Analysis of stratospheric NO₂ trends above Kiruna using ground-based zenith sky DOAS observations

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SUMMARY

INTRODUCTION

MEASUREMENTS

ANALYSIS METHODS

RESULTS

SUMMARY

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1. Stratospheric NO$_2$ influence the ozone chemistry. 
   Destruction of ozone or acting as a buffer

2. Major source of stratospheric NOx : N$_2$O 
   - Mostly coming from soil 
   - Life time around 120 years, almost no reaction in Troposphere 
   - Approximately, 90% of N$_2$O in stratosphere is destroyed by photolysis. 
   - Previous studies show that due to rising N$_2$O emission, NO$_2$ increases and O$_3$ decreases.

Several studies show long term NO$_2$ trends, but those are focused on the middle-latitude and southern hemisphere. Here, we study long-term NO$_2$ trend for the northern hemisphere at high-latitude.

3. In this study, we use the ground-based zenith sky DOAS measurement at Kiruna (67°N), Sweden.
4. Trend analysis method: Modified linear regression methods (by Bodeker al., 1998 and modified by Hendrick et al., 2012).
Results: Stratospheric NO$_2$ VCDs over Kiruna

- Negative trend
- Statistically not significant

- Trend relative to year 1997
  - 1997 – 2006: $-0.22 \pm 3.6 \%$/decade
  - 1997 – 2009: $-0.18 \pm 2.4 \%$/decade
  - 1997 – 2015: $-0.05 \pm 1.3 \%$/decade

Measured monthly mean NO$_2$

Calculated NO$_2$ using the multiple linear regression model

Linear trend
The trend of stratospheric NO$_2$ over Kiruna (1997 – 2009) is slightly negative (-0.18±2.4%/decade), but no significant. Here, this study is comparable with F. Hendrick et al. (2012) study.

F. Hendrick et al. (2012) shows the trend of stratospheric NO$_2$ VCDs (1990 – 2009) at Jungfraujoch (46.5°N) using SAOZ and FTIR measurements, -3.7±1.1%/decade and -3.6±0.9%/decade, respectively. → Strong decreasing trends

What is the reason for this discrepancy?
- Different site: Kiruna (67°N) and Jungfraujoch (45°N)
- Different measurement covered period
Come and visit my PICO screen

**PICO4.10** between **14:00-15:00**
1. Stratospheric NO\textsubscript{2} influence the ozone chemistry.
   - Middle and upper stratosphere (25 – 40 km): NO\textsubscript{x} destruction of ozone
     \[\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2\]
     \[\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2\]
     \[\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad \text{[Crutzen, 1970]}\]

   - Below 25km: acting as a buffer against halogen-catalyzed O\textsubscript{3} loss through the formation of reservoir species (ClONO\textsubscript{2}, BrONO\textsubscript{2}).
     \[\text{ClO} + \text{NO}_2 \rightarrow \text{ClONO}_2\]
     \[\text{BrO} + \text{NO}_2 \rightarrow \text{BrONO}_2\]

2. Major source of stratospheric NO\textsubscript{x} : N\textsubscript{2}O
   - Mostly coming from soil
   - Life time around 120 years, almost no reaction in Troposphere
   - Approximately, 90% of N\textsubscript{2}O in stratosphere is destroyed by photolysis.
   - Previous studies show that due to rising N\textsubscript{2}O emission, NO\textsubscript{2} increases and O\textsubscript{3} decreases.

Several studies show long term NO\textsubscript{2} trends, but those are focused on the middle-latitude and southern hemisphere. Here, we study long-term NO\textsubscript{2} trend for the northern hemisphere at high-latitude.
Diurnal cycle of reactive nitrogen compounds for different periods. In most cases (left), $N_2O_5$ is accumulated during night and photolised during day. During polar summer, photolysis of $NO_2$ determines the diurnal cycle of $NO_2$.

[Lambert et al., 2002]
# Literature review

<table>
<thead>
<tr>
<th>Study</th>
<th>Measurement period</th>
<th>Site</th>
<th>Instrument</th>
<th>Trend analysis</th>
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</thead>
<tbody>
<tr>
<td>Dirksen et al. (2011)</td>
<td>1981 – 2010</td>
<td>New Zealand (45°S)</td>
<td>Ground-based zenith sky DOAS</td>
<td>+5% /decade</td>
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<td>McLinden et al. (2001)</td>
<td>1981 – 1999</td>
<td></td>
<td>3D Chemical Transport model</td>
<td>+2.5%/decade</td>
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<td>F.Hendrick et al. (2012)</td>
<td>1990 – 2010</td>
<td>Jungfraujoch (46.5°N)</td>
<td>SAOZ, FTIR</td>
<td>-3.7± 1.1%/decade -3.6±0.9%/decade</td>
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<tr>
<td></td>
<td>2000 – 2010</td>
<td>Harestua (60.2°N)</td>
<td>Ground-based UV/Vis spectrometer</td>
<td>-3.9±3.1%/decade</td>
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**Comparable data**

Gruzdev et al. (2009): Kiruna (67.8°N), Sodankyla (67.4°N)
F.Hendrick et al. (2012): Harestua (60.2°N)
Ground-based zenith sky DOAS

- Geometry of zenith sky DOAS

Differential Optical Absorption Spectroscopy (DOAS) technique:
Remote sensing method to detect trace gases and aerosols in the atmosphere using measured spectra of scattered sunlight.
Each trace gas has the property to absorb particular wavelengths of the light.
Based on Lambert Beer’s law, we investigate the absorption of different species from measured spectrum.

Slant column densities (SCDs)

During twilight time, a long light path in stratosphere

Modified from (http://www.doas-bremen.de/maxdoas_instrument.htm)
Ground-based zenith sky DOAS

- **Measurement site**: Kiruna, Sweden: 67.84°N, 20.41°E
  Good place to study the polar stratospheric chemistry.
  Located in the arctic circle and is often situated under the polar vortex.
  Mountain wave induced Polar Stratospheric Clouds (PSCs) develop.

- **Installation of Zenith Sky DOAS**
  Measurement starts: December of 1996 and since then performed automatic measurements up to now.
  Wavelength range: 300nm to 400nm

  - Fitting window: 356 – 392 nm
  - Fitted species: NO₂, O₄, O₃, Ring effect
  - Daily based twilight reference spectra
  - NO₂ vertical columns retrieved using Langley plot methods, integrating profile
NO$_2$ VCDs retrieval

- **Langley plot method**
  - NDACC Climatology AMFs LUT
  - Langley plot method
  - VCDs

- **Integrating profile**
  - Zenith sky DOAS meas.
  - dSCDs
  - Ground-based profile
  - Integrating profile

**Equation:**

\[
VCD(\theta) = \frac{DSCD(\theta) + SCD_{ref}}{AMF(\theta)}
\]

**Legend:**
- $DSCD(\theta)$: Actual amount of NO$_2$ in the reference spectrum
- $AMF(\theta)$: Mean scattering height depends on SZA
- Based on the Optimal Estimation Method
- Forward model (RTM + Photochemical model)

[Hendrick et al., 2004]
Trend analysis: Approaching method

- Modified linear least squares regression model
  (developed by Bodeker al., 1998 and modified by Hendrick et al., 2012)

\[ M(t) = A(N_A = 2) + B(N_B = 2) \times t + C(N_C = 2) \times QBO(t) + D(N_D = 0) \]
\[ \times Solar\;flux(t) + E(N_E = 1) \times Aerosols(t) + \epsilon \]

M(t) : Modeled NO₂ at decimal month(t).
  Including offset, linear trend, QBO, Solar activity, Seasonality, and stratospheric aerosol amount. → Assumption: each parameter contributes to NO₂ variability and residual

A – E : Model coefficients calculated using a standard linear least squares regression fit to the measured NO₂ data.
  Calculated using Fourier series to fit seasonality.

\[ = \left[ C_0 + C_1 \sin \left(\frac{2\pi t}{12}\right) + C_2 \cos \left(\frac{2\pi t}{12}\right) + C_3 \sin \left(\frac{4\pi t}{12}\right) + C_4 \cos \left(\frac{4\pi t}{12}\right) \right] \times QBO(t) \]
Trend analysis : Predictors

- **Stratospheric aerosol optical thickness**: GISS/NASA simulations data Altitude range (15 – 20 km) and Latitude (66.5°N) (GISS/NASA, http://data.giss.nasa.gov/modelforce/strataer/)

No data 2013 – 2015: Assume minimum optical thickness (0.001)
Dataset: Time series of measured stratospheric NO$_2$ VCDs

- Time series of Zenith Sky DOAS and satellite observation of stratospheric NO$_2$ VCDs (1997 – 2015), (GOME, SCIAMACHY, and GOME2)

Here, we can check the strong seasonal variations and consistent measurements.
Results: Trend analysis (AM)

- NO$_2$ VCDs derived from Langley plot method

Stratospheric NO$_2$ VCDs over Kiruna

Trend relative to year 1997
1997 – 2006: -0.22 ± 3.6 %/decade
1997 – 2009: -0.18 ± 2.4 %/decade
1997 – 2015: -0.05 ± 1.3 %/decade

Measured monthly mean NO$_2$

Calculated NO$_2$ using the multiple linear regression model

Linear trend

Iteration 2
Results: Trend analysis (PM)

- NO$_2$ VCDs derived from Langley plot method

Stratospheric NO$_2$ VCDs over Kiruna

Trend relative to year 1997
- 1997 – 2006: $-0.16 \pm 2.7$ %/decade
- 1997 – 2009: $-0.14 \pm 1.9$ %/decade
- 1997 – 2015: $-0.04 \pm 1.0$ %/decade

- Measured monthly mean NO$_2$
- Calculated NO$_2$ using the multiple linear regression model
- Linear trend
Results: Trend analysis (AM)

- NO₂ VCDs derived from integrating the profile

Stratospheric NO₂ VCDs over Kiruna

Trend relative to year 1997
- 1997 – 2006: -0.22±2.3 %/decade
- 1997 – 2009: -0.17±2.0 %/decade
- 1997 – 2015: -0.05±1.1 %/decade

Measured monthly mean NO₂

Calculated NO₂ using the multiple linear regression model

Linear trend

Iteration 4
Results: Trend analysis (PM)

- NO₂ VCDs derived from integrating the profile

![Graph showing Stratospheric NO₂ VCDs over Kiruna](image)

Trend relative to year 1997
- 1997 – 2006: -0.28±2.9 %/decade
- 1997 – 2009: -0.20±2.1 %/decade
- 1997 – 2015: -0.07±1.0 %/decade

- Measured monthly mean NO₂
- Calculated NO₂ using the multiple linear regression model
- Linear trend

Iteration 5
Here, I have NO$_2$ trend analysis results using two different NO$_2$ VCDs derived from Langley plot method and integrating profile. These two results show similar results to each other. Kiruna measurements show negative trends over 1997 – 2006, 1997 – 2009, and 1997 – 2015. However, those trend values are statistically not significant within the 95% confidence. (p-value: 0.87 – 0.92).

And it shows strong seasonality (p-value:0.057). However, QBO(p-value:0.952), Solar activity (p-value:0.922) and AOD (p-value:0.972) do not significantly contribute to stratospheric NO$_2$ trend.
The trend of stratospheric NO$_2$ over Kiruna (1997 – 2009) shows slightly negative (-0.18±2.4%/decade), but no significant. Here, this study is comparable with F. Hendrick et al. (2012) study.

F. Hendrick et al. (2012) shows the trend of stratospheric NO$_2$ VCDs (1990 – 2009) at Jungfraujoch (46.5°N) using SAOZ and FTIR measurements, -3.7±1.1%/decade and -3.6±0.9%/decade, respectively. → Strong decreasing trends

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Acknowledgement

- Satellite nadir (GOME, SCIAMACHY and GOME2) stratospheric VCDs have been retrieved with scientific product created at the IUP Bremen.
- Stratospheric aerosol optical thickness: GISS/NASA simulations data, altitude range (15 – 20 km) and Latitude (66.5°N), (GISS/NASA, http://data.giss.nasa.gov/modelforce/strataer/)

- F.Hendrick et al., ACP (2012) : Analysis of stratospheric NO₂ trends above Jungfraujoch using ground-based UV-visible, FTIR, and satellite nadir observations
- G.E.Bodeker et al., JGR (1998) : Trends and variability in vertical ozone and temperature profiles measured by ozon sondes at Lauder, New Zealand

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