Analysis of stratospheric NO_2 trends above Kiruna using ground-based zenith sky DOAS observations

Myojeong Gu[1], Carl-Fredrik Enell[2], François Hendrick[3], Janis Pukite[1], Michel Van Roozendael[3], Ulrich Platt[4], Uwe Raffalski[5], and Thomas Wagner[1]

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(1) Max-Planck Institute for Chemistry, Mainz, Germany, myojeong.gu@mpic.de,(2) EISCAT Scientific Association, Kiruna, Sweden, (3) Institut d'Aéronomie Spatiale de Belgique (IASB-BIRA), Brussels, Belgium (4)Institute for Environmental Physics, University of Heidelberg, Heidelberg, Germany, (5) Swedish Institute of Space Physics, Kiruna, Sweden

Analysis of stratospheric NO_2 trends above Kiruna using ground-based zenith sky DOAS observations

PICO4.10

2-minute-madness

1. Stratospheric NO_2 influence the ozone chemistry.
   Destruction of ozone or acting as a buffer

2. Major source of stratospheric NOx :N_2O
   - Mostly coming from soil
   - Life time around 120 years, almost no reaction in Troposphere
   - Approximately, 90% of N_2O in stratosphere is destroyed by photolysis.
   - Previous studies show that due to rising N_2O 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).

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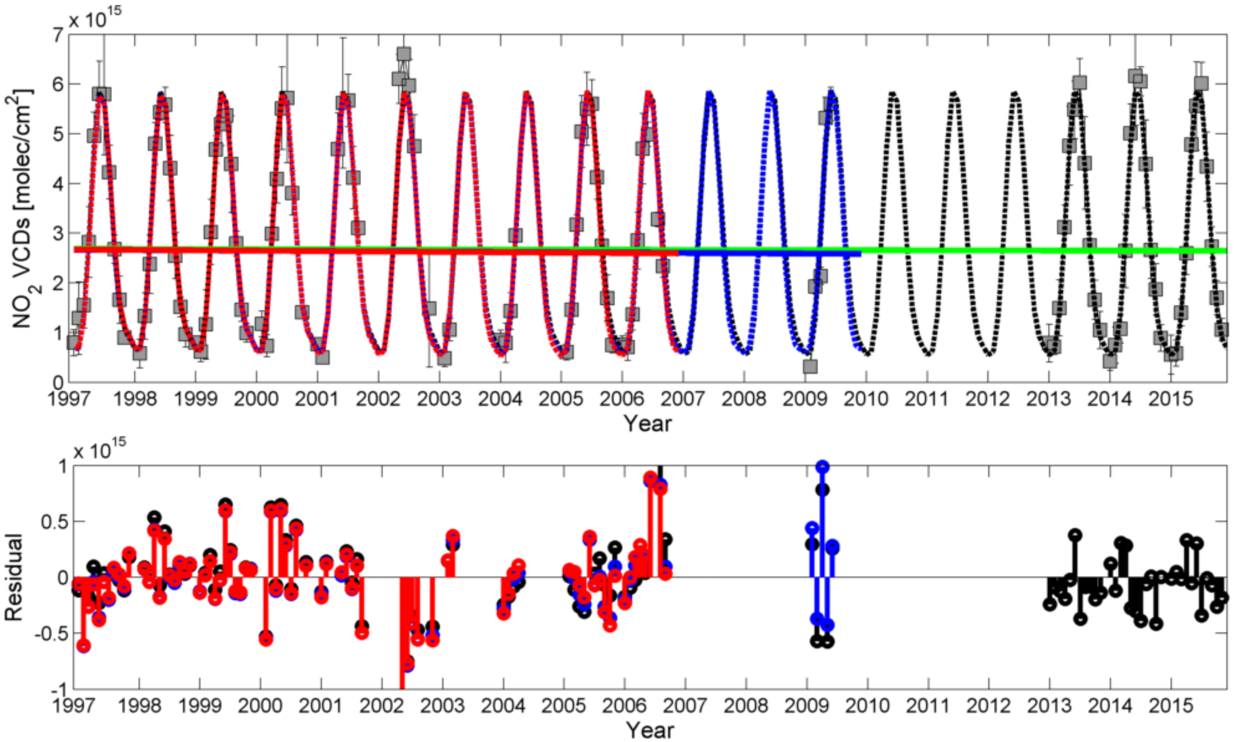
2-minute-madness

5. Results : 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

- Negative trend
- Statistically not significant

Measured monthly mean NO_2

Calculated NO_2 using the multiple linear regression model

Linear trend

Analysis of stratospheric NO_2 trends above Kiruna using ground-based zenith sky DOAS observations

PICO4.10

2-minute-madness

6. 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

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PICO4.10 between **14:00-15:00**

Introduction: Chemistry

1. Stratospheric NO_2 influence the ozone chemistry.

   -Middle and upper stratosphere (25 – 40 km): NO_x destruction of ozone

   $NO + O_3 \rightarrow NO_2 + O_2$

   $NO_2 + O \rightarrow NO + O_2$

   $NO_2 + h\nu \rightarrow NO + O$ [Crutzen, 1970]

   -Below 25km: acting as a buffer against halogen-catalyzed O_3 loss through the formation of reservoir species ($ClONO_2$, $BrONO_2$).

   $ClO + NO_2 \rightarrow ClONO_2$

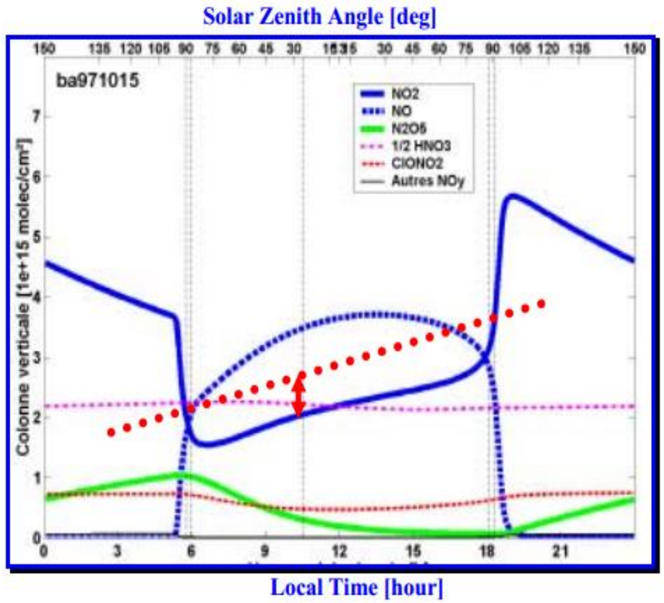
   $BrO + NO_2 \rightarrow BrONO_2$

2. Major source of stratospheric NOx :N_2O
   - Mostly coming from soil
   - Life time around 120 years, almost no reaction in Troposphere
   - Approximately, 90% of N_2O in stratosphere is destroyed by photolysis.
   - Previous studies show that due to rising N_2O emission, NO_2 increases and O_3 decreases.

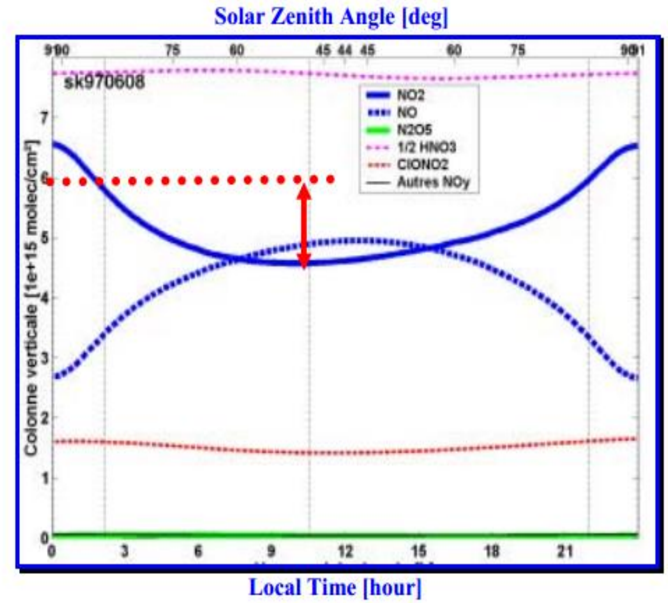
Several studies show long term NO_2 trends, but those are focused on the middle-latitude and southern hemisphere. Here, we study long-term NO_2 trend for the northern hemisphere at high-latitude.

Iteration 1

Day/night Alternance



Polar Summer



[Lambert et al., 2002]

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.

Literature review

	Measurement period	Site	Instrument	Trend analysis
Liley et al. (2000)	1981 – 1991	New Zealand (45°S)	Ground-based zenith sky DOAS	+5% /decade
Dirksen et al. (2011)	1981 – 2010	New Zealand (45°S)	Ground-based zenith sky DOAS	+5% /decade
McLinden et al. (2001)	1981 – 1999		3D Chemical Transport model	+2.5%/decade
Gruzdev et al. (2009)	1983 – 2007	23 NDACC stations	FTIR and ground-based zenith sky DOAS	Mid latitude in SH: positive trend NH: negative trend
Cook & Roscoe (2009)	1990 – 2007	Antarctic	Ground-based zenith sky DOAS	1990 – 2000: +10%/decade 2000 – 2007: -20%/decade
F.Hendrick et al. (2012)	1990 – 2010	Jungfraujoch (46.5°N)	SAOZ, FTIR	-3.7± 1.1%/decade -3.6±0.9%/decade
	2000 – 2010	Harestua (60.2°N)	Ground-based UV/Vis spectrometer	-3.9±3.1%/decade

Literature review

	Measurement period	Site	Instrument	Trend analysis
Liley et al. (2000)	1			
Dirksen et al. (2011)	1			
McLinden et al. (2001)	1			
Gruzdev et al. (2009)	1			
Cook & Roscoe (2009)	1			
F.Hendrick et al. (2012)	1			
	2			

Table 1. Stations for NO_2 observations and annual estimates of linear trends in column NO_2 content.

Station	Latitude	Longitude	Organization responsible for observations	Period of observations	Trend* (% per decade) Morning	Trend* (% per decade) Evening	Trend* (10^{13} cm^{-2} per decade) Morning	Trend* (10^{13} cm^{-2} per decade) Evening
1. Ny-Alesund	78.9° N	11.9° E	NILU	1991, 1993–2003	−3.5 ± 6.7 −4.9 ± 6.8	−0.7 ± 7.1 −2.8 ± 6.3	−0.8 ± 1.6 −1.2 ± 1.6	−0.2 ± 1.9 −0.7 ± 1.7
2. Thule	76.5° N	68.8° W	DMI	1990–2004				
3. Scoresbysund	70.5° N	22.0° W	SA	1996–2007	4.7 ± 7.2 3.2 ± 7.1	2.8 ± 6.6 2.4 ± 6.4	1.5 ± 2.3 1.0 ± 2.3	1.0 ± 2.4 0.9 ± 2.4
4. Kiruna	67.8° N	20.4° E	NIWA	1991–2006	−0.3 ± 4.0 −3.1 ± 3.8	−2.3 ± 3.0 **−4.1 ± 2.9**	−0.1 ± 1.2 −1.0 ± 1.2	−0.9 ± 1.2 **−1.7 ± 1.2**
5. Sodankyla	67.4° N	26.6° E	SA	1995–2007	**−4.6 ± 3.3** **−4.2 ± 3.2**	0.5 ± 3.0 **−2.9 ± 2.9**	**−1.4 ± 1.0** **−1.3 ± 1.0**	0.5 ± 1.9 **−1.0 ± 1.0**
6. Zhigansk	66.8° N	123.4° E	SA	1992–2007	**7.2 ± 5.4** **7.9 ± 4.6**	**7.7 ± 5.1** **9.1 ± 4.3**	**2.0 ± 1.5** **2.2 ± 1.3**	**2.6 ± 1.8** **3.1 ± 1.5**
7. Harestua	60.2° N	10.8° E	IASB	1994–2007	1.7 ± 5.5 3.8 ± 5.2	0.5 ± 4.2 2.2 ± 4.1	0.4 ± 1.4 1.0 ± 1.3	0.2 ± 1.6 0.8 ± 1.4
8. Zvenigorod	55.7° N	36.8° E	IAP	1990–2007	**−6.8 ± 3.3** **−8.0 ± 3.6**	**−6.7 ± 2.7** **−7.4 ± 2.9**	**−1.8 ± 0.9** **−2.1 ± 1.0**	**−2.6 ± 1.1** **−2.9 ± 1.1**
9. Jungfraujoch (UV–visible)	46.6° N	8.0° E	IASB	1990–2007	**−10 ± 2.8** **−9.9 ± 2.8**	**−12 ± 2.4** **−11 ± 2.4**	**−2.6 ± 0.7** **−2.5 ± 0.8**	**−4.6 ± 0.9** **−4.2 ± 0.9**
(infrared)			IAG	1990–2006	−1.5 ± 3.2		−0.4 ± 1.1	
10. Moshiri	44.4° N	142.3° E	RCAST	1991–2002				
11. OHP	43.9° N	5.7° E	SA	1992–2007				
12. Issyk-Kul	42.6° N	77.0° E	KNU	1983–2005	**2.5 ± 2.1** **2.7 ± 2.1**	0.6 ± 1.5 0.5 ± 1.4	**0.81 ± 0.67** **0.88 ± 0.67**	0.33 ± 0.78 0.25 ± 0.76
				1990–2005	2.4 ± 2.9	**2.4 ± 2.1**	0.76 ± 0.94	**1.3 ± 1.1**
13. Mauna Loa	19.5° N	155.6° W	NIWA	1996–2006	−1.3 ± 4.2 2.2 ± 4.4	−1.8 ± 3.7 2.1 ± 4.0	−0.4 ± 1.1 0.6 ± 1.2	−0.7 ± 1.5 0.8 ± 1.6

❖ Comparable data

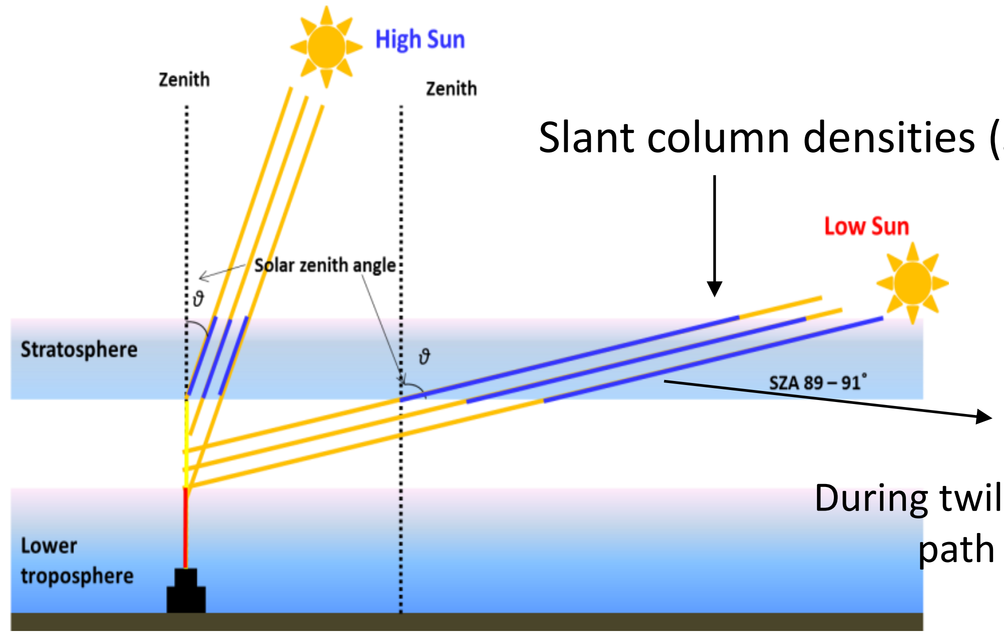
Gruzdev et al. (2009): Kiruna (67.8°N), Sodankyla(67.4°N)

F.Hendrick et al.(2012): Harestua (60.2°N)

Iteration 4

Ground-based zenith sky DOAS

❖ Geometry of zenith sky DOAS



Slant column densities (SCDs)

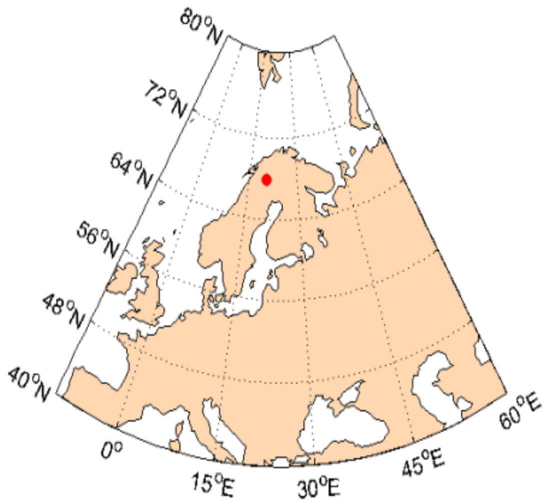
During twilight time, a long light path in stratosphere

Modified from (http://www.doas-bremen.de/maxdoas_instrument.htm)

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.

Iteration 1

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 : NO_2, O4, O_3, Ring effect
- Daily based twilight reference spectra
- NO_2 vertical columns rerieved using Langley plot methods, integrating profile

Iteration 2

NO_2 VCDs retreival

❖ Langley plot method

NDACC Climatology AMFs LUT

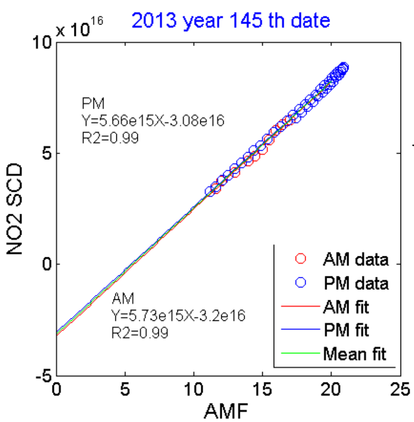
Zenith sky DOAS meas.

dSCDs

Langley plot method

VCDs

Plotting the DSCD(θ) as a function of AMF(θ)



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

SCD_{ref} : Actual amount of NO_2 in the reference spectrum

❖ Integrating profile

IASB-BIRA algorithm

Ground-based profile

Integrating profile

- Mean scattering height depends on SZA
- Based on the Optimal Estimation Method
- Forward model (RTM + Photochemical model)

[Hendrick et al., 2004]

Iteration 1

Trend analysis : Approaching method

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

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

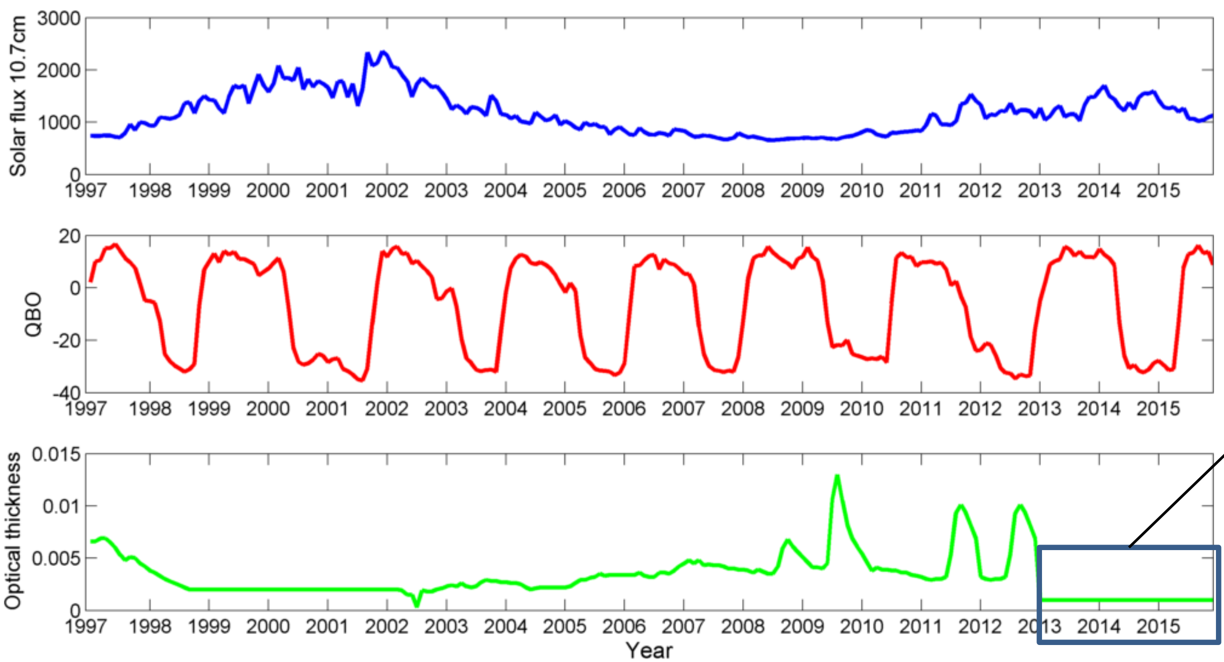
M(t) : Modeled NO_2 at decimal month(t) .
Including offset, linear trend, QBO, Solar activity, Seasonality, and stratospheric aerosol amount. → Assumption: each parameter contributes to NO_2 variability and residual

A – E :Model coefficients calculated using a standard linear least squares regression fit to the measured NO_2 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

- QBO : Quasi-Biennial-Oscillation (QBO), Singapore monthly mean zonal wind at 30hPa
  (FU-Belin, http://www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo)
- Solar activity : radio frequency 10.7cm Solar Flux data
  (The National Research Council of Canada, http://www.spaceweather.ca/solarflux/sx-3-en.php)
- 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/)

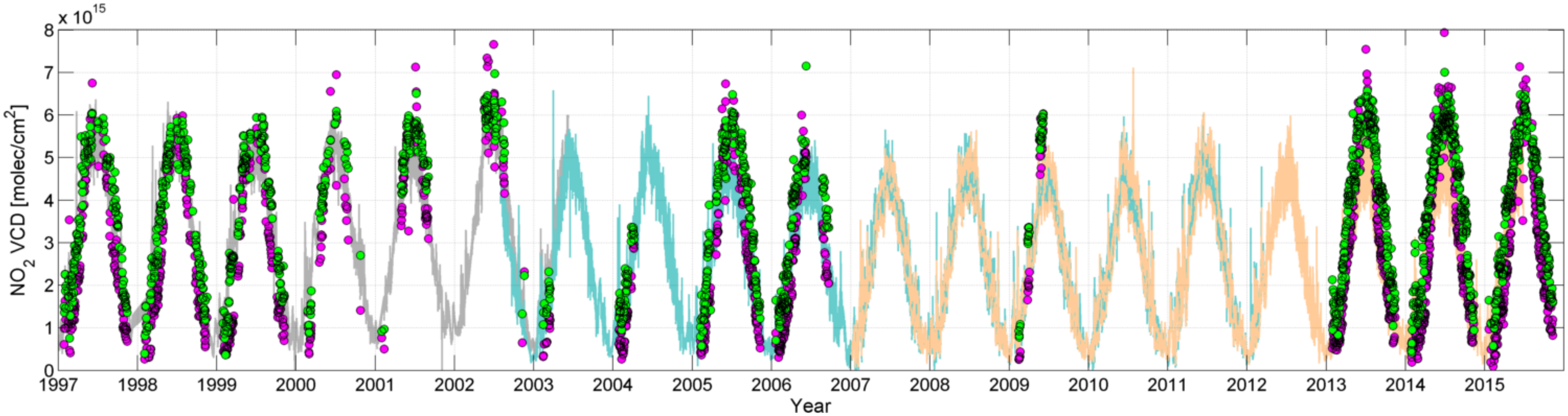


No data 2013 – 2015
:Assume minimum optical thickness (0.001)

Iteration 3

Dataset: Time series of measured stratospheric NO_2 VCDs

❖ Time seires of Zenith Sky DOAS and satellite obesrvation of stratospheric NO_2 VCDs (1997 – 2015), (GOME, SCIAMACHY, and GOME2)



DOAS @ AM

DOAS @ PM

GOME

SCIAMACHY

GOME-2

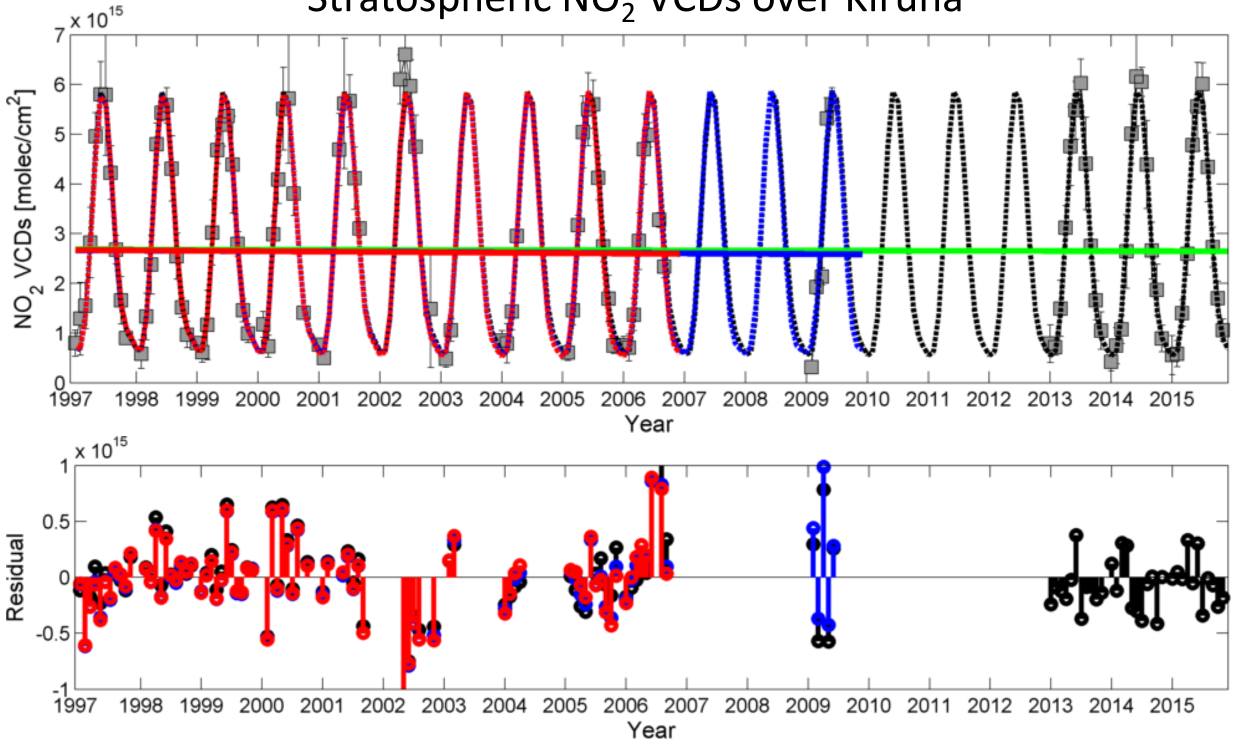
Here, we can check the strong seasonal variations and Consistent measurements.

Iteration 1

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

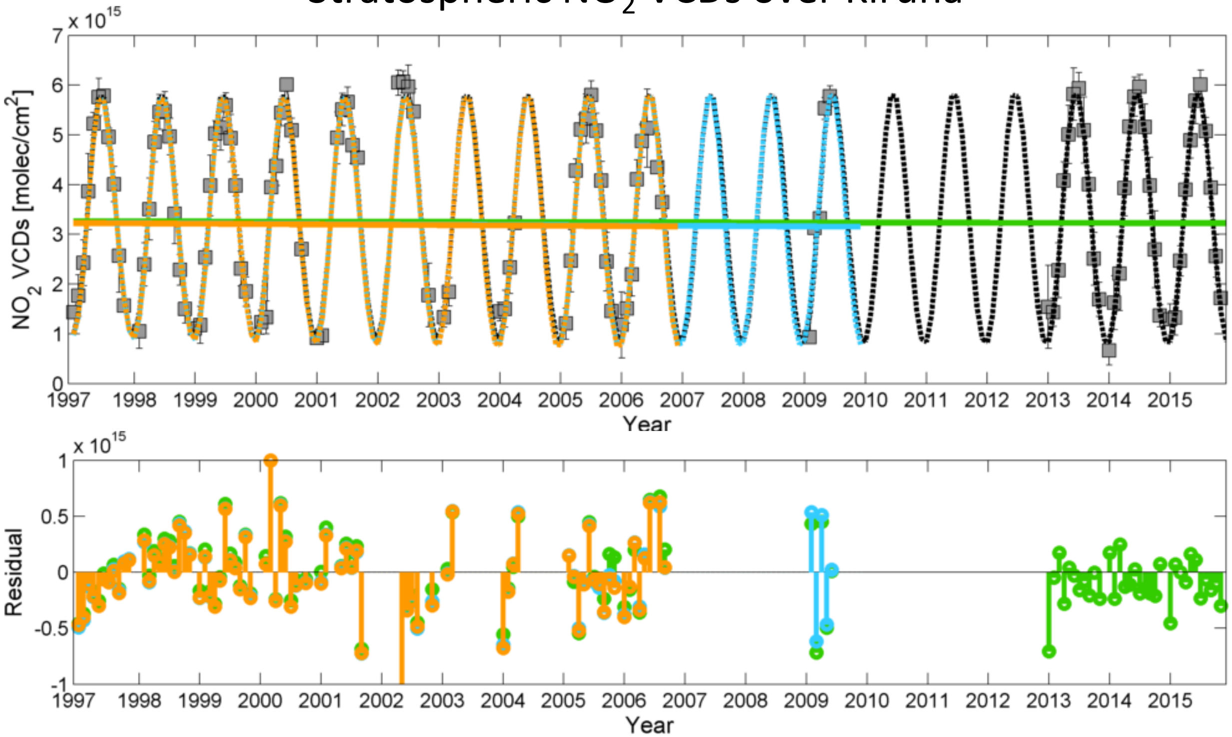
Linear trend

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±2.7 %/decade

1997 – 2009 : -0.14±1.9 %/decade

1997 – 2015 : -0.04±1.0 %/decade

Measured monthly mean NO_2

Calculated NO_2 using the multiple linear regression model

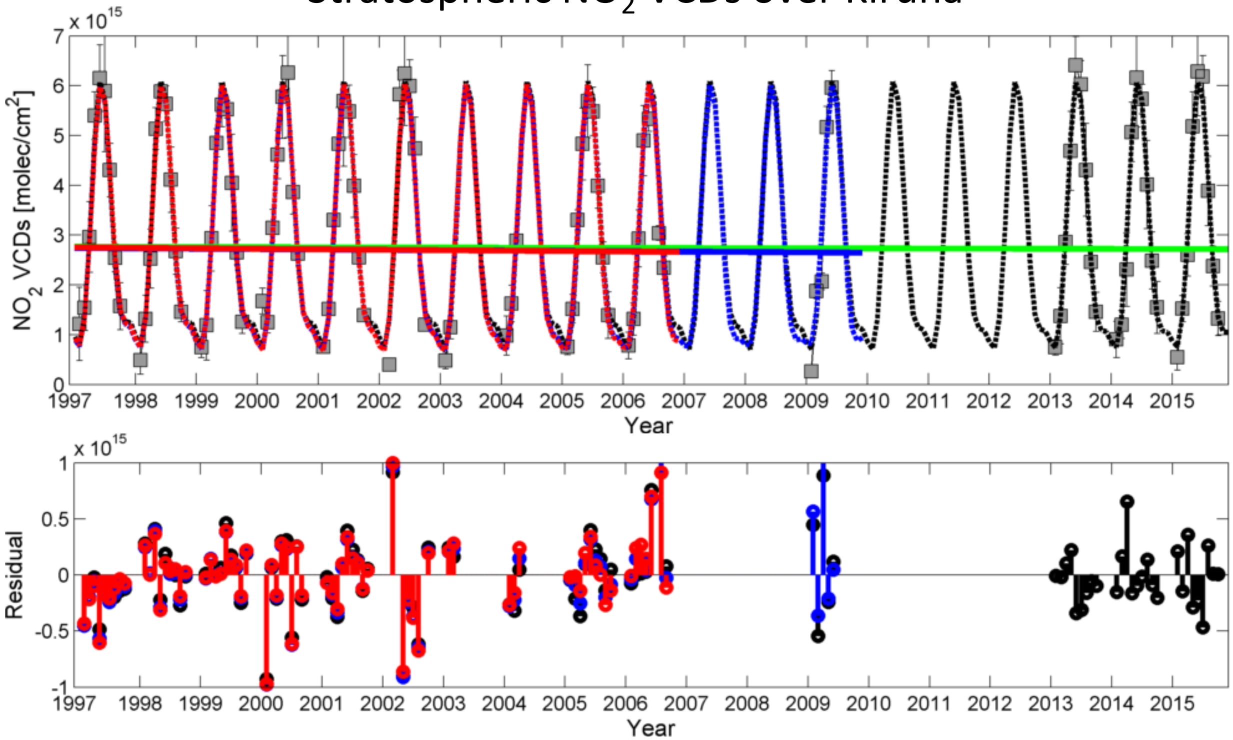
Linear trend

Iteration 3

Results: Trend analysis (AM)

❖ NO_2 VCDs derived from integrating the profile

Stratospheric NO_2 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 NO_2

Calculated NO_2 using the multiple linear regression model

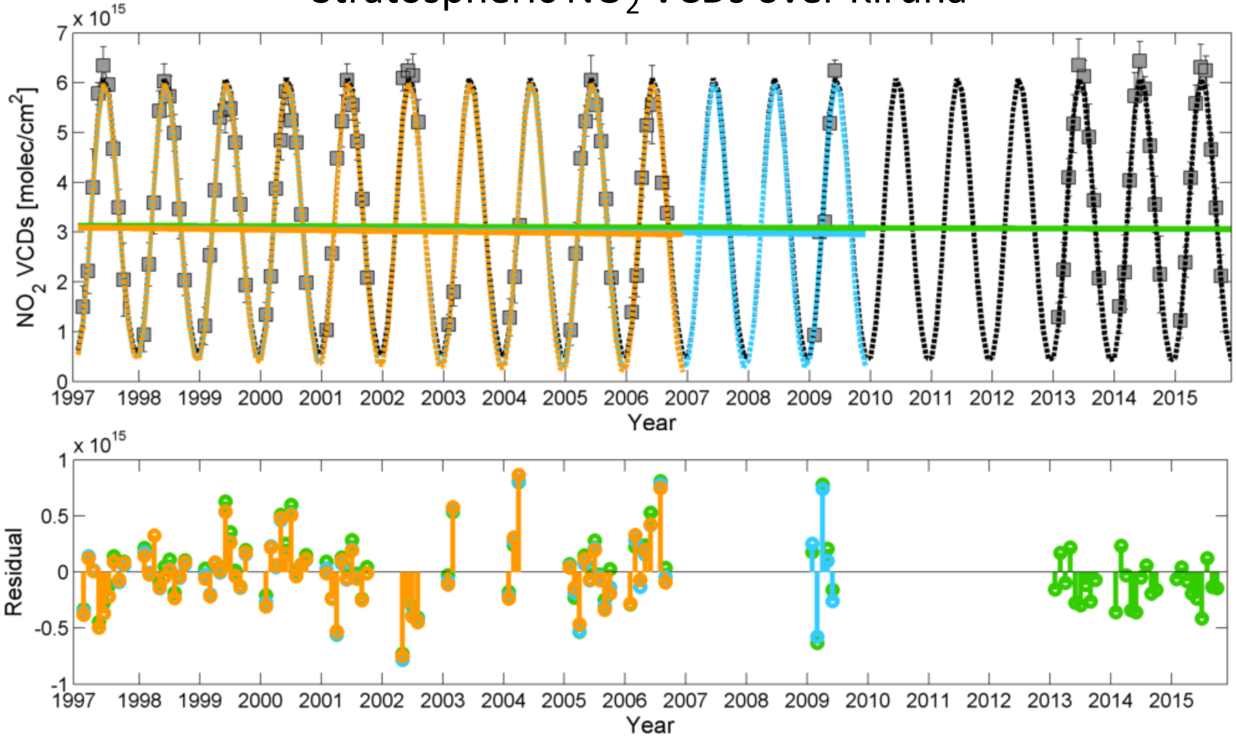
Linear trend

Iteration 4

Results: Trend analysis (PM)

- NO_2 VCDs derived from integrating the profile

Stratospheric NO_2 VCDs over Kiruna



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 NO_2

Calculated NO_2 using the multiple linear regression model

Linear trend

Iteration 5

Summary

❖ NO_2 VCDs Trend relative to year 1997 [%/decade]

	Langley plot method		Integrating profile	
Period	Morning	Evening	Morning	Evening
1997 – 2006	-0.22±3.6	-0.16±2.7	-0.22±3.0	-0.28±2.9
1997 – 2009	-0.18±2.4	-0.14±1.9	-0.17±2.0	-0.02±1.9
1997 – 2015	-0.05±1.3	-0.04±1.0	-0.05±1.1	-0.07±1.1
	photochemical reaction not included		Photochemistry included	

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.

Iteration 1

Summary

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

What is the reason for this discrepancy?

- Different site : Kiruna (67°N) and Jungfraujoch (45°N)
- Different measurement covered period

Iteration 2

Acknowledgement

- Satellite nadir (GOME, SCIAMACHY and GOME2) stratospheric VCDs have been retrieved with scientific product created at the IUP Bremen.
- QBO : Quasi-Biennial-Oscillation (QBO), Singapore monthly mean zonal wind at 30hPa
  (FU-Belin, http://www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo)
- Solar activity : radio frequency 10.7cm Solar Flux data
  (The National Research Council of Canada, http://www.spaceweather.ca/solarflux/sx-3-en.php)
- 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 NO_2 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

We would like to thank François Hendrick for consistent help and advice on the NO_2 profile algorithm and Caroline Fayt, Udo Frieß, and Mega Octaviani for advice to analysis.