Nitrogen Oxide Emissions

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Overview

1. What is the role of nitrogen in the atmosphere?
2. What is NO\textsubscript{x}?
3. What is it doing in the troposphere?
4. Why should we care?
5. Where does it come from?
6. Is it changing with time?
Nitrogen in the Atmosphere

- nitrogen is needed to sustain life
- 99% of the nitrogen is in the form of $N_2$ which can only be used by a small number of microbes
- in most regions of the earth, there is not enough nitrogen available to sustain human population
- anthropogenic emissions of reactive nitrogen are in the form of fossil fuel burning, biomass burning and industrial production of $NH_3$
- as only a small fraction of the reactive nitrogen can be used, most of it is entering the atmosphere and accumulates

- nitrogen accumulation contributes to loss of biodiversity, acid deposition, acidification of soils and waters, coastal eutrophication, forest productivity changes and is linked to ozone smog formation, climate change and stratospheric ozone depletion
The Nitrogen Cycle

Simplified NOx Chemistry in the Troposphere

adapted from M. Jenkin
Some facts on NO\textsubscript{x} in the Troposphere

- NO and NO\textsubscript{2} are rapidly converted into each other and are therefore combined to
  \[ \text{NO}_x = \text{NO} + \text{NO}_2 \]
- the ratio \([\text{NO}] / [\text{NO}_x]\) is about 0.2 at the surface but increases towards higher altitudes (temperature dependence of \(\text{O}_3 + \text{NO}\) reaction)
- the atmospheric lifetime of NO\textsubscript{x} is short close to the surface (hours) and increases towards higher altitudes (days)
- 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\textsubscript{x}
  \(\Rightarrow\) NO\textsubscript{x} is found close to its sources
- PAN has a long lifetime and can be transported and re-release NO\textsubscript{x} when temperature increases

Ehhalt D.H. et al. (1992) Sources and distribution of NO\textsubscript{x} in the upper troposphere at northern mid-latitudes. J Geophys Res 97: 3725–3738
Why should we care about NOx in the Troposphere?

NOx
• is a key species in tropospheric ozone formation
• leads to formation of HNO₃ and thereby acid rain
• contributes to eutrophication
• acts as a greenhouse gas (NO₂, at least locally)
• acts indirectly on climate through ozone formation
• can contribute to aerosol formation
Sources of NOx in the Troposphere

Main sources of NO\textsubscript{x} (in Tg N / yr) are

- fossil fuel combustion \hphantom{.}22.0 (15 – 29)
- fires \hphantom{.}6.7 (3 – 10)
- microbial soil emissions \hphantom{.}5.5 (3.3 – 7.7)
- lightning \hphantom{.}2.0 (1 – 4)
- oxidation of biogenic NH\textsubscript{3} \hphantom{.}1.0 (0.5 – 1.5)
- aircraft \hphantom{.}0.5 (0.5 – 0.6)
- stratosphere \hphantom{.}0.5 (0.4 – 0.6)

Anthropogenic NOx Sources

- 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: EA

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Soil Sources of NOx

- NO and N₂O are emitted from microbial activities in the soil, both during nitrification (NH₄⁺ → NO₃⁻) and denitrification (NO₃⁻ → N₂)
- 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 NOₓ emitted is lost by NO₂ deposition
- NOₓ soil emissions seem to be underestimated in current models
- potential for increases as use of fertilizers increases, but strong dependence on actual practices used
- potential for link to climate as dependence on both T and humidity is strong and N₂O is greenhouse gas
Soil Sources of NOx: Example

- Chouteau, Hill and Liberty Counties in North-Central Montana, USA
- harvested cropland, low population density, no large stationary NOx sources
- NO2 columns retrieved from SCIAMACHY satellite data are large after fertilisation and subsequent precipitation

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\textsubscript{x}
- the amount of NO\textsubscript{x} emitted per biomass burned varies strongly between different biomass types (savannah, tropical rain forests, boreal forests)
- large amounts of NO\textsubscript{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\textsubscript{x} in the upper troposphere
NOx from Biomass Burning: Example

- 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\textsubscript{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\textsubscript{x} in models often parameterised by cloud height or convective precipitation

- the relevance of lightning NO\textsubscript{x} is that it is injected in the upper troposphere, where ozone formation is very efficient
NOx from Lightning: Example

- NO\textsubscript{2} columns retrieved from GOME satellite data
- coincident measurements of clouds, lightning and NO\textsubscript{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
The global View: Satellite NO2 Measurements

SCIAMACHY tropospheric NO\textsubscript{2} columns 2006

anthropogenic pollution

biomass burning

ships

transport

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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\textsubscript{2} or other species influenced by NO\textsubscript{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)

$\rightarrow$ 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
NO\textsubscript{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\textsubscript{2} levels have fallen as expected, but not the ozone levels.
Satellite NO2 Trends: The Global Picture

GOME annual changes in tropospheric NO2

Δ VC NO2 [molec cm⁻² yr⁻¹]

- 6.0 10¹⁴

A. Richter et al., Increase in tropospheric nitrogen dioxide over China observed from space, Nature, 437 2005
Satellite NO2 Trends: US Power Plants

- GOME NO$_2$ time-series shows non-significant trend in USA
- after 2000, clear decrease (> 30%) in NO$_2$ in Ohio-valley area
- no change in urban areas
- size and geographical pattern consistent with model simulations

Satellite NO2 Trends: US Power Plants

NO$_2$ columns in summer over the US – measurement and WRF model run

US Power Plant NOx reductions: Effect on ozone

- NO\textsubscript{x} reductions lead to large NO\textsubscript{2} reductions locally
- O\textsubscript{3} reductions significant but smaller and much less locally
- depend strongly on meteorological conditions and on VOC distribution
- unexpectedly small effect in northern US

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

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**NOx Emissions from 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)

Summary

- Nitrogen is one of the key elements for life
- $\text{NO}_x$ ($\text{NO} + \text{NO}_2$) in the troposphere is relevant for ozone chemistry, acid deposition
- $\text{NO}_x$ emissions are both natural (soils, lightning, fires) and anthropogenic (fossil fuels, fires), the latter dominating
- Uncertainties on emissions are very large, in particular for natural sources
- Satellite measurements provide interesting insights in many aspects of $\text{NO}_x$ emissions and chemistry
- $\text{NO}_x$ 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)