Nitrogen Oxides in the Troposphere

sources, distributions, impacts, and trends

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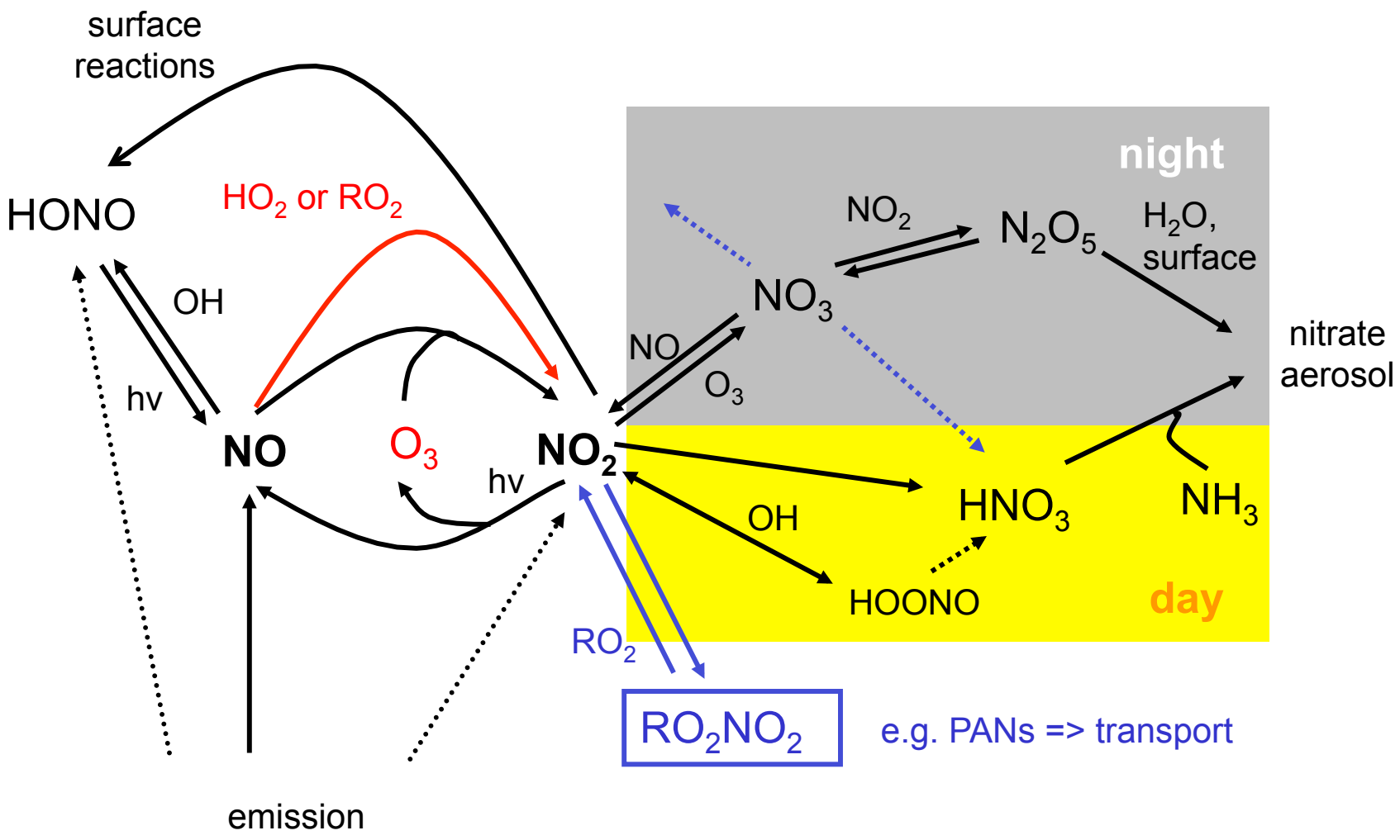
Overview

1. What is NO_x?
2. What is it doing in the troposphere?
3. Why should we care?
4. Where does it come from?
5. How can it be measured?
6. Is it changing with time?

Simplified NOx Chemistry in the Troposphere



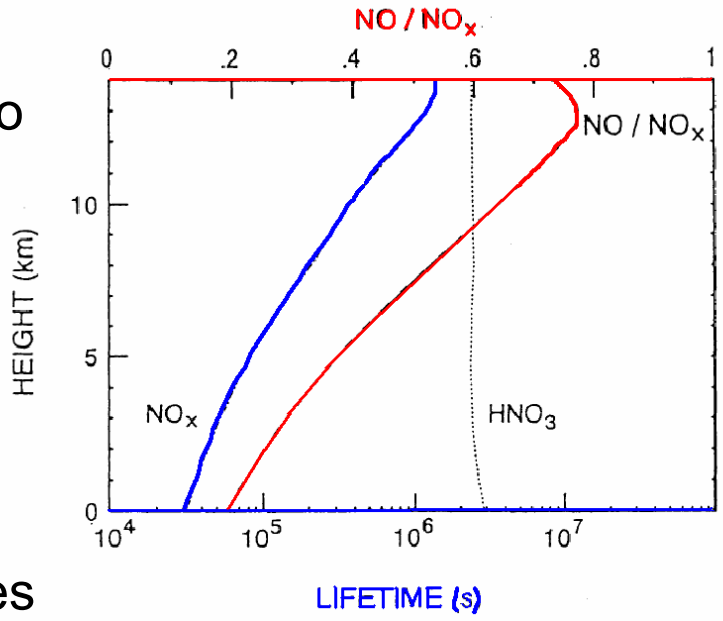
adapted from M. Jenkin

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)



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

- lifetime is longer in winter than in summer (lower [OH])

- 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

Why should we care about NOx in the Troposphere?

NOx

- is a key species in tropospheric ozone formation
- leads to formation of HNO_3 and thereby acid rain
- contributes to eutrophication
- acts as a greenhouse gas (NO_2, at least locally)
- acts indirectly on climate through ozone formation
- can contribute to aerosol formation

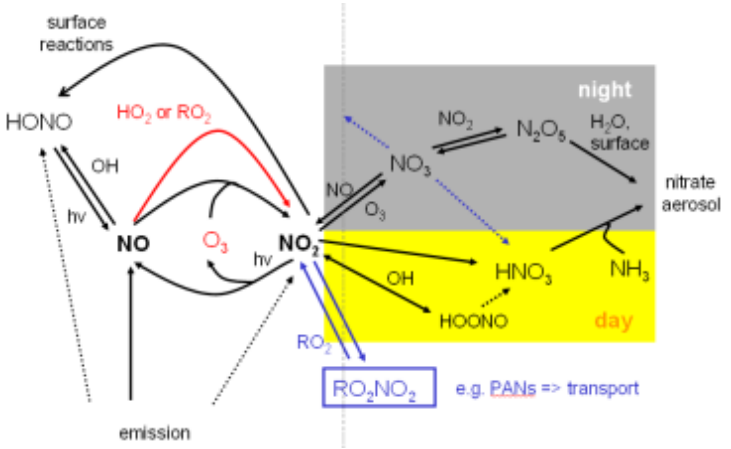
The Role of NOx in Ozone Chemistry

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

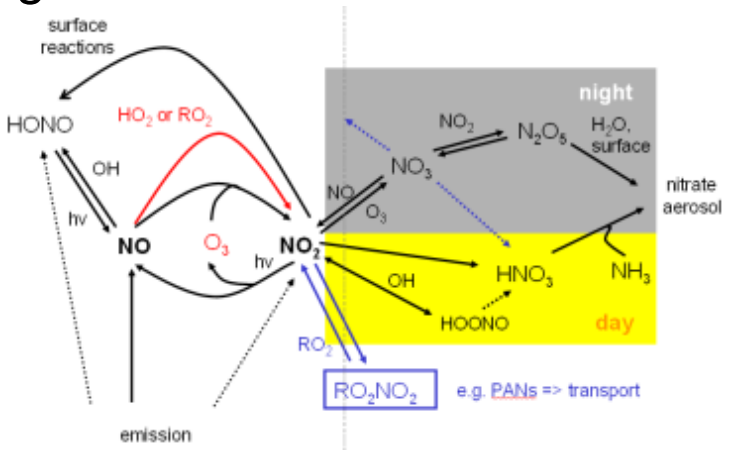
- if NO is oxidized to NO_2 by HO_2 or RO_2 instead of O_3, ozone is catalytically formed by NO
- how much O_3 can be formed in the presence of NO_x is eventually limited by the amount of CO, CH_4, and other hydrocarbons available
- at high NO_x concentrations, O_3 levels are reduced by reaction with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

NOx and acid Rain

- normal rain should have a pH of about 5, but much lower values are often observed in industrialised areas
- SO_2 emissions have been the main reason for acid rain
- as SO_2 emissions decrease, NO_x becomes relatively more important

- HNO_3 is formed through several paths and its wet and dry deposition is one of the main sinks for nitrogen oxides:

$$NO_2 + OH + M \rightarrow HONO_2 + M$$
$$N_2O_{5(g)} + H_2O_{(g,l)} \rightarrow 2HNO_{3(g,\,aq)}$$
$$NO_{3(aq)} + H_2O_{(l)} \rightarrow HNO_{3(aq)} + OH_{(aq)}$$
$$NO_3 + RH \rightarrow HNO_{3(g)} + R$$



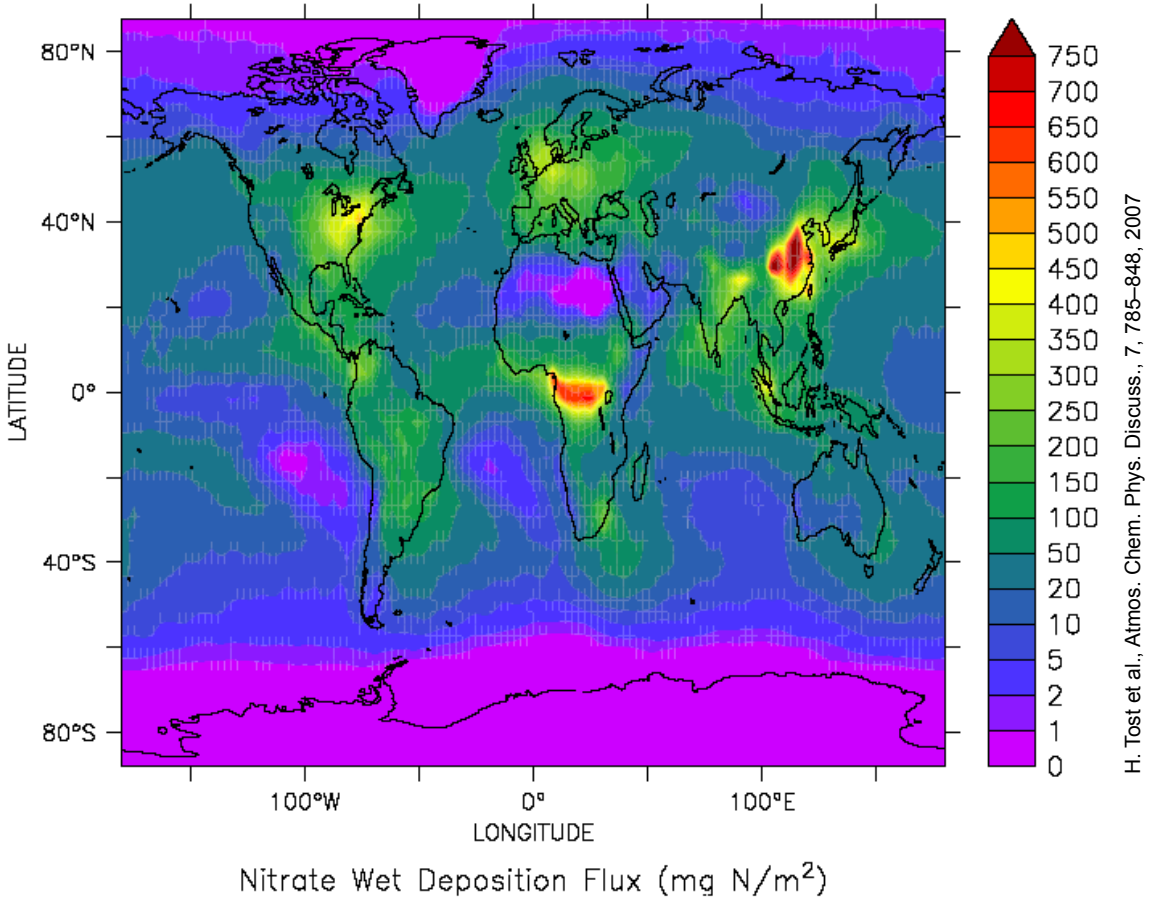
- the effects of acid rain are most pronounced on freshwater fish and forest ecology, but also on buildings

NOx and acid Rain: Example

Amount of nitrate that is deposited depends on

- NO_x emitted
- efficiency of nitrate formation
- precipitation

ECHAM5/MESSy1 model results



Sources of NOx in the Troposphere

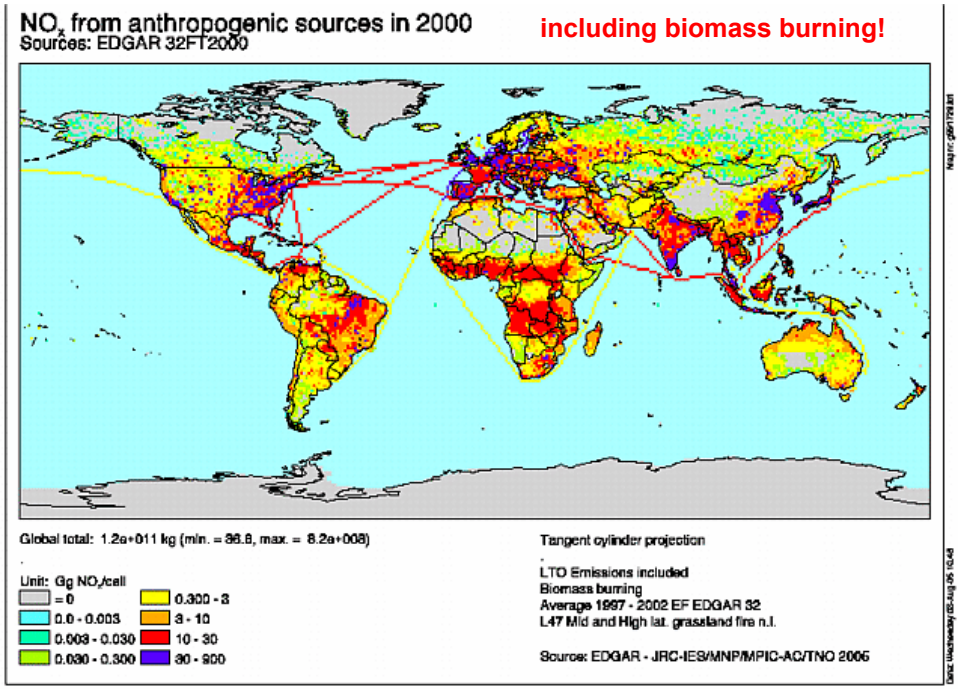
R. Delmas et al., Nutrient Cycling in Agroecosystems, 48, 51 – 60, 1997

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)

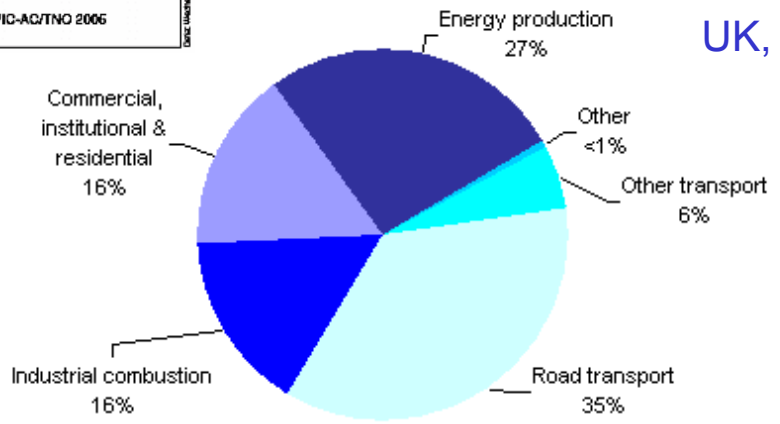
Anthropogenic NOx Sources

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

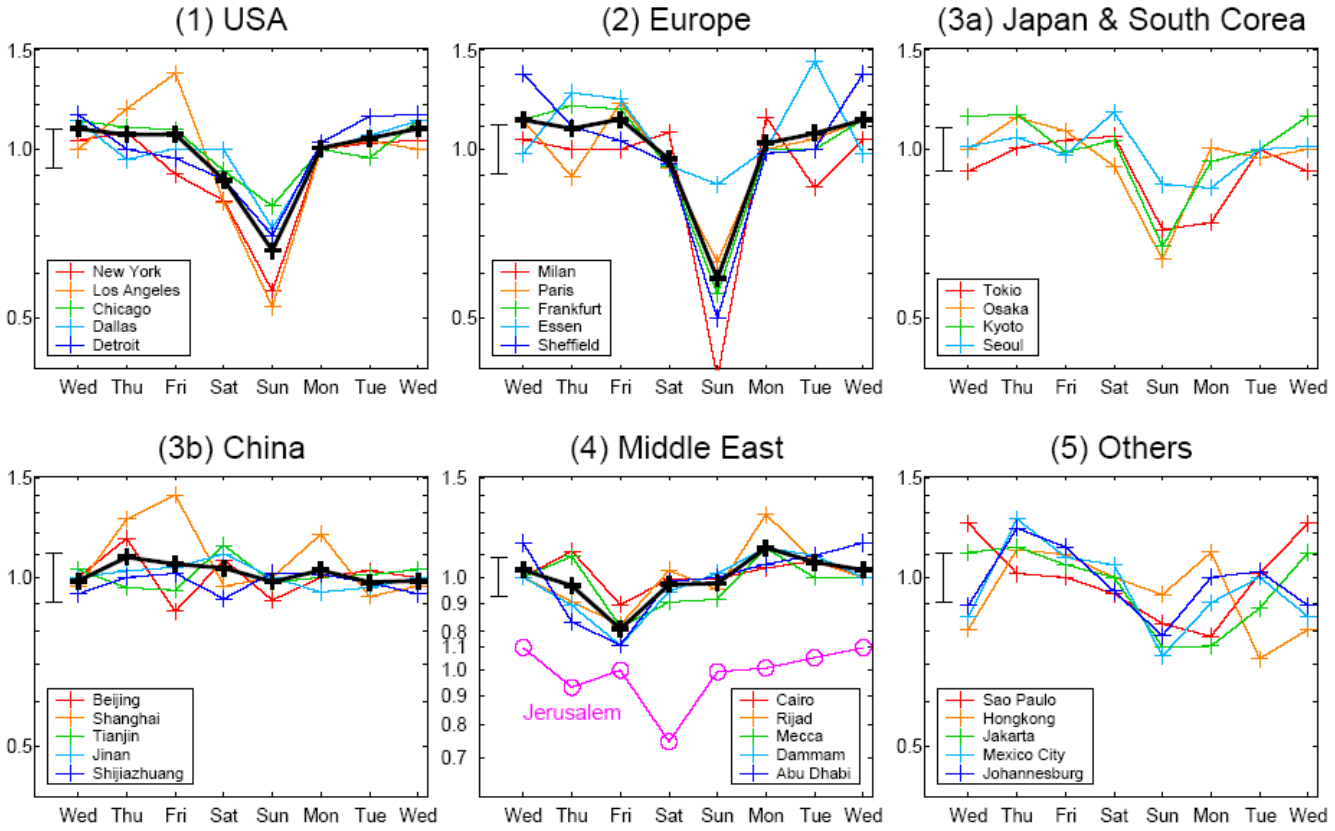


Total emissions of oxides of nitrogen = 1.67 million tonnes

Source: NAEI

http://www.environment-agency.gov.uk/commondata/103196/11628997?referrer=/yourenv/eff/1190084/air/1158715/1162725/

Anthropogenic NOx Sources: Example



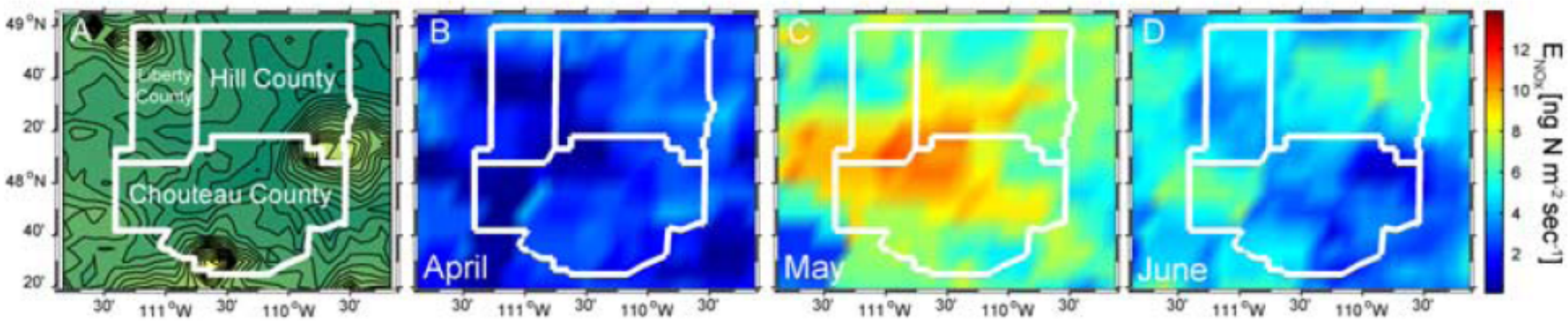
Beirle et al., Atmos. Chem. Phys., 3, 2225–2232, 2003

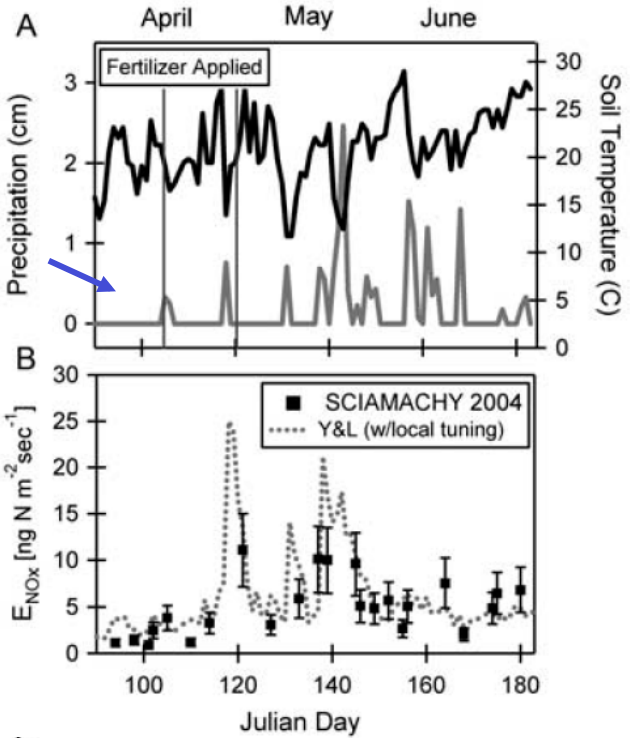
- Normalised tropospheric NO_2 columns retrieved from GOME satellite measurements show clear weekly cycle over industrialised areas
- anthropogenic NO_x emissions dominate

Soil Sources of NOx

- NO and N_2O are emitted from microbial activities in the soil, both during nitrification ($NH_4^+ \rightarrow NO_3^-$) and denitrification ($NO_3^- \rightarrow N_2$)
- function of soil moisture and texture, inorganic nitrogen availability, the carbon to nitrogen ratio, temperature and precipitation
- typical parameterisation using T, precipitation and fertilisation
- usually observed as strong pulses after fertilisation and rain
- in ecosystems with dense vegetation cover (e.g. rain forests), part of the NO_x emitted is lost by NO_2 deposition
- NO_x soil emissions seem to be underestimated in current models
- potential for increases as use of fertilizers increases, but strong dependence on actual practices used

Soil Sources of NOx: Example





- Chouteau, Hill and Liberty Counties in North-Central Montana, USA
- harvested cropland, low population density, no large stationary NO_x sources
- NO_2 columns retrieved from SCIAMACHY satellite data are large after fertilisation and subsequent precipitation

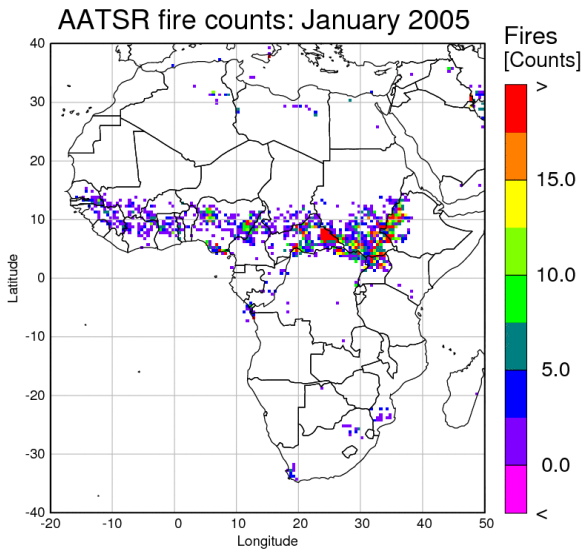
Bertram, T. H., et al., (2005), Satellite measurements of daily variations in soil NOx emissions, Geophys. Res. Lett., 32, L24812, doi:10.1029/2005GL024640

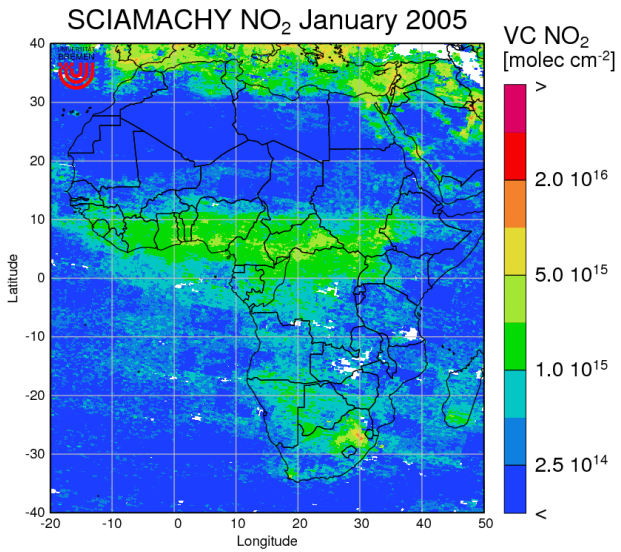
NOx from Biomass Burning

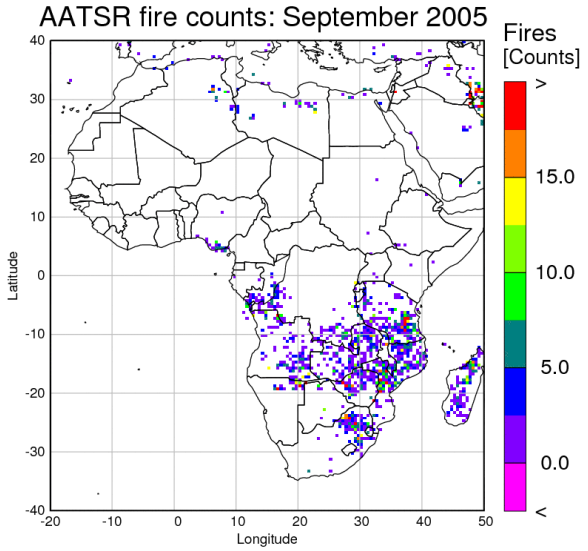
- biomass burning is happening on large scales on a regular basis as part of
  - agricultural practices
  - wild fires
  - domestic fires
- it is a significant source of NO_x
- the amount of NO_x emitted per biomass burned varies strongly between different biomass types (savannah, tropical rain forests, boreal forests)
- large amounts of NO_x are emitted in the tropics, much less e.g. in Alaska or Siberia
- in big fires, enough heat is produced to start pyroconvection and to inject NO_x in the upper troposphere

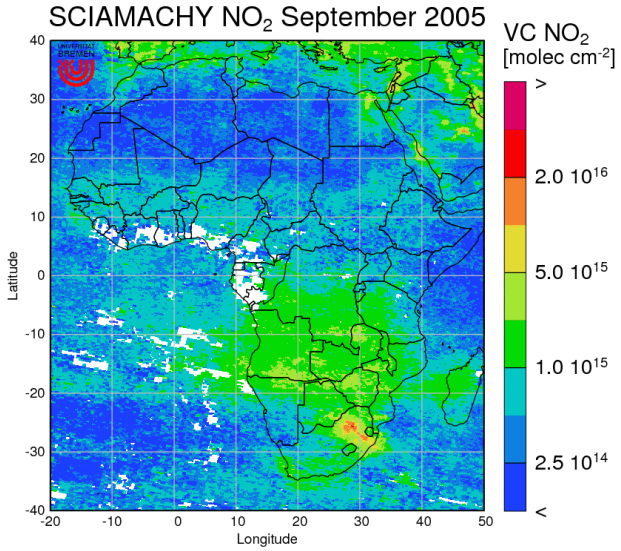
NOx from Biomass Burning: Example

http://dup.esrin.esa.int/ionia/wfa/index.asp









- fires detected by AATSR satellite instrument using IR signature
- NO_2 retrieved from SCIAMACHY measurements
- seasonality of fires and NO_2 is in good agreement
- biomass burning is main NO_x source

NOx from Lightning

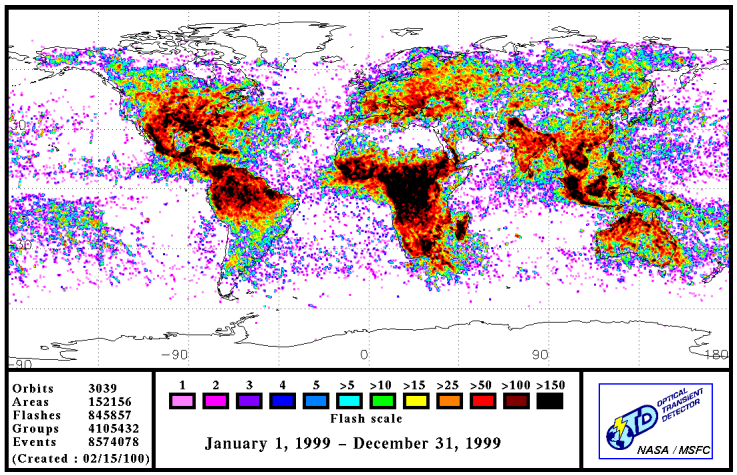
- at very high temperatures (> 2000 K)

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

  $O + N_2 \rightarrow NO + N$

  $N + O_2 \rightarrow NO + O$

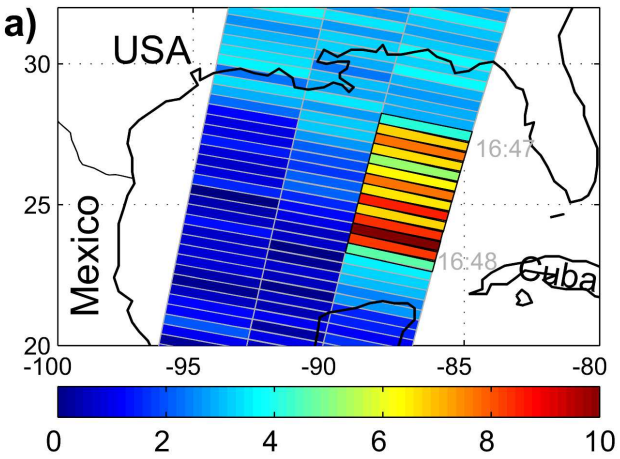
  (*Zel'dovitch mechanism*).
- lightning NO_x is computed from the product of lightning dissipation energy and NO yield per Joule of discharge
- estimates have varied dramatically in the past: 1.2 Tg ... 200 Tg N / yr
- recent estimates cluster around 2..5 Tg N / yr
- estimates are based on lightning counts 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



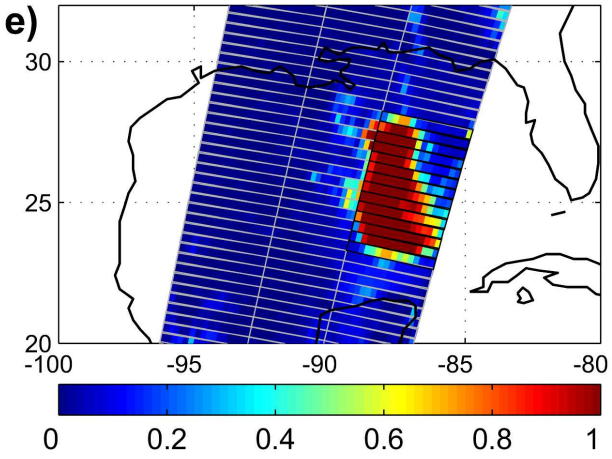
http://thunder.nsstc.nasa.gov/data/OTDsummaries/

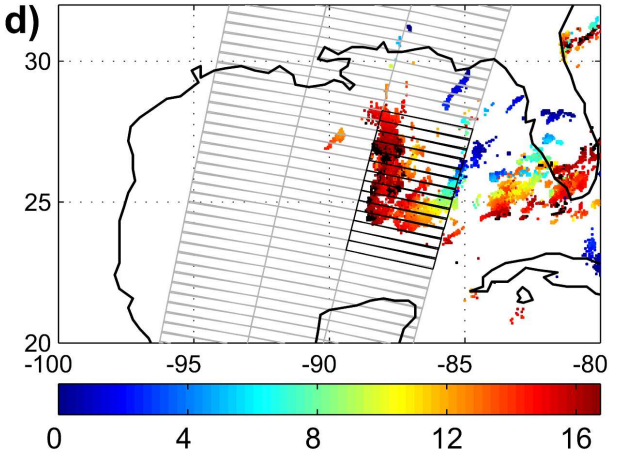
NOx from Lightning: Example

GOME trop. NO_2SCD (10^{15} molec/cm^2)



Cloud fraction





NLDN flashes (time of last lightning event)

- NO_2 columns retrieved from GOME satellite data
- coincident measurements of clouds, lightning and NO_2 in space and time
- no indication for pollution impact
- direct evidence without a priori assumptions

Beirle et al., Estimating the NOx produced by lightning from GOME and NLDN data: a case study in the Gulf of Mexico Atmos. Chem. Phys., 6, 1075-1089, 2006

Measurements of NOx

Challenges

- high spatial and temporal variability
- what is a representative measurement location?
- vertical distribution

Techniques

- in-situ using chemiluminescence
- locally using absorption spectroscopy
- globally using remote sensing in the visible spectral range

in-situ NOx Measurements

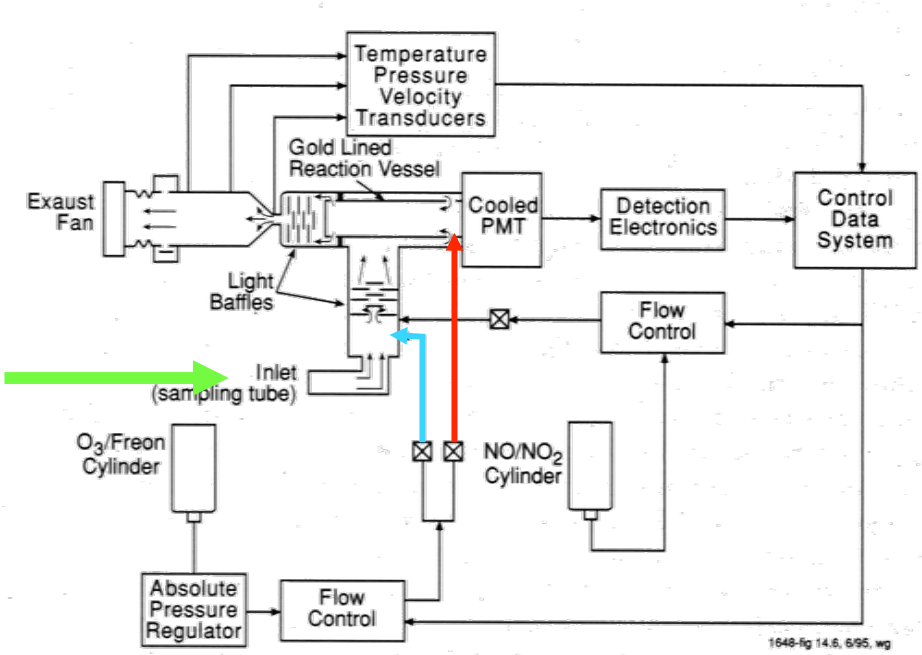


Figure 11.6. *Chemiluminescent detector for NO. The sample air is mixed with ozone in the reaction vessel, and the photons from the resulting chemiluminescence are detected by the photomultiplier tube. If the ozone is added before the reaction chamber, the luminescence takes place outside the view of the PMT and gives a background level (Ridley and Howlett, 1974).*

Idea:

In some exothermic reactions, part of the energy is released as photons that can be measured by a photomultiplier.

$O_3 + NO \rightarrow NO_2^* + O_2$

$NO_2^* \rightarrow NO_2 + h\nu$

$NO_2^* + M \rightarrow NO_2 + M$

The emitted intensity depends on the effectiveness of quenching which is proportional to the pressure and the concentrations of $[O_3]$ and [NO].

If pressure and $[O_3]$ concentration are kept constant, the intensity is proportional to the concentration of the NO.

Long Path DOAS measurements

Instrument:

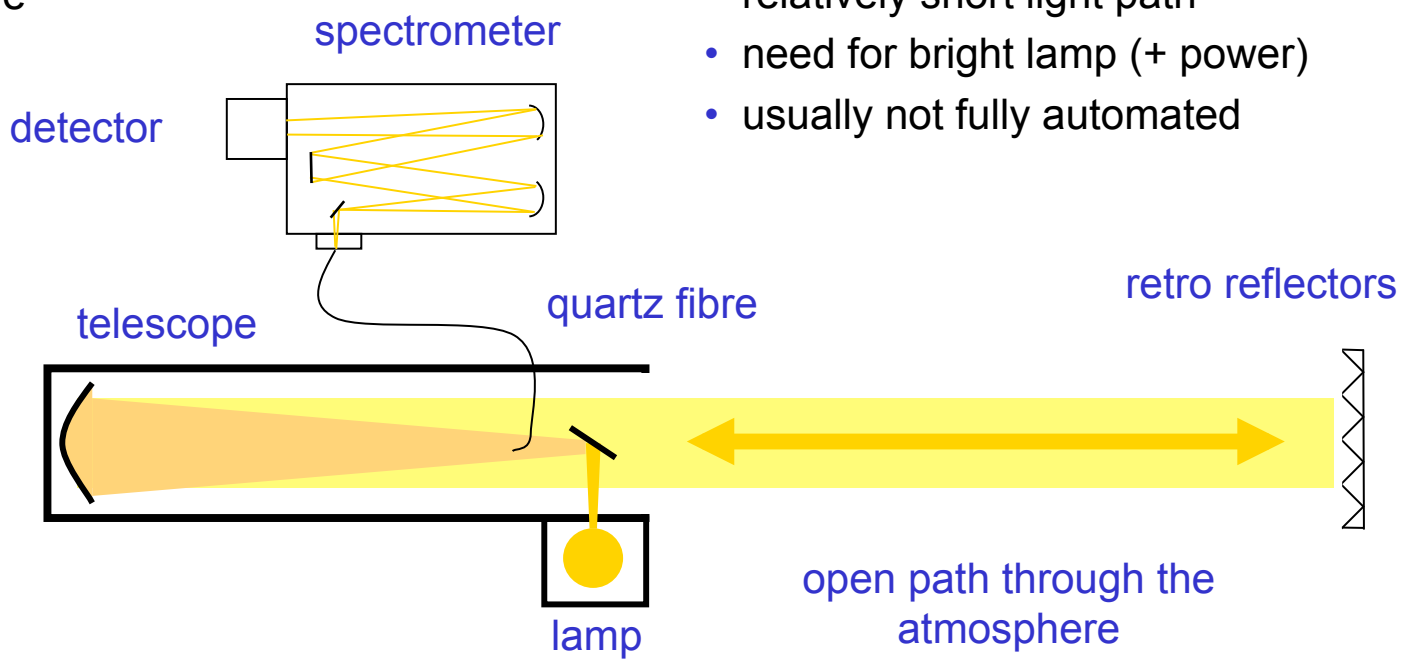
- open path Differential Optical Absorption Spectroscopy (DOAS) system using a lamp as light source
- retro reflectors for simplified set-up
- white cells (multi reflection) for enhanced light path possible

advantages:

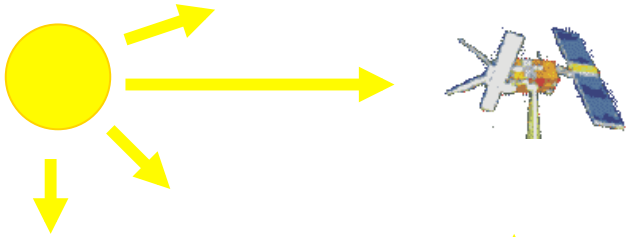
- measurements at night
- well defined light path
- extension to UV (no ozone layer in between)

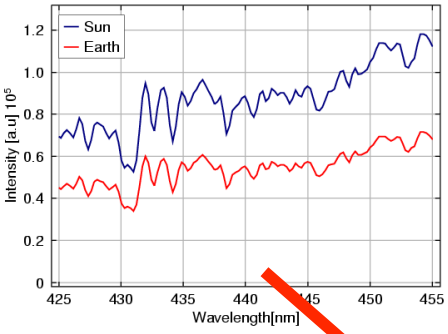
disadvantages:

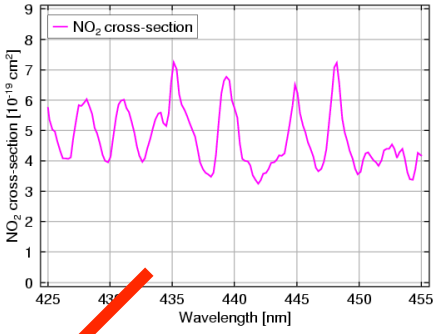
- relatively short light path
- need for bright lamp (+ power)
- usually not fully automated

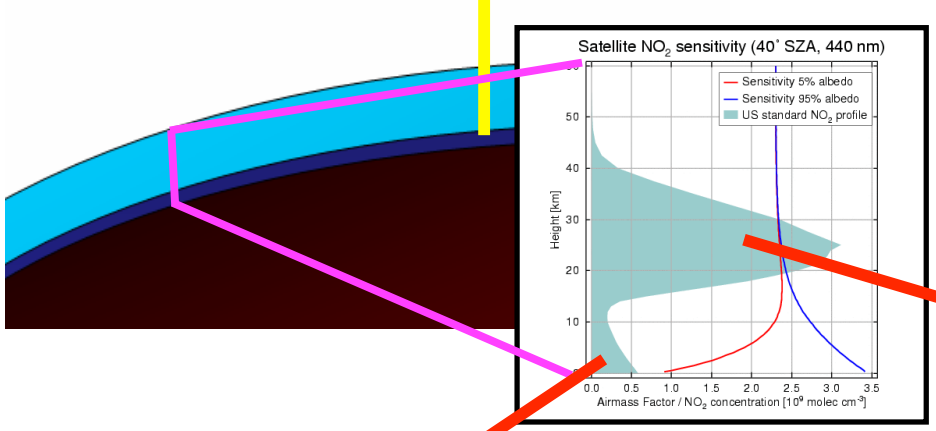


Satellite NO_2 Measurements









DOAS analysis

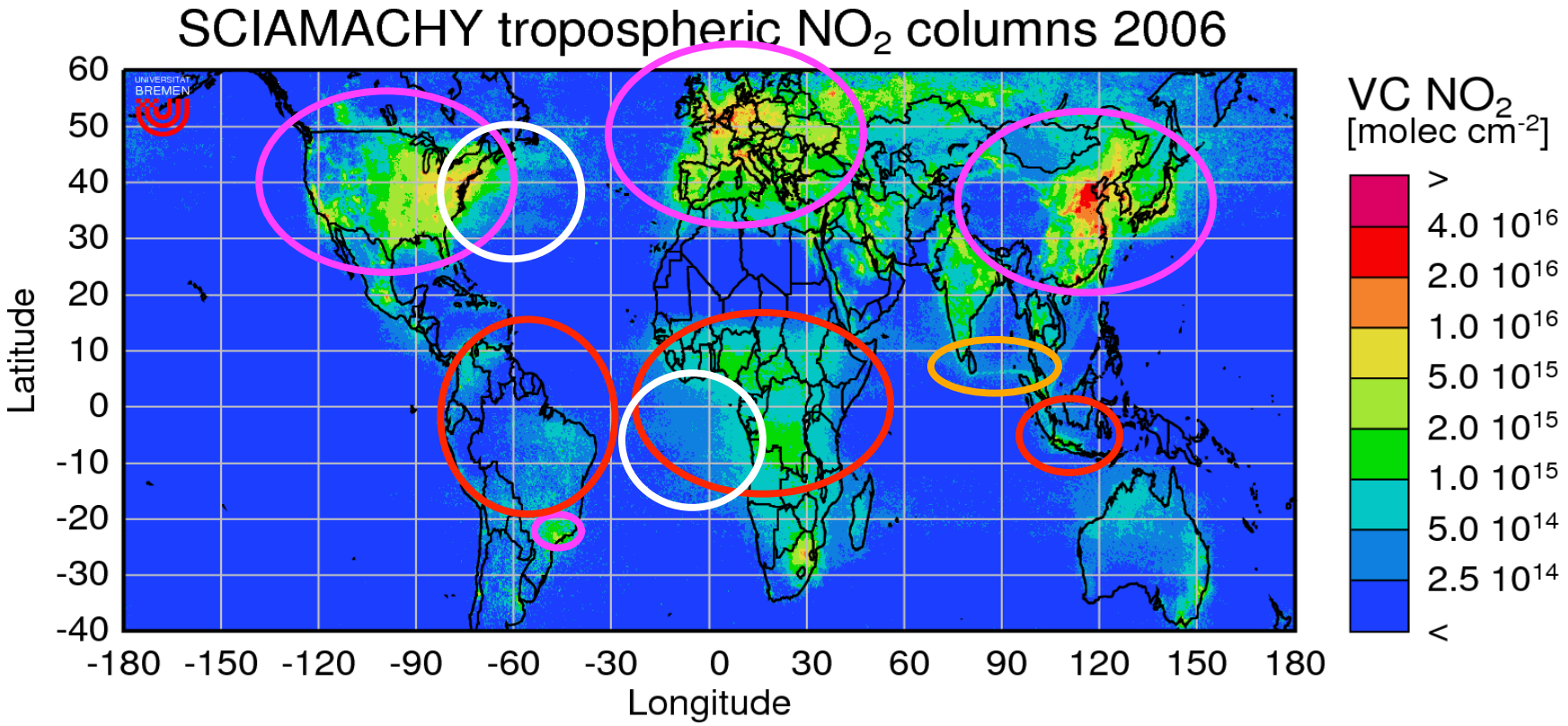
Total Slant Column

Tropospheric Slant Column

SCIATRAN RTM (airmass factor)

Tropospheric Vertical Column

Satellite NO_2 Measurements: Example



anthropogenic pollution

biomass burning

ships

transport

Satellite NO_2 instruments

GOME

- 07.95 – 06.03 (full coverage)
- 4 channels 240 – 790 nm
- 0.2 – 04 nm FWHM
- nadir viewing
- 320 x 40 km^2 ground pixel
- sun-synchronous orbit
- global coverage in 3 days

GOME-2

- similar to GOME
- launched 10.06
- 80 x 40 km^2 ground pixel
- global coverage in 1.5 days

SCIAMACHY

- 08.02 – today
- 8 channels 240 – 1700 nm and 2 – 2.4 µm
- 0.2 – 04 nm (1.5 nm) FWHM
- nadir viewing + limb + solar / lunar occultation
- 60 x 30 km^2 typical ground pixel
- sun-synchronous orbit
- global coverage in 6 days

OMI

- imaging spectrometer
- launched 07.04
- 13 x 24 -120 x 24 km^2 ground pixel
- global coverage in 1 day

NOx Emission Estimates

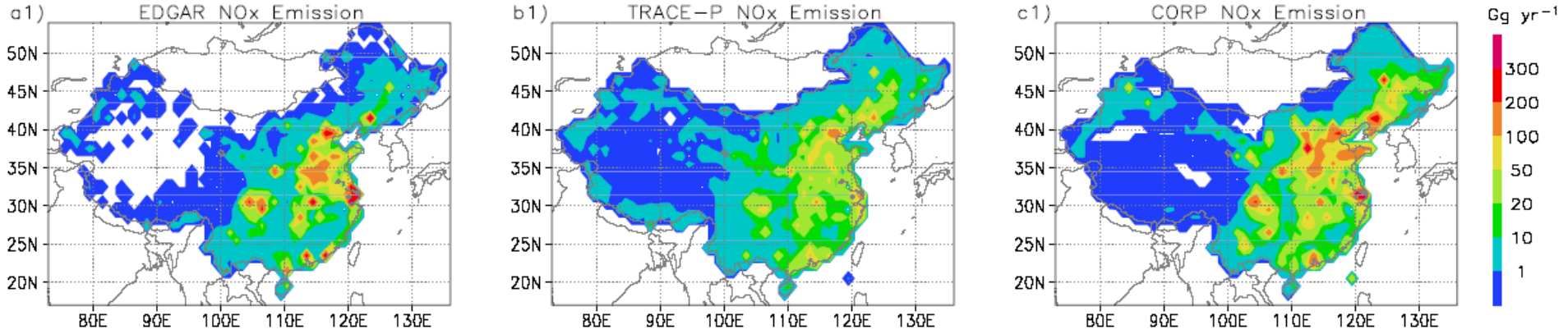
"bottom up"

- using statistical data on activities (e.g. number and type of cars, average mileage, average fuel consumption)
- and data on emission factors (x g NO emitted per l fuel)

"top down"

- using measurements of e.g. NO_2 or other species influenced by NO_x
- applying a model to establish the connection between emissions and atmospheric concentrations (or columns)
- iterating emissions in the model to improve agreement between model prediction and measurements
- the more measurements, the better => satellite data should be optimal, but accuracy and lack of vertical resolution is a problem

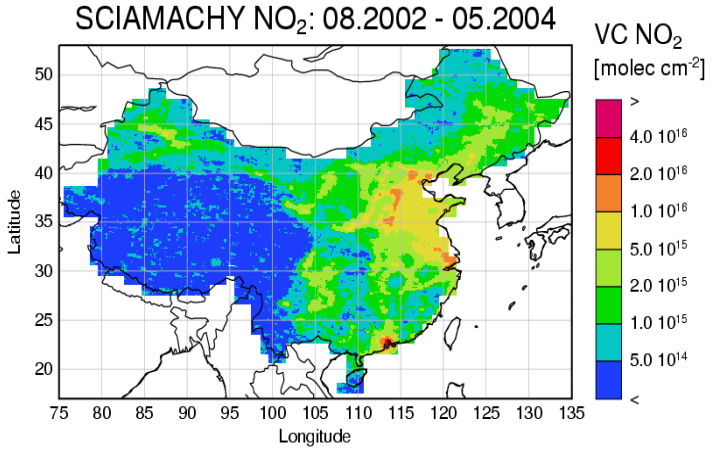
Example: Bottom up Emission Estimates for China



Problem:

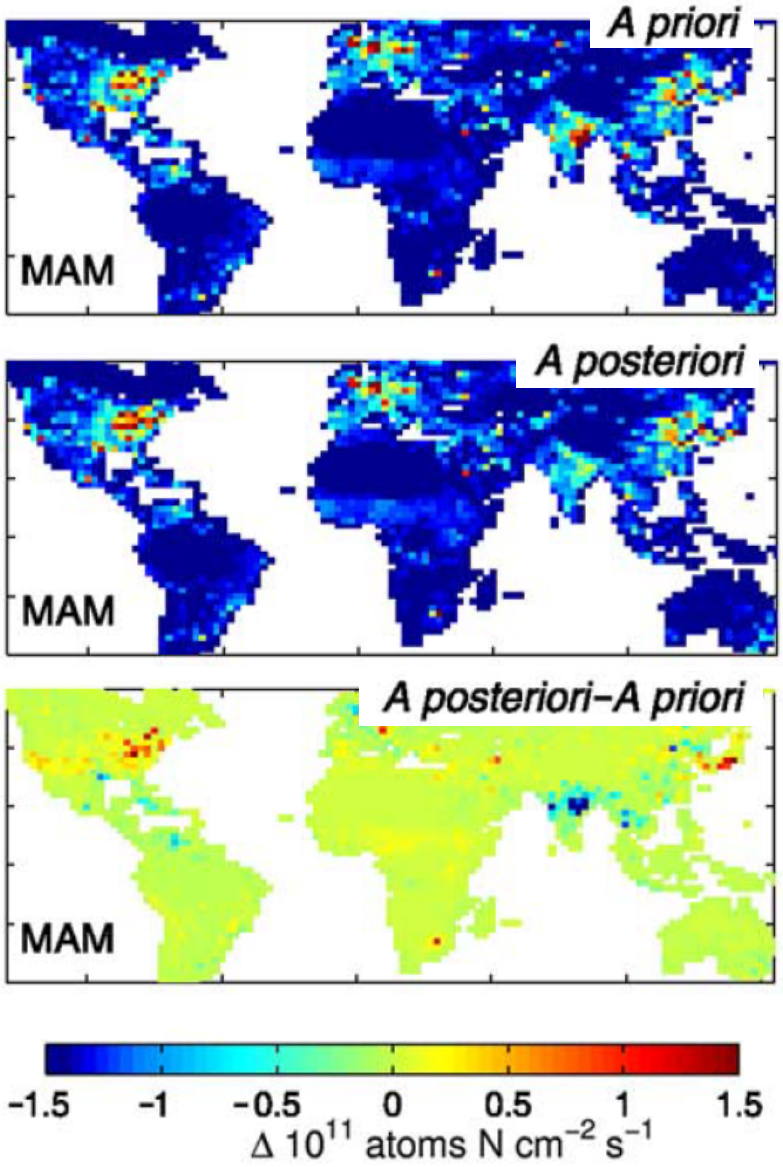
- depending on the data source and approach used, emission inventories differ significantly
- political considerations can interfere (in both directions)

→ comparison with independent data e.g. from satellites can help



Ma, J. et al., Comparison of model-simulated tropospheric NO2 over China with GOME-satellite data, *Atmospheric Environment*, **40, 593–604, 2006**

Example: Top Down Emission Estimates



Approach:

- GEOS-CHEM model
- GOME NO_2 columns
- linearized relation between NO_x emission and NO_2 column determined for each grid cell from model
- error weighted combination of a priori (GEIA) and a posteriori emissions
- improved emission inventory with reduced uncertainties

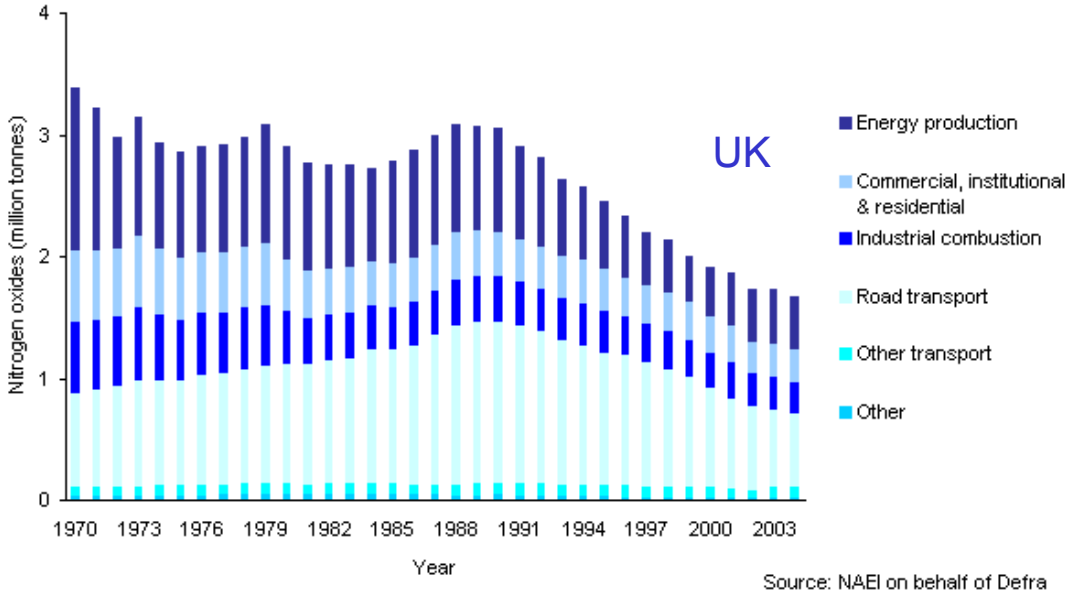
Martin, R. et al.,, Global inventory of nitrogen oxide emissions constrained by space-based observations of NO2 columns, *J. Geophys. Res.*, **108**(D17), 4537, doi:10.1029/2003JD003453, 2003.

NOx Emission Trends

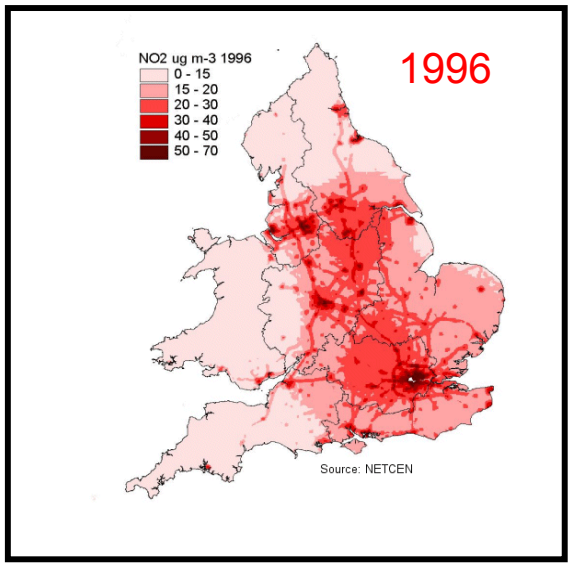
NO_x emissions in Europe, the US and Japan are decreasing:

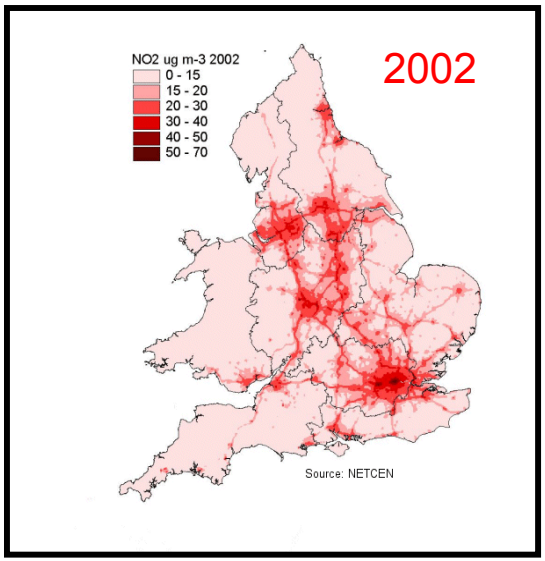
- switch from coal and oil to natural gas
- use of catalytic converters
- "export" of heavy industry

As a result, NO_2 levels have fallen as expected, but not the ozone levels.



Source: NAEI on behalf of Defra

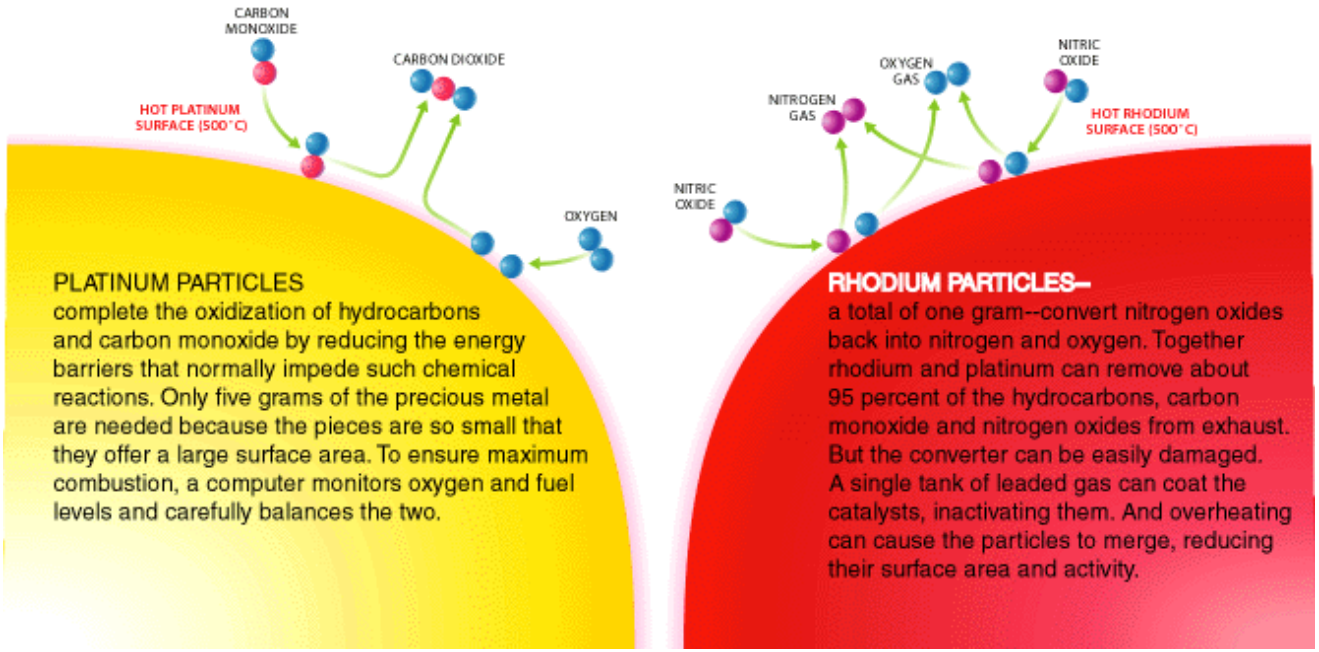




http://www.environment-agency.gov.uk/commondata/103196/1162888?referrer=/yourenv/eff/1190084/air/1158715/1162725/

NOx reductions: Catalytic Converter

In principle, if fuel would be fully oxidized, cars should only emit H_2O and CO_2. However, in practice not all hydrocarbons are oxidized and NO is formed from N_2 and O_2.



oxidation of hydrocarbons and CO on platinum

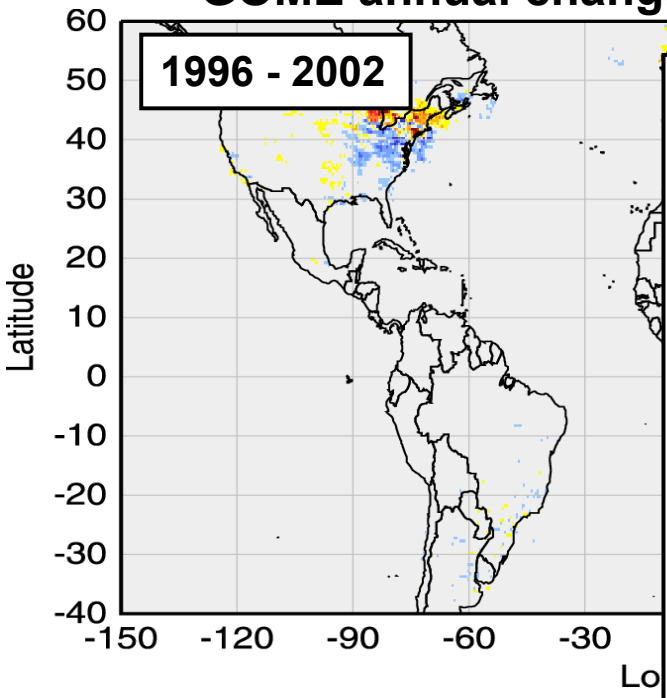
$2CO + O_2 \rightarrow 2\ CO_2$

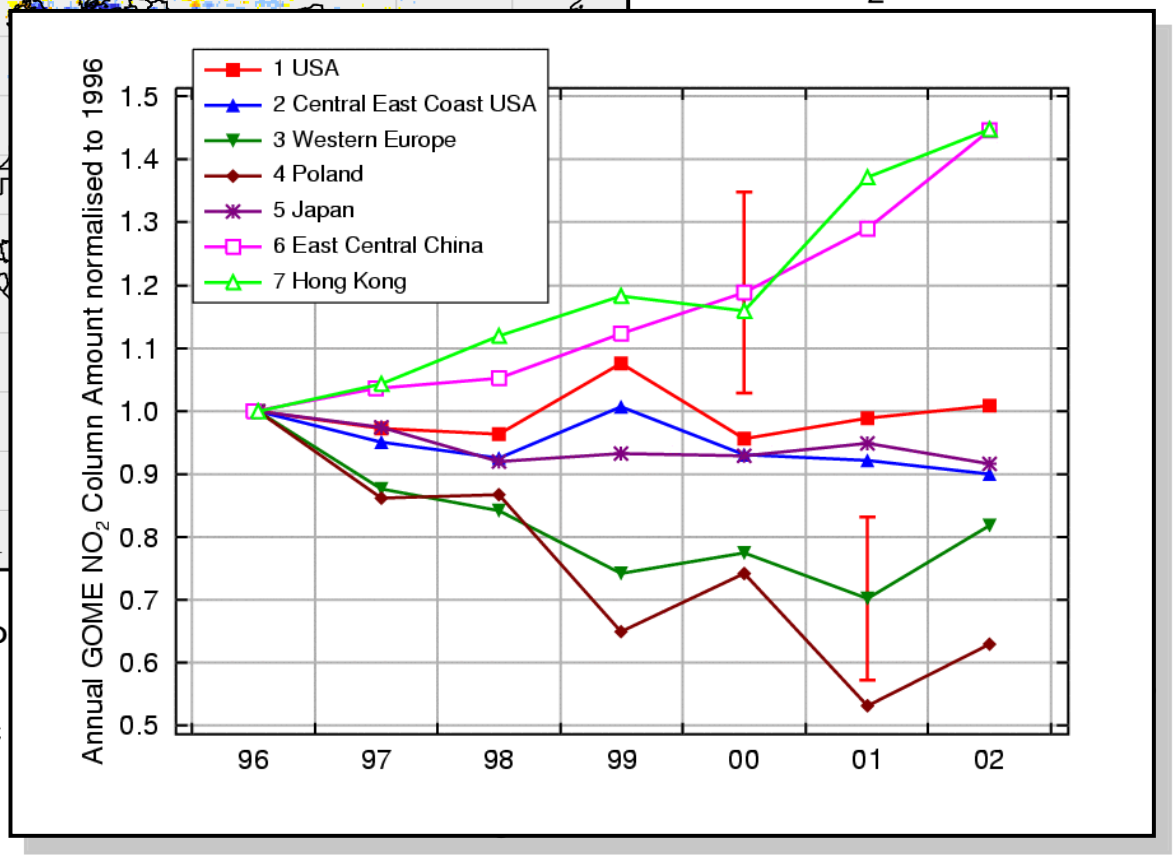
conversion of NO to N_2 and O_2 using H_2 and CO from the exhausts on rhodium:

$2NO \rightarrow N_2 + O_2$

Satellite NO_2 Trends: The Global Picture

GOME annual changes in tropospheric NO_2

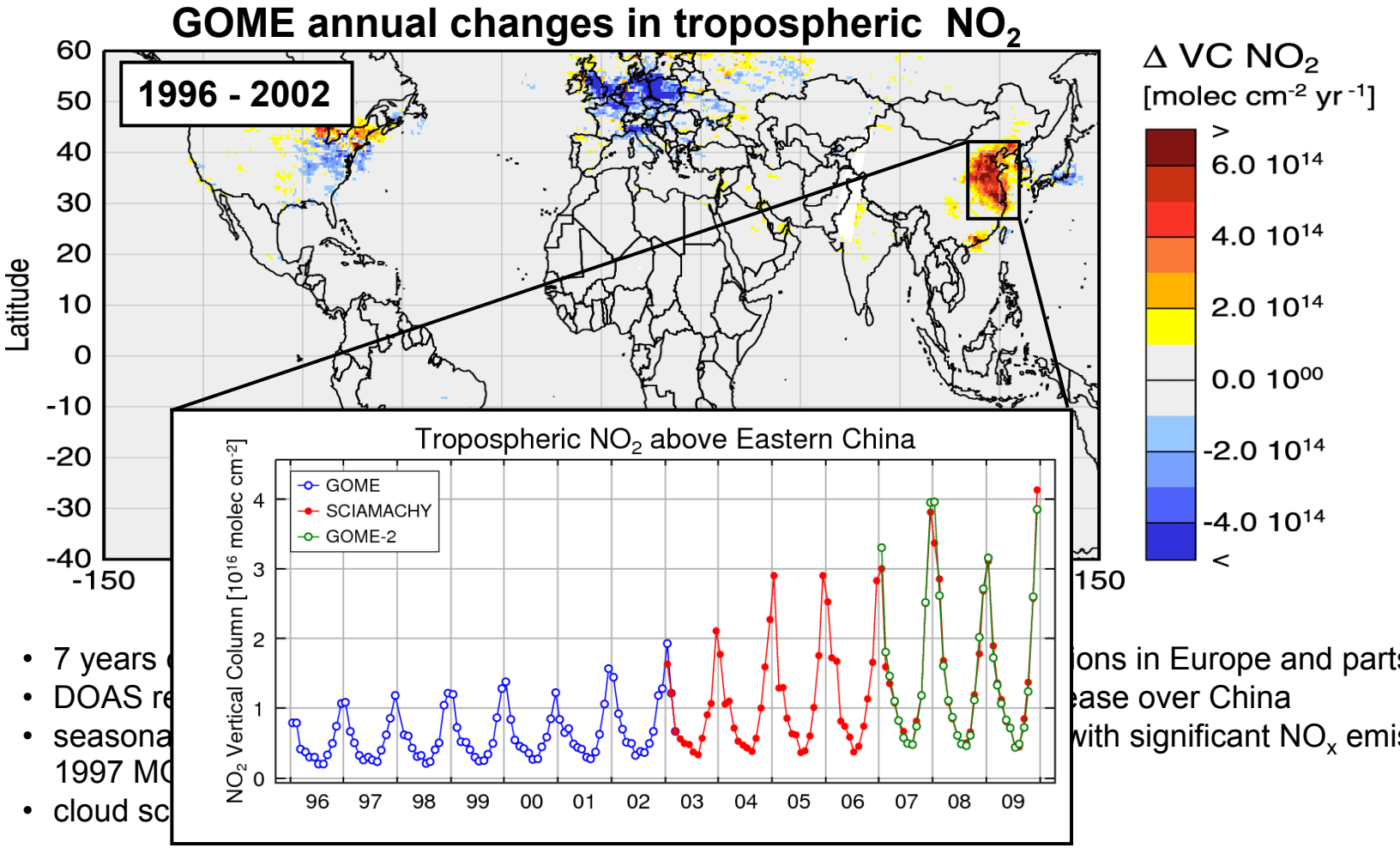




- 7 years of GOME satellite data
- DOAS retrieval + CTM-stratospheric
- seasonal and local AMF based on 1997 MOART-2 run
- cloud screening

A. Richter et al., Increase in tropospheric nitrogen dioxide over China observed from space, *Nature*, **437** 2005

Satellite NO_2 Trends: The Global Picture



- 7 years (
- DOAS re
- seasona
  1997 MC
- cloud sc

ions in Europe and parts of the US
ease over China
with significant NO_x emission

A. Richter et al., Increase in tropospheric nitrogen dioxide over China observed from space, *Nature*, **437** 2005

Satellite NO2 Trends: Caveats

What can explain the observed increase in NO_2 over China?

- A GOME **instrument drift**

  => this should affect Japan as well but not SCIAMACHY
- A change in viewing conditions as a result of changes in **cloud cover, aerosol loading or vertical transport**

  => there is no indication for this from the GOME data themselves
- A change in **NO to NO_2 partitioning** at constant NO_x levels, for example as a result of a change in O_3
- A change in **NO_2 losses**, for example as a result of decreased OH concentrations
- An increase in NO_2 concentrations as a result of increased **NO_x emissions**

Satellite NO_2 Trends over large cities

Table 1. The Observed Trend for Several Cities in the Period 1996–2006[a]

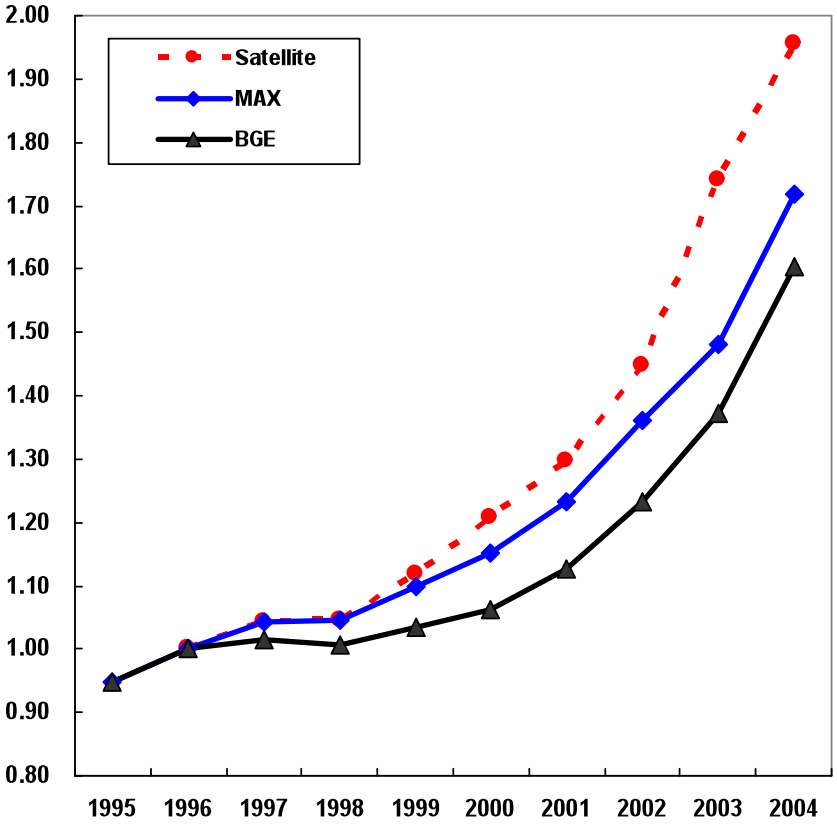
	Center Coordinates Grid Cell (lat./lon.)	Mean Concentration NO_2 in 1996 [10^{15} molec/cm^2]	Linear Trend in NO_2 [10^{15} molec/cm^2/a]	Annual Growth Rate (%, Reference Year 1996)
		Biggest Megacities		
Tokyo	35.5°/139.5°	10.9	−0.23 ± 0.19	−2.1 ± 2
Mexico City	19.5°/−99.5°	7.5	0.13 ± 0.05	1.7 ± 1
Seoul	37.5°/126.5°	10.4	0.13 ± 0.13	1.3 ± 1
New York	40.5°/−74.5°	12.9	−0.03 ± 0.17	−0.3 ± 1
Sao Paulo	−23.5°/−46.5°	4.9	0.11 ± 0.11	2.2 ± 2
Bombay	18.5°/72.5°	2.3	0.07 ± 0.03	3.0 ± 1
Delhi	28.5°/77.5°	4.1	0.30 ± 0.06	7.4 ± 1
Shanghai	30.5°/121.5°	5.2	1.5 ± 0.24	29 ± 5
Los Angeles	34.5°/−118.5°	11.0	−0.10 ± 0.11	−0.9 ± 1
Osaka	34.5°/135.5°	9.0	0.00 ± 0.11	0.0 ± 1
Jakarta	−6.5°/106.5°	3.7	−0.03 ± 0.04	−0.7 ± 1
Calcutta	22.5°/88.5°	2.6	0.06 ± 0.03	2.2 ± 1
Cairo	30.5°/31.5°	4.0	0.05 ± 0.04	1.3 ± 1
Manila	14.5°/120.5°	2.6	−0.14 ± 0.04	−5.6 ± 1
Karachi	24.5°/67.5°	1.7	0.02 ± 0.02	1.4 ± 1
Moscow	55.5°/37.5°	6.9	0.14 ± 0.27	2.1 ± 4
Buenos Aires	−34.5°/−58.5°	3.3	−0.08 ± 0.06	−2.5 ± 2
Dacca	23.5°/90.5°	2.3	0.03 ± 0.02	1.4 ± 1
Rio de Janeiro	−22.5°/−43.5°	3.8	−0.06 ± 0.07	−1.6 ± 2
Beijing	39.5°/116.5°	11.1	1.2 ± 0.29	11 ± 3
London	51.5°/−0.5°	8.2	0.06 ± 0.17	0.7 ± 2
Tehran	35.5°/51.5°	4.1	0.26 ± 0.05	6.5 ± 1
		Other interesting cities		
Novosibirsk	55.5°/83.5°	1.3	0.13±0.03	11±3
Omsk	54.5°/73.5°	0.84	0.08±0.04	9.9±4
Ruhr (Cologne)	50.5°/6.5°	11.0	−0.40±0.12	−3.6±1

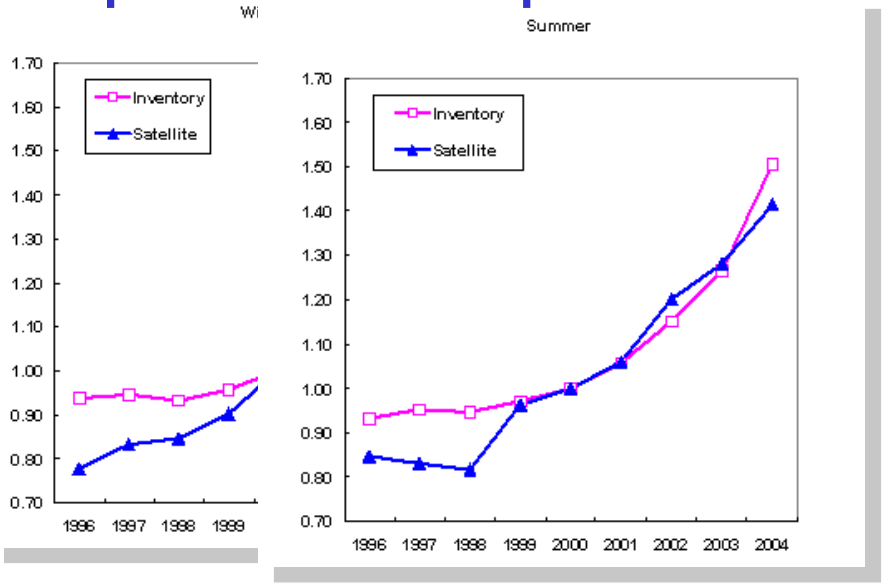
[a]The 22 biggest megacities are ordered by population number.

van der A, R. J.et al. (2008), Trends, seasonal variability and dominant NOx source derived from a ten year record of NO2 measured from space, *J. Geophys. Res.*, 113, D04302, doi: 10.1029/2007JD009021.

NO_2 Trends: Comparison with bottom up estimates

How do the satellite derived trends compare to bottom up estimates?



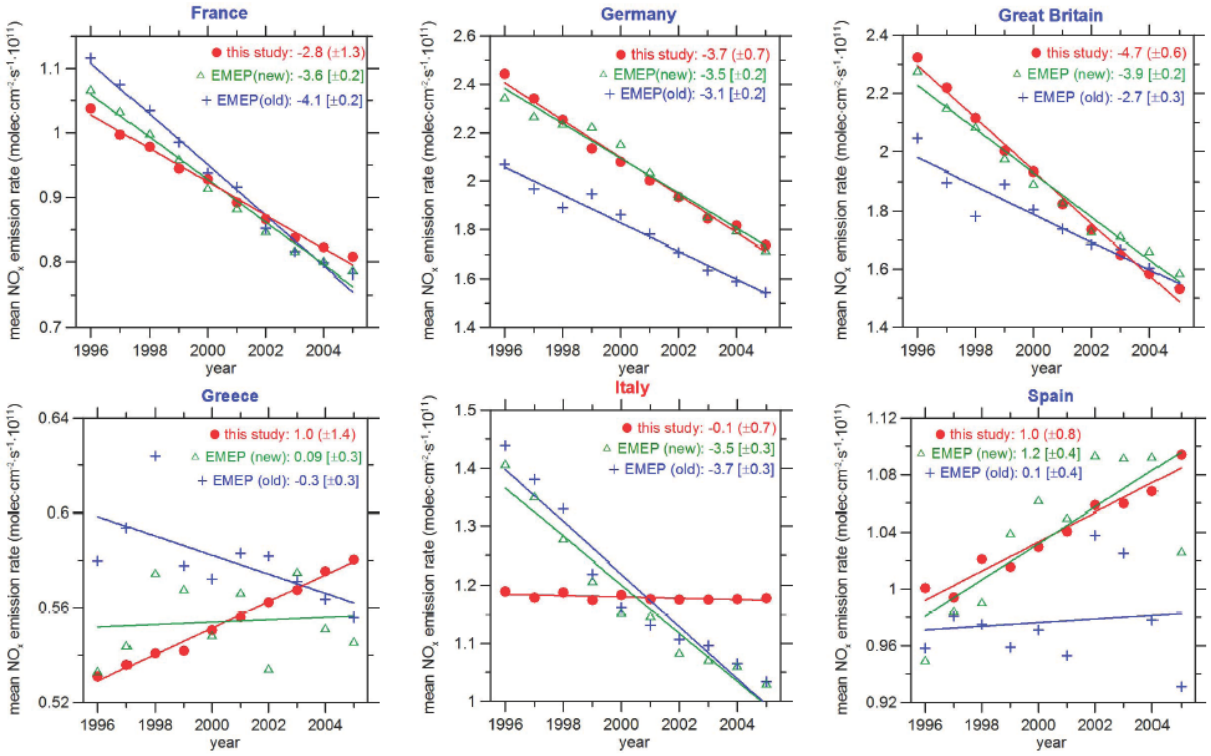


- the latest bottom-up inventories agree qualitatively with satellite data
- summer values agree even quantitatively
- satellite problems in winter?
- strong seasonality in emissions?

Q. Zhang et al., NOx emission trends for China, 1995–2004: The view from the ground and the view from space, J. Geophys. Res., 112, D22306, doi: 10.1029/2007JD008684., 2007

NO_2 Trends above Europe

How do the satellite derived trends compare to bottom up estimates?

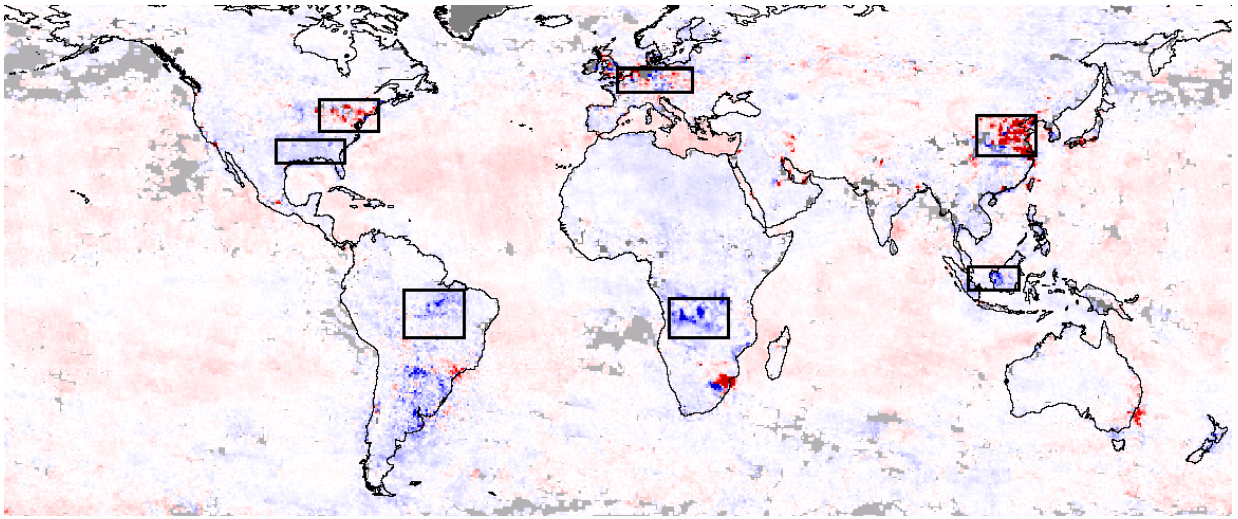


- GOME and SCIAMACHY data over Europe + CHIMERE
- Comparison to two versions of EMEP emissions
- Excellent agreement in some regions, disagreement in others

Konovalov, I.et al., Satellite measurement based estimates of decadal changes in European nitrogen oxides emissions, Atmos. Chem. Phys., **8**, 2623-2641, 2008

Diurnal variation of NOx emissions

SCIA – OMI tropospheric NO_2 August 2006



SCIAMACHY:
morning orbit (10:00 LT)

OMI:
noon orbit (13:30 LT)

expected changes in

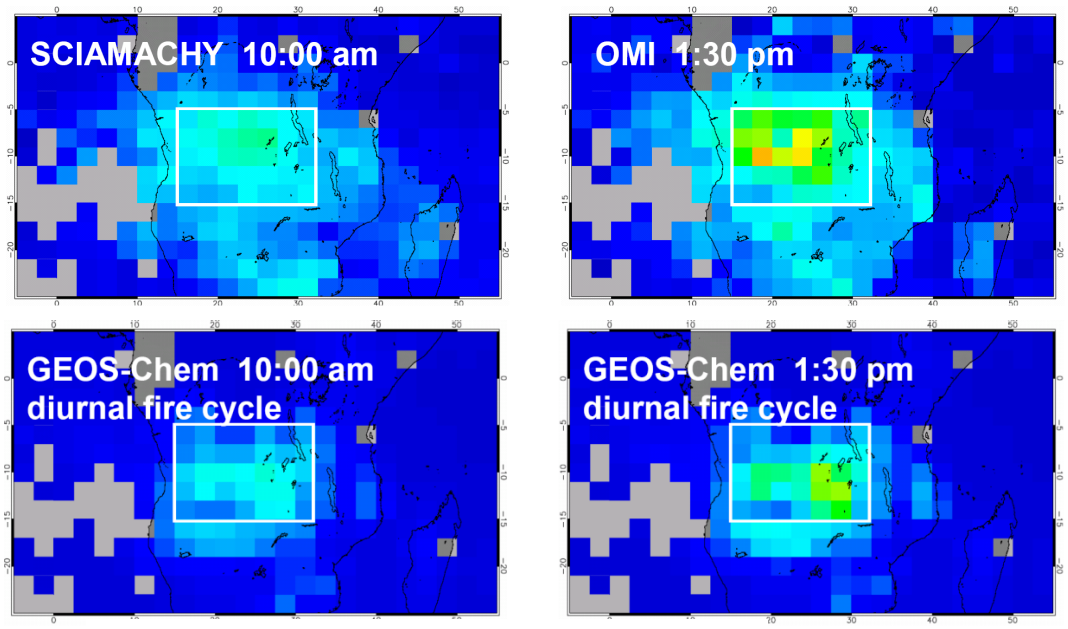
- **photochemistry**
  => less NO_2 around noon
- **emissions**
  => depends on sources

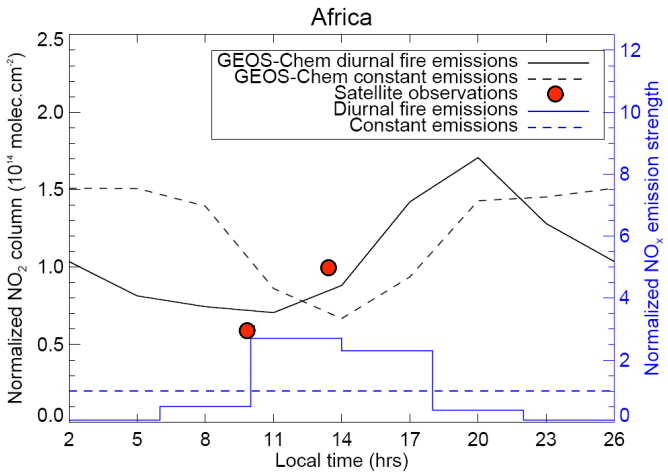
=> SCIAMACHY 10-40% higher than OMI for most anthropogenic source regions

=> SCIAMACHY lower than OMI for biomass burning regions

F. Boersma et al., Intercomparison of SCIAMACHY and OMI tropospheric columns:
observing the diurnal evolution of chemistry and emissions from space *J. Geophys. Res., 113*, D16S26, doi:10.1029/2007JD008816

Diurnal variation of NOx emissions



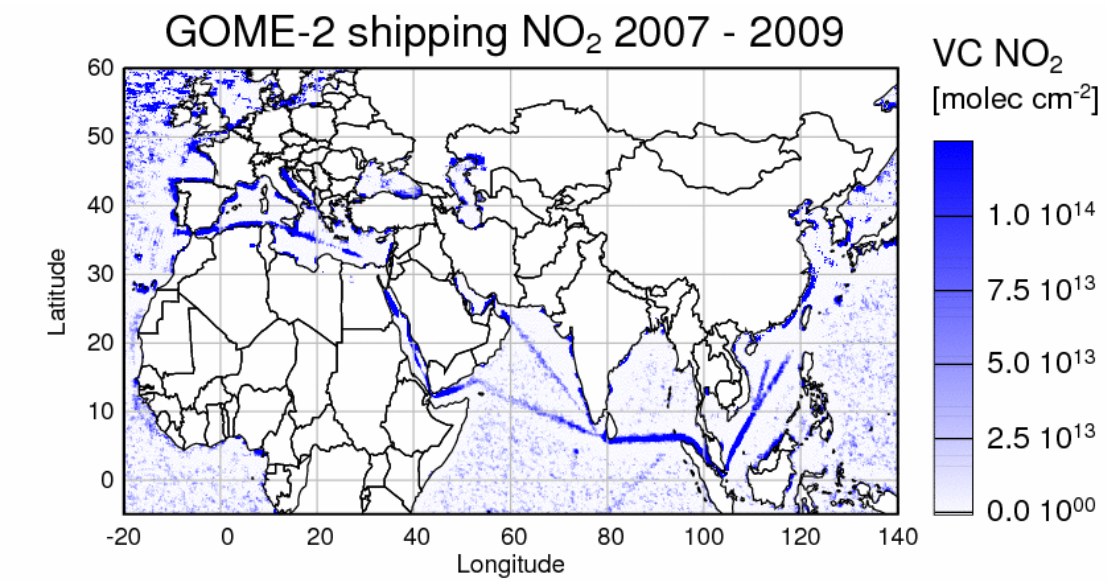


Comparison with **GEOS-Chem:**

- diurnal variation over biomass burning not correct
- diurnal emission profile needs to be taken into account
- better agreement is achieved
- but: it's only two points...

F. Boersma et al., Intercomparison of SCIAMACHY and OMI tropospheric columns: observing the diurnal evolution of chemistry and emissions from space *J. Geophys. Res., 113*, D16S26, doi: 10.1029/2007JD008816

NOx Emissions from Shipping

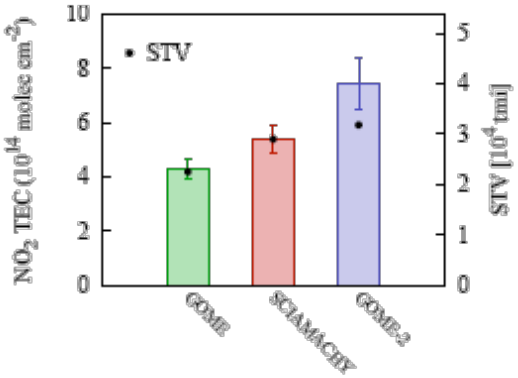


Ship emissions:

- large source of NO_x, SO_x and aerosols
- relevant input into marine boundary layer
- well defined NO_2 patterns in Red Sea and Indian Ocean in GOME-2 data
- consistent with pattern of shipping

With estimate of NO_2 lifetime, NO_x emissions can be estimated => agreement within error bars.

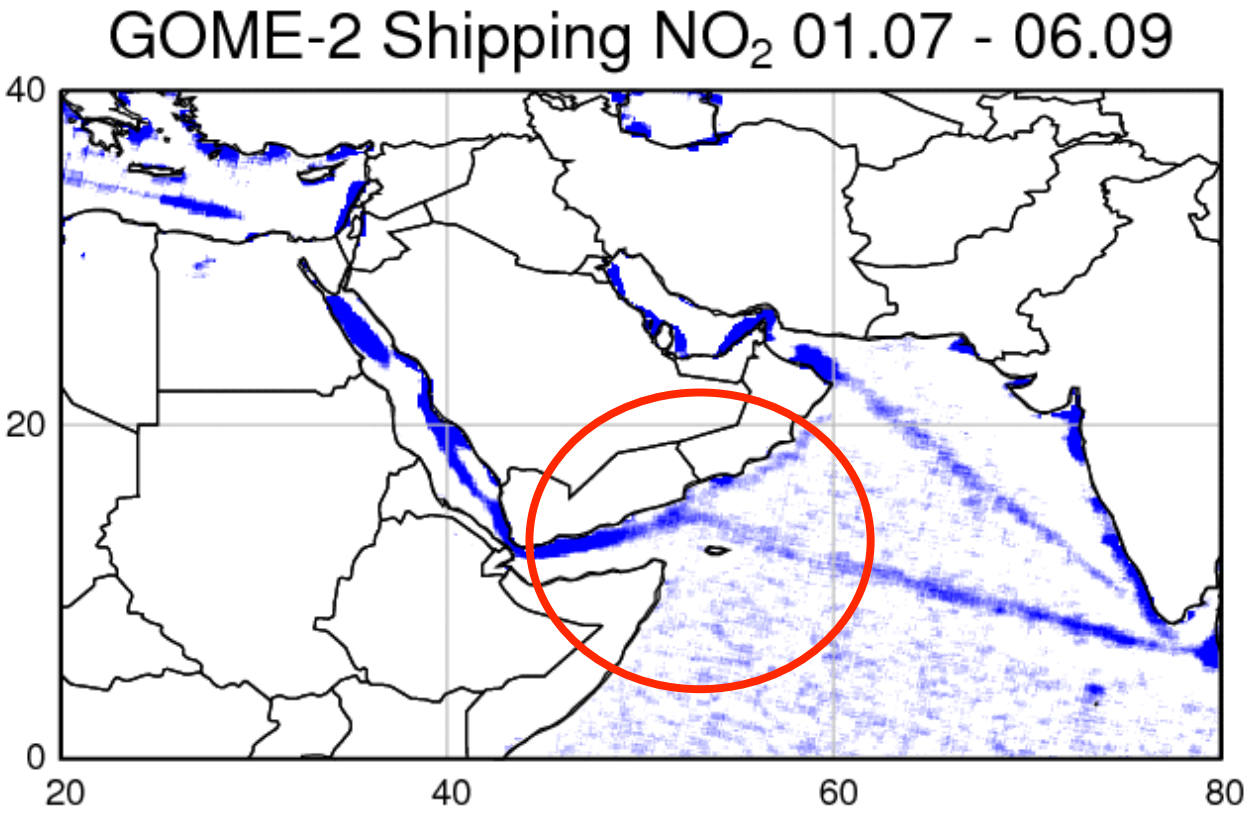
But: error bars still large (mainly from lifetime)



Franke et al., Atmos. Chem. Phys. Discuss., 8, 15997–16025, 2008

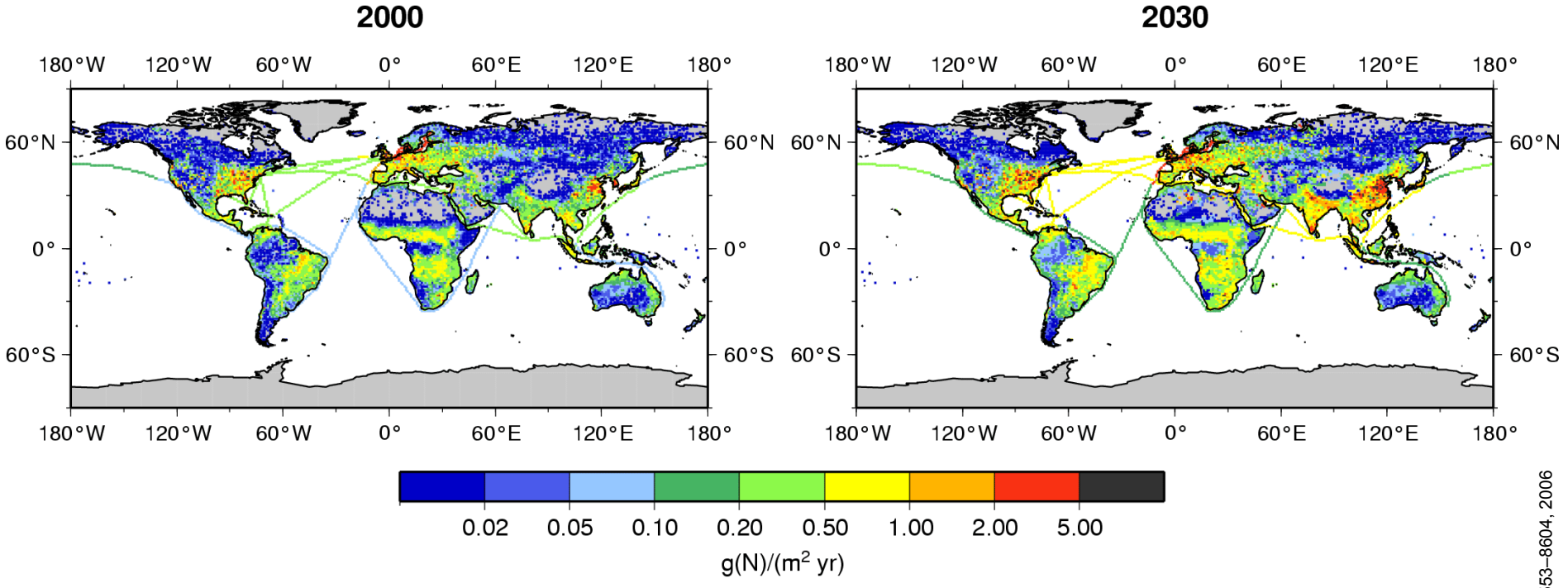
A. Richter et al., Satellite Measurements of NO2 from International Shipping Emissions, *Geophys. Res. Lett.*, **31**, L23110, doi:10.1029/2004GL020822, 2004

Temporal change in shipping NOx



- Pattern of ship emissions in the vicinity of Yemen changed since 2007
- Probably in response to pirate attacks

NOx Emission Trends: predictions



- more or less constant in industrialised areas
- increases in developing countries
- large increases in Asia
- large increases from shipping

Eyring et al., Atmos. Chem. Phys. Discuss., 6, 8553–8604, 2006

Are Emissions changing from NO to NO_2?

Conventional Wisdom:

- all NO_x is emitted as NO
- rapid conversion to NO_2 via reaction with O_3

Recent Developments:

- measurements hint at up to 20% of NO_2 emissions
- oxidizing particulate traps in diesel engines oxidize NO
- this is going to increase!

Effects:

- change in NO_2 concentrations in rural areas
- effect on top-down emission estimates
- shift in NO_x / NO_y chemistry

Summary

- NO_x ($NO + NO_2$) in the troposphere is relevant for ozone chemistry, acid deposition
- NO_x emissions are both natural (soils, lightning, fires) and anthropogenic (fossil fuels, fires), the latter dominating
- NO_x can be measured in-situ, NO_2 also by spectroscopic methods both locally and from satellite
- satellite measurements provide interesting insights in many aspects of NO_x emissions and chemistry
- NO_x emissions are changing with decreasing values in the already industrialised countries (improved technology, fuel changes) and increasing values in the industrialising countries (intensified used of fossil fuels)
- technological changes can have unexpected results on NO_x emissions (e.g. diesel engines, soot filters)

=> we are not going to run out of interesting NO_x topics anytime soon!