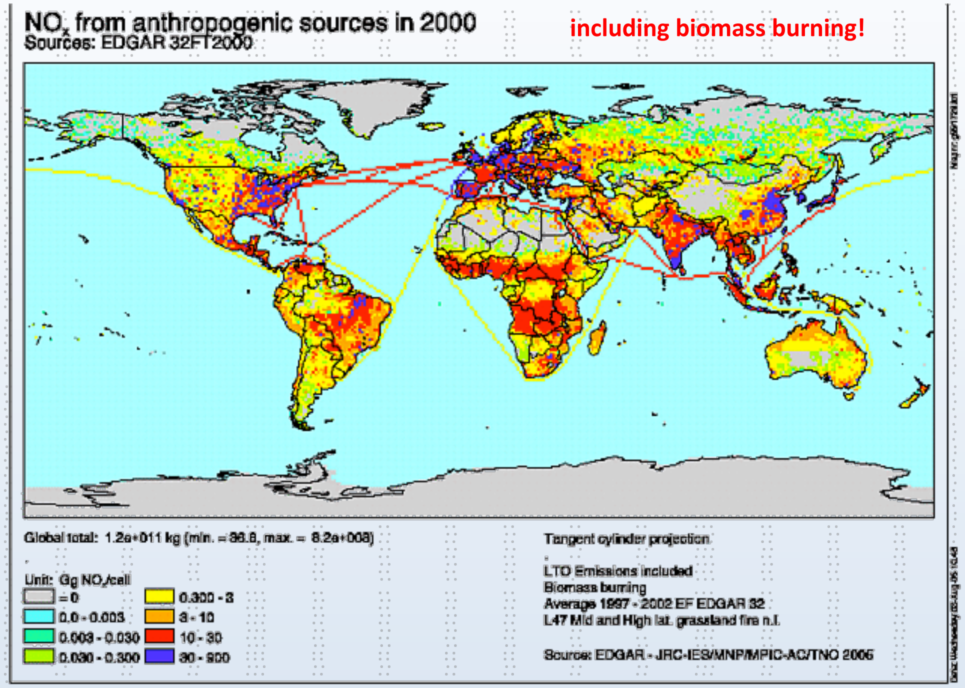
R. Delmas et al., Nutrient Cycling in Agroecosystems, 48, 51 – 60, 1997

**Main sources of $NO_x$ (in Tg N / yr) are**

| | |
|---|---|
| • fossil fuel combustion | 22.0 (15 – 29) |
| • fires | 6.7 (3 – 10) |
| • microbial soil emissions | 5.5 (3.3 – 7.7) |
| • lightning | 2.0 (1 – 4) |
| • oxidation of biogenic $NH_3$ | 1.0 (0.5 – 1.5) |
| • aircraft | 0.5 (0.5 – 0.6) |
| • stratosphere | 0.5 (0.4 – 0.6) |

From Andreas Richter

# Anthropogenic $NO_x$ Sources

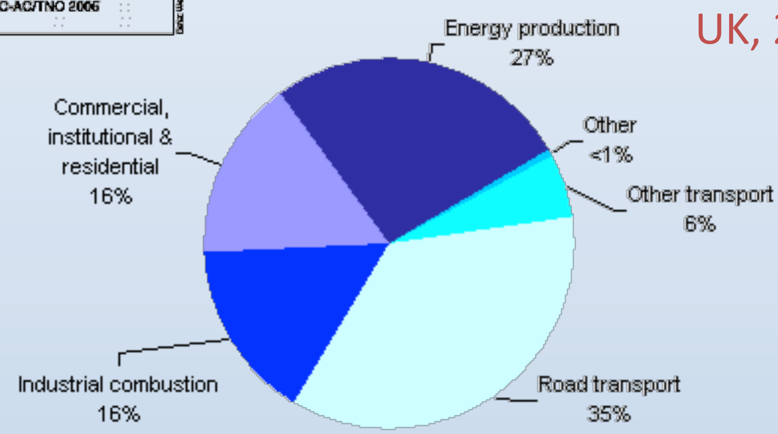



http://www.mnp.nl/edgar/model/v32ft2000edgar/edgarv32ft-prec/edgv32ft-nox-map.jsp

- **anthropogenic emissions centered in a few industrialised areas**
- **largest emissions in cities and from power plants**
- **emissions per capita very unevenly distributes => future?**

- **road transport has large importance**
- **energy production is second, depending on energy mix**

UK, 2004

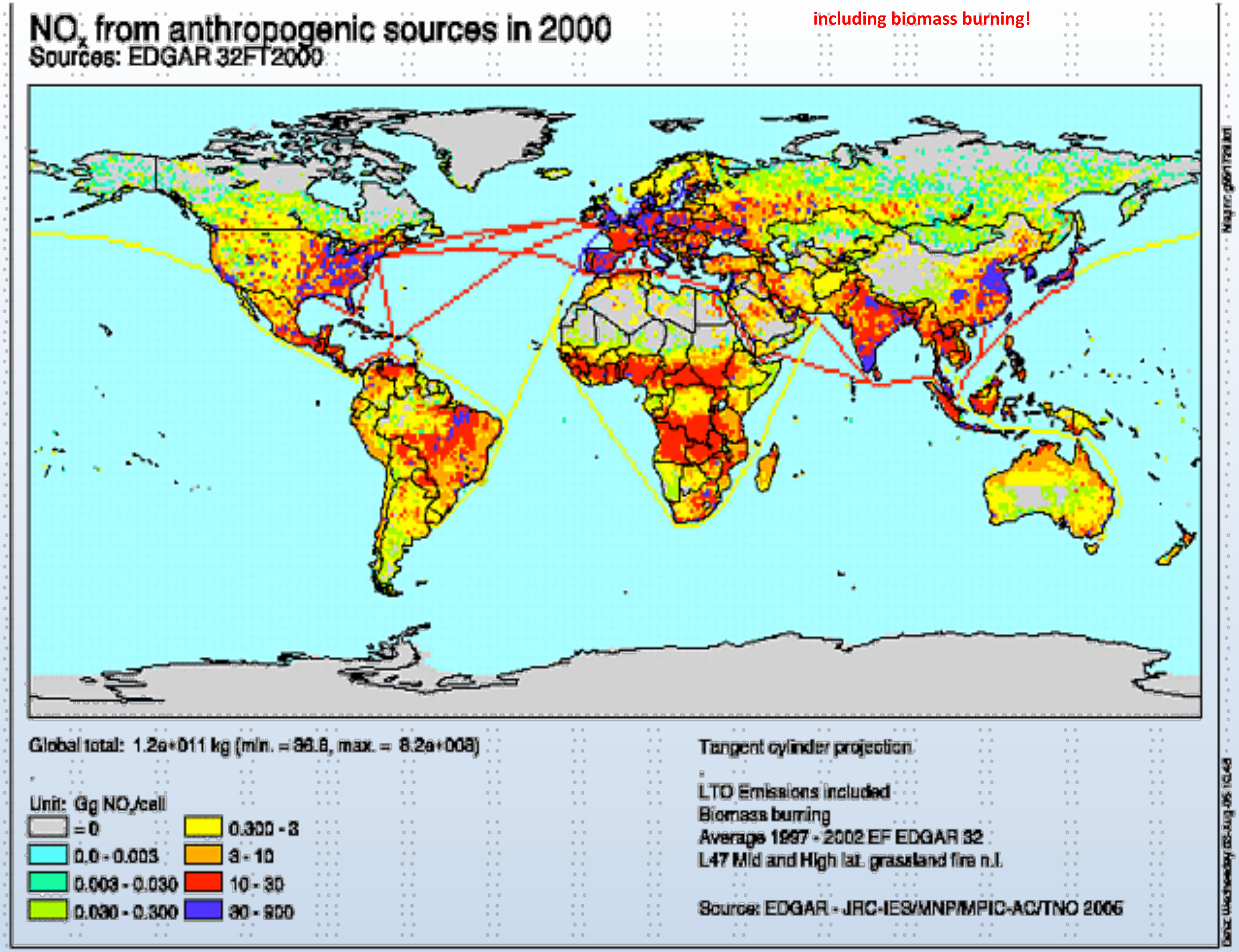



Total emissions of oxides of nitrogen = 1.67 million tonnes

Source: NAEI

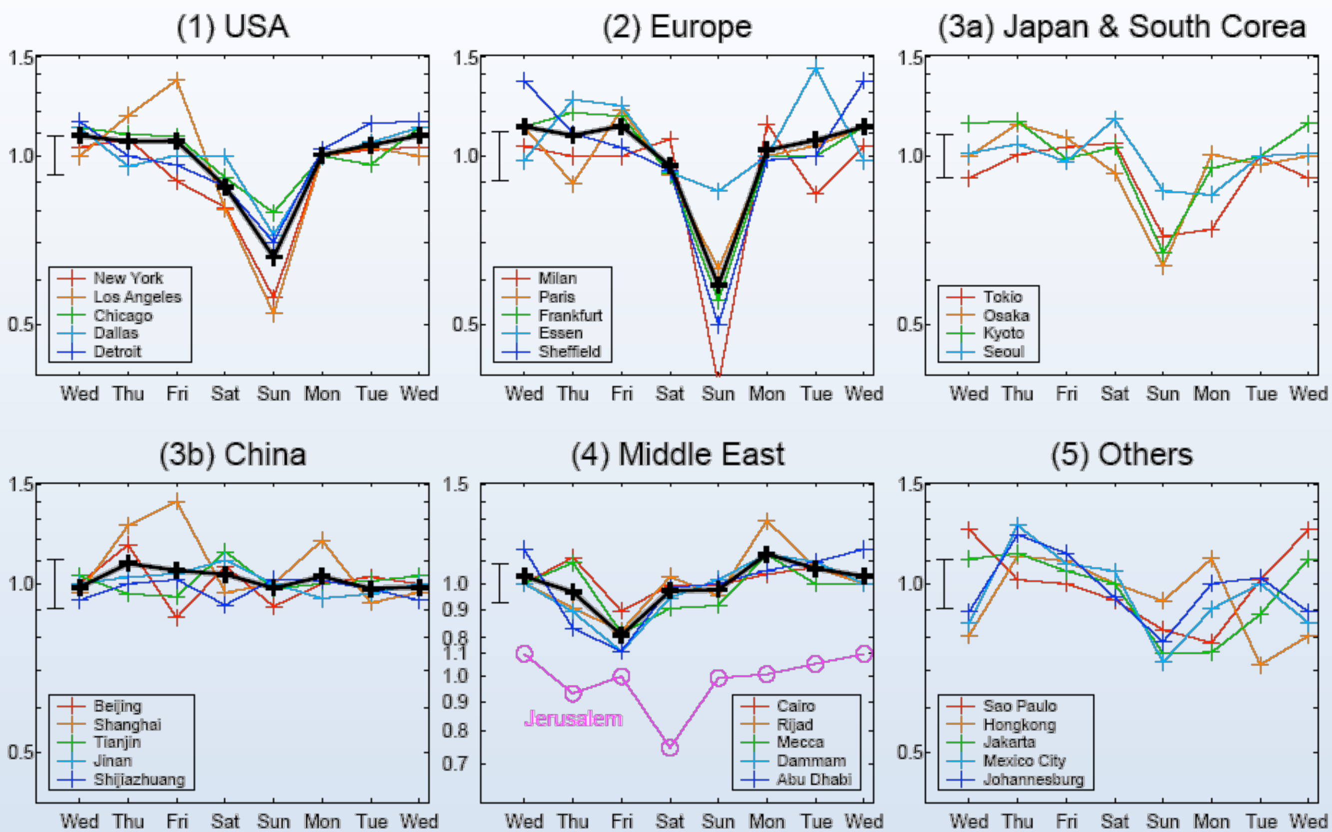
http://www.environment-agency.gov.uk/commondata/103196/1162897?referrer=/yourenv/eff/1190084/air/1158715/1162725/

From Andreas Richter



NO$_x$ from anthropogenic sources in 2000
Sources: EDGAR 32FT2000
including biomass burning!
Global total: 1.2e+011 kg (min. = 86.8, max. = 8.2e+008)
Unit: Gg NO$_x$/cell
= 0
0.0 - 0.003
0.003 - 0.030
0.030 - 0.300
0.300 - 3
3 - 10
10 - 30
30 - 300
Tangent cylinder projection
LTO Emissions included
Biomass burning
Average 1997 - 2002 EF EDGAR 32
L47 Mid and High lat. grassland fire n.i.
Source: EDGAR - JRC-IES/MNP/MPIC-AC/TNO 2005

# Anthropogenic $NO_x$ Sources: Example




Beirle et al., Atmos. Chem. Phys., 3, 2225–2232, 2003

- **Normalised tropospheric $NO_2$ columns retrieved from GOME satellite measurements show clear weekly cycle over industrialised areas**
- **anthropogenic $NO_x$ emissions dominate**

From Andreas Richter

# $NO_x$ from Lightning

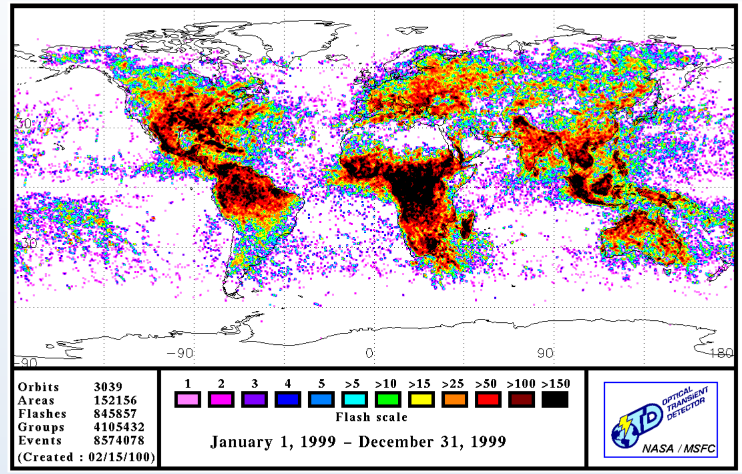
- at very high temperatures (> 2000 K)

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

  $O + N_2 \rightarrow NO + N$

  $N + O_2 \rightarrow NO + O$

  (*Zel'dovitch mechanism*).




http://thunder.nsstc.nasa.gov/data/OTDsummaries/

- lightning $NO_x$ is computed from the product of lightning dissipation energy and NO yield per Joule of discharge
- estimates have varied dramatically in the past: 1.2 Tg ... 200 Tg N / yr
- recent estimates cluster around 2.5 Tg N / yr
- estimates are based on lightning counts from space and in situ measurements of NO in individual thunderstorms
- lightning $NO_x$ in models often parameterised by cloud height or convective precipitation
- the relevance of lightning $NO_x$ is that it is injected in the upper troposphere, where ozone formation is very efficient

From Andreas Richter