



**Report on consistency between satellite
observations used for assimilation and
NORS validation data**

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1. Applicable and reference documents

NORS Description of Work

2. Acronyms

DIAL	Differential Absorption LIDAR
DOAS	Differential Optical Absorption Spectroscopy
DOFS	Degrees Of Freedom for Signal
FTIR	Fourier Transform Infrared Spectroscopy
GB	Ground-based
MACC-II	Monitoring Atmospheric Composition and Climate II
MAXDOAS	Multi-Axis Differential Optical Absorption Spectroscopy
MRD	Mean Relative Difference.
MW	Microwave Radiometry
NDACC	Network for the Detection of Atmospheric Composition Change
NORS	Demonstration Network Of ground-based Remote Sensing Observations in support of the Copernicus Atmosphere Service
PC	Partial Columns
SZA	Solar Zenith Angle
VMR	Volume Mixing Ratio

3. Introduction

The scope of the present work is to report on the consistency between satellite observations used for assimilation by Copernicus Atmospheric Service and NORS products. For this purpose a bibliographic search has been carried out to collect the previous works where NORS products from NORS/NDACC stations and satellite data are involved.

It should be taken into account that there is a wide range of different techniques and instrumentation as well as retrieval procedures in the literature for this purpose and that there is not a standard procedure defined to undertake validations.

In the literature, satellite products are compared with GB products, both obtained from different instruments based on different techniques and atmospheric scanning methods. Even for identical techniques, the retrieval settings, collocation criteria or time window differ for most of the works considered in this report. In addition, in any case, the data have to be transformed to be comparable, taking into account the characteristics of instrumentation, behaviour of the retrieved specie, atmospheric region and data availability

This report is structured as follows:

1. Definition of NORS products by technique, specie and atmospheric region
2. Description of satellite data used by Copernicus assimilation
3. Assessment of consistency between NORS products and validations found in literature classified by NORS product.

4. Description of NORS Products

NORS considers ground-based products from six NDACC stations that monitor atmospheric species using four different techniques.

NORS pilot stations are:

- Ile de La Réunion (21°S, 55°E)
- Izaña (28°N, 16°W)
- Observatoire de Haute-Provence (OHP, 44°N, 6°E)
- Bern (47°N; 7°E)
- Jungfraujoch(47°N, 8°E)
- Ny Ålesund (79°N, 12°E)

OHP, Bern and Jungfraujoch will be referred from here as Alps station.

Techniques involved in NORS project are:

- Differential Optical Absorption Spectroscopy (DOAS/MAXDOAS instrumentation)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Differential Absorption LIDAR (DIAL)
- Microwave Radiometry (MW)

The distribution of different techniques in NORS stations can be found in Table 1.

Key atmospheric species in NORS are:

- ozone (O₃),
- nitrogen dioxide (NO₂),
- carbon monoxide (CO),
- formaldehyde (HCHO)
- methane (CH₄) as well as
- aerosol extinction.

Table 1. NORS/NDACC station techniques.

	DOAS	MAXDOAS	FTIR	O₃ DIAL	O₃ MW
Réunion	X		X	X	
Izaña	X	X	X		
Alps	X	X	X	X	X
Ny Ålesund	X	X			

These species are presented in different products depending on the technique and atmospheric region ranging from total column to vertical profiles. Referring to the technique, molecule and atmospheric region, NORS products can be defined as:

- DOAS/MAXDOAS Stratospheric O₃ column
- DOAS/ MAXDOAS Stratospheric NO₂ column
- DOAS Tropospheric NO₂ column
- DOAS Stratospheric NO₂ profile MAXDOAS LT NO₂ Profile and column (NO₂ lower tropospheric profile and column)
- MAXDOAS LT HCHO Profile (HCHO low tropospheric profile)

- MAXDOAS LT Aerosol extinction Profile (Aerosol extinction low tropospheric profile)
- FTIR Stratospheric O₃ column
- FTIR Stratospheric CO column
- FTIR Stratospheric CH₄ column
- FTIR Tropospheric O₃ column
- FTIR Tropospheric CO column
- FTIR Tropospheric CH₄ column
- DIAL O₃ Stratospheric Profile (O₃ profile between 10 and 50 km.)
- MW O₃ Stratospheric Profile (O₃ profile between 20 and 70 km)

5. NORS products and satellite products used for assimilation in the COPERNICUS Atmospheric Service.

Bibliographic search has been done taking into account the satellite products used by MACCII (http://www.gmes-atmosphere.eu/about/project/macc_input_data/) and NORS data products, listed in the Table 2

Table 2. NORS data products and satellite products used by MACCII.

NORS Product	Satellite	Satellite product	NDACC technique
Stratospheric O ₃ column	GOME-2 SEVIRI OMPS SCIAMACHY	O ₃ total column	DOAS, MAXDOAS, FTIR
O ₃ profile between 10 and 50 km / O ₃ profile between 20 and 70 km	MLS	O ₃ profile between 10 and 50 km	O ₃ DIAL, O ₃ MW
	OMI	O ₃ profile	
	SBUV-2	O ₃ nadir profile	
	MIPAS	O ₃ profile	
	GOME	O ₃ profile	
Lower tropospheric NO ₂ profile	OMI		MAXDOAS
Tropospheric O ₃ column	IASI		FTIR
Stratospheric NO ₂ column	OMI GOME-2 SCIAMACHY	Total NO ₂ column	DOAS, MAXDOAS, FTIR
NO ₂ profile			DOAS
Tropospheric NO ₂ column	OMI GOME-2	Tropospheric NO ₂ column	DOAS, MAXDOAS
Lower tropospheric HCHO profile ⁽³⁾			MAXDOAS
aerosol extinction profile	VIIRS MODIS	AOD	MAXDOAS
Tropospheric CO column	IASI	CO total column	FTIR

	MOPITT	CO vertical profile	
Stratospheric CO column	IASI	CO total column	FTIR
	MOPITT	CO vertical profile	
Tropospheric CH ₄ column/ Stratospheric CH ₄ column	SCIAMACHY IASI TANSO		FTIR

6. Assessment of consistency between NORS products and validations found in literature classified by NORS product.

6.1. Ozone products

- MW O₃ Profile
- DIAL O₃ Profile
- FTIR Stratospheric O₃ column
- DOAS/MAXDOAS Stratospheric O₃ column.

Relevant literature taken into account for analyzing the consistency of NORS ozone products can be consulted in

Table 3.

Table 3. Papers for NORS ozone products

Papers	DOAS	DIAL	MW	FTIR	IASI	MIPAS	HALOE	SAGE I, II, III	SBUV/2	GOMOS	ACE FTS	ACE MAESTRO	MLS	SCIA	GOME GOME-2	OMI AURA DOAS	TOM V7/V8
Brinksma 2006		X												X			
Cortesi 2007		X	X	X		X											
Delcloo 2013			X												X		
Dumitru 2006			X				X	X									
Dupuy 2009		X		X							X	X					
Gil-Ojeda 2012	X													X	X	X	X
Hendrick 2011	X													X	X	X	X
Hocke 2005			X										X				
Nair 2011		X					X	X	X	X			X				
Palm 2010			X										X				
Pastel 2013	X													X	X	X	X
Senten 2008				X			X				X						
Steinbrecht 2009		X	X				X	X		X				X			
Studer 2013			X			X					X		X				
Viatte 2011				X	X										X	X	

6.1.1. Consistency between NORS ozone products and Satellite data.

6.1.1.1. MW O₃ Profiles.

In this section main result for the validation of Ozone profiles from a range of satellite products considered in MACCII using microwave radiometers (MWR) at NORS/NDACC stations of Ny-Alesund and Bern are presented. Most literature found is

related to Bern/Payerne MWR and only two references involving Ny-Alesund have been found.

A summary of the result of comparisons is displayed in Table 4.

Table 4. Main results of the MW O₃ profile comparison

NORS product	Station	Differences	Satellite	Reference	Comments
MW O ₃ Profile	Bern	Relative differences of $\pm 5\%$ in January between 25-55 km	OMI/Aura	Hocke et al., 2005	Comparison was made through SOMORA/Payerne radiometer.
		$\pm 7\%$ average agreement was achieved in the altitude range 20–50 km	GOME	Calisesi et al., 2005	This work states a procedure to regrid the MW radiometers to satellite ozone comparison.
		Consistency between datasets < 5%	SBUV-MOD, SAGE, SAGE II, HALOE, SCIAMACHY and GOMOS	Steinbrecht et al., 2009	This work is not to validate O ₃ measurements but to obtain a trend on temperature and ozone in the upper stratosphere between 35-45 km). Only consistency between data series is checked
		VMR <10% HALOE between 25-45 km $\pm 20\%$ between 20 and 70 km. VMR $\pm 20\%$ SAGE between 20 and 45 Km.	HALOE	Dumitru et al., 2006	Comparison of mean relative differences of vertical profiles
		Average difference close to 0% between 30-40 km. Differences were to -10% near 20 km.	GOME-2/MetOp B	Delcloo and Kreher, 2013.	EUMETSAT validation report
		Agreement within 5% in the stratosphere	Aura-MLS	Studer et al., 2013	Currently under discussion at AMT
	Mean difference within 10% for 50 to 0.1 hPa region	MIPAS, ACE-FTS	Currently under discussion at AMT		
	Ny Alesund	Observed differences fit within the total error budget (mean within $\pm 7\%$)	MIPAS	Cortesi et al., 2007	Comparison of O ₃ partial column time series.
		Agreement within 10% in the middle and upper stratosphere	Aura-MLS and TIMED-SABER	Palm et al., 2010	This manuscript introduces the OZORAM ground-based millimetre wave radiometer

Microwave limb sounder provides nearly continuous measurements of stratospheric ozone vertical profiles in VMR units between 20 and 70 km over typically 1h with a vertical resolution of 8 to 12 km. This low vertical resolution poses additional problems

for comparison and dedicated methods have been developed (Calisesi et al 2005) in order to compare Ozone MWR data to satellite data.

Calisesi et al., 2005 stated a procedure to re-grid the SOMORA MW radiometer profiles to compare with GOME ozone data. Results of the comparison give an average agreement of $\pm 7\%$ between 20-25 km after removing the smoothing effects.

Payerne is an observatory close to Bern where GROMOS MWR operates since 1994. GROMOS MWR, located in Bern, was intercompared with the SOMORA one in **Hocke et al., 2005**. SOMORA MWR was also used to validate OMI-Aura ozone profiles. Due to the proximity of both radiometers and to the consistency of measurements, no further comparison of GROMOS to OMI-Aura was performed. This work can be considered as a validation study of OMI-Aura data with Bern MW radiometer.

For this comparison, OMI profiles within a distance of 800 km around the Payerne station and within a time difference of 1h were taken into consideration.

To transform both satellite and GB profiles into comparable magnitudes and taking into account the lower vertical resolution of MW radiometer, Rodgers Optimal Estimation Method was used to adjust OMI profiles to MWR, interpolating into the vertical grid of the MW radiometer. The period of comparison was the year 2005. During this period, agreement of $\pm 5\%$ in the relative differences of profiles was observed for the month of January between 25 and 55 km.

The MWR at NDACC Bern station has been in operation since 1994 and provides continuously ozone profiles up to 75 km. As shown by **Dumitru et al., 2006**, its comparison with HALOE measurements shows differences of less than 10% with no systematic bias between 1995 and 2002. The comparison with SAGE II, deployed only until 2000, shows a good agreement with mean relative differences of $\pm 20\%$ between 20 and 45 km. On the other hand, above 45 km, SAGE II ozone values were larger than the MWR ozone measurements by around 50% indicating an overestimation of SAGE II ozone values at the stratopause.

Collocation criterion used in this work was $\pm 5^\circ$ latitude and $\pm 15^\circ$ longitude for both satellite instruments and ± 1 h for HALOE and ± 2 h for SAGE II.

As in the work of Hocke et al. (2005), SAGE II and HALOE profiles were interpolated to GB-MWR radiometer vertical grid and afterwards convolved with the corresponding AVKs.

Cortesi et al., 2007 made an ozone profile validation of MIPAS instrument using measurements of different GB instrumentation at different stations based on the off-line processor version 4.61. Concerning MWR of NORS/NDACC stations only Ny Alesund was included in this work although several NDACC MWRs were considered for this validation.

To compare ozone profiles from MWR and MIPAS is necessary to transform units into density number, using the ECMWF or NCEP meteorological analysis of pressure and temperature.

The collocation criteria were 500 km from ground-based station to tangent point and 15 min of time difference.

The strategy of the validation consisted of two steps; first, an investigation on partial ozone columns at different pressure levels was carried out to make a re-grouping of stations with a similar behaviour and to make a separation between layers dominated by

dynamics and layers dominated by photochemistry. Based on this classification, time series of ozone partial columns was used to identify the time periods where the agreement had a constant behaviour.

Moreover, in order to make a proper comparison, the different way of scanning the atmosphere from both instruments should be taken into account. For this purpose the uncertainties of the measurements and the retrievals of MIPAS and the GB instrument, the smoothing differences associated to vertical, horizontal smoothing differences and the spatial separation of the two ozone profiles were considered in Cortesi et al. (2007). Vertical smoothing was estimated by means of averaging kernels associated with MIPAS retrieval profiles that were degraded to MWR measurements.

However, MIPAS AKV for the study of horizontal smoothing were not available due to the nature of MIPAS measurements, in this case, uncertainties associated to horizontal smoothing were calculated through the horizontal component of atmospheric noise associated to MIPAS measurements.

The ozone partial column difference induced by the spatial/temporal separation of two ozone profiles (the GB and MIPAS) was estimated using BASCOE ozone fields and the difference in the geolocation.

Observed differences fit within the total error budget (mean within $\pm 7\%$) for Northern NDACC stations considered in this work.

Bern MW radiometer data series was also used by **Steinbrecht et al. (2009)** to obtain an ozone and temperature trend in the upper stratosphere. The period of analysis in which MWR data from Bern were used was from 1994 to 2008. In order to generate a data series long enough they built a consistent series using data from different sources. To state the consistency, a comparison between GB data and satellite data was necessary.

Satellite data were obtained from SAGE I, SAGE II, HALOE, GOMOS and SCIAMACHY (limb ozone profiles).

The differences between different satellites and GB instrument were taken into account in this work. For example: GOMOS samples in the dark part of the orbit, SCIAMACHY samples many profiles per day over the sunlit part of the globe, SAGE and HALOE only measure when the sun rises or sets and MWR radiometers provide nearly continuous measurements.

The strategy for comparisons, after a quality data control and removal of the unrealistic profiles, was to transform both GB and satellite measurements to a comparable magnitude. For this purpose, ground-based profiles between 35 and 45 km were averaged to give monthly mean profiles for each instrument and station whereas for satellite instruments, after a removal of unrealistic ozone profiles, zonal monthly mean profiles were obtained by averaging all satellite profiles within $\pm 5^\circ$ latitude of the station.

Palm et al., 2010 introduces the OZORAM ground-based millimetre wave radiometer. The OZORAM instrument is located in Ny-Alesund and provides ozone profiles from 30 to 70 km with a temporal resolution of 1 h. The paper presents an error discussion of the retrieved profiles concluding that the spectroscopic error dominates the error due to measurement noise up to the stratopause, the error pattern due to spectroscopic uncertainties leads to an oscillation in the uncertainty of the retrieved profile, and the error due to a wrong temperature of the cold calibration load is negligible. An estimation of the OZORAM ozone profiles accuracy is carried out from September

2008 till summer 2010 by comparison with profiles measured by MLS onboard EOS-AURA and SABER onboard TIMED. Significant correlation is found between the profiles measured by OZORAM and the MLS instrument up to 70 km altitude at night and 55 km during the day. Even though, absolute levels of MLS and OZORAM differ considerably at night. The SABER night time data correlates significantly with OZORAM profiles while the day time data only correlate at about 60 km altitude. In general, the agreement between OZORAM and satellite instruments is within 10% in the middle and upper stratosphere and 30% in the lower mesosphere.

The validation report O3M SAF (Delcloo and Kreher, 2013), finds a low bias of about 10% in GOME-2/MetOp B when compared to Bern MWR above 40 km. Average difference was close to 0% between 30-40 km but below 30 km differences were up to -10% for Bern MWR near 20 km. For this study, only GOME2 profiles with overall convergence and successful retrieval in the quality processing status were taken into account with ground pixels centre closer than 200 km and with a time difference of less than 2h.

Studer et al., (2013) (currently under discussion at AMT) has presented an inter-comparison of stratospheric ozone profiles derived from GROMOS radiometer at Bern with MIPAS, SABER, MLS and ACE-FTS satellite instruments. The coincidence criterion for this study was 1.8° in latitude (± 200 km), 10.5° in longitude (± 800 km) and 15 minutes in time with respect to MW radiometer observation.

Satellite vertical resolution was reduced to GROMOS altitude resolution by convolving each profile with the corresponding AVK matrix of GROMOS.

Mean difference between satellite and lidar and GROMOS instrument was within 10% for the 50 to 0.1 hPa region. The overall agreement between GROMOS and AURA/MLS was within 5% in the stratosphere.

Conclusions.

The main advantage of ozone microwave limb sounder is its capacity of providing nearly continuous measurements of stratospheric ozone vertical profiles.

Validation of satellite datasets with MWR data indicates a good consistency between measurements even when comparing long data series.

NORS/NDACC MWR instruments are of great utility to check satellite performance due to the large coincidence of common measurements in short periods of time, and can be used to state the measurement condition of satellite .

6.1.1.2. DIAL O₃ Profiles

In this section main results in the validation of Ozone profiles from a range of satellite products considered in MACCII using Differential Absorption LIDAR at NORS/NDACC stations of Ny-Alesund and OHP are presented.

Most literature found is related to OHP station where a great activity on validation of vertical profiles of satellite instrumentation has been carried out. DIAL from Ny Alesund have participated in the validation of MIPAS and ACE-FTS and ACE-MAESTRO products.

A summary of the result of the comparisons can be found in Table 5

Table 5. Main results of the DIAL O₃ profile comparison

NORS product	Station	Differences	Satellite	Reference	Comments
DIAL O ₃ Profiles	OHP	Tropical to midlatitude LIDARS: between 20 and 40 km differences were 5% but between 21 and 24 km range differences increase to 10%.	MIPAS	Cortesi et al., 2007	Mean Relative difference is lower than $\pm 5\%$ between 15 and 40 km. Bias up to $\pm 5\%$ outside this range
	OHP	$\pm 4\%$ at 23 and 26 km $\pm 5\%$ at 29 km $\pm 10\%$ at 35 km	SBUV/2 (1985-2007)	Nair et al., 2011	Comparison of partial columns about 4 km of the profile (16-19, 19-23, 23-27, 28-32, 33-37 and 38-42 km)
	OHP	Monthly Mean of Relative differences $\leq 5\%$ between 19-23 and 23-27 km 10% 28-32 and 33-37 km $> 10\%$ 16-20 and 38-42 km	SAGE II (1985-2005)	Nair et al., 2011	Comparison of partial columns about 4 km of the profile (16-19, 19-23, 23-27, 28-32, 33-37 and 38-42 km)
	OHP		SAGE III	Nair et al., 2011	Comparison of partial columns about 4 km of the profile (16-19, 19-23, 23-27, 28-32, 33-37 and 38-42 km)
	OHP	$\pm 5\%$ at all altitudes except between 16-20 and 38-42 with differences $> 10\%$	HALOE (1991-2005)	Nair et al., 2011	Comparison of partial columns about 4 km of the profile (16-19, 19-23, 23-27, 28-32, 33-37 and 38-42 km)
	OHP	Best Agreement between 23-27 km and 28-32 km with differences of $\pm 10\%$	MLS/UARS (1995-2000)	Nair et al., 2011	Comparison of partial columns about 4 km of the profile (16-19, 19-23, 23-27, 28-32, 33-37 and 38-42 km)
	OHP	$\pm 5\%$ at all altitudes except between 16-20 and 38-42 with differences of $\pm 10\%$	MLS/Aura (2005-2010)	Nair et al., 2011	Comparison of partial columns about 4 km of the profile (16-19, 19-23, 23-27, 28-32, 33-37 and 38-42 km)
	OHP	Exhibits small variations at all altitudes from 2002 to 2005. After 2005 GOMOS had high noise in the detector and differences increase.	GOMOS	Nair et al., 2011	Comparison of partial columns about 4 km of the profile (16-19, 19-23, 23-27, 28-32, 33-37 and 38-42 km)
	OHP	MRD -7% 15-37 km MRD $< -18\%$ below 15 km	ACE MAESTRO	Dupuy et al., 2009	Relative differences of the time series between Feb 21 st 2004 to August 31 st 2006

		MRD ~ +8% 37-41 km			
OHP		MRD $\pm 10\%$ between 15-42 km	ACE-FTS	Dupuy et al., 2009	Relative differences of the time series between Feb 21 st 2004 to August 31 st 2006 DIAL profiles smoothed to ACE-FTS
OHP				Eckert et al., 2014	
Ny Alesund		High latitude MIPAS O ₃ is low biased with respect to DIAL and differences remains always below 7% from 15 km to 40 km. Differences increase at the lowest tangent point of MIPAS at 12 km with a negative bias of -20%.	MIPAS	Cortesi et al., 2007	Mean Relative difference is lower than $\pm 5\%$ between 15 and 40 km. Bias up to $\pm 5\%$ outside this range
Ny Alesund		MRD -7% 15-37 km MRD <-18% below 15 km MRD ~ +8% 37-41 km	ACE MAESTRO	Dupuy et al., 2009	Relative differences of the time series between Feb 21 st 2004 to August 31 st 2006
Ny Alesund		Mean Relative differences $\pm 10\%$ between 15-42 km	ACE-FTS	Dupuy et al., 2009	Relative differences of the time series between Feb 21 st 2004 to August 31 st 2006 DIAL profiles smoothed to ACE-FTS
OHP		Difference between datasets <5%	SBUV-MOD	Steinbrecht et al., 2009	This work is not to validate O ₃ measurements but to obtain a trend on temperature and ozone in the upper stratosphere between 35-45 km). Only consistency between data series is checked.
OHP		Difference between datasets <5%	SAGE I	Steinbrecht et al., 2009	This work is not to validate O ₃ measurements but to obtain a trend on temperature and ozone in the upper stratosphere between 35-45 km). Only consistence between data series is checked.
OHP		Difference between datasets <5%	SAGE II	Steinbrecht et al., 2009	This work is not to validate O ₃ measurements but to obtain a trend on temperature and ozone in the upper stratosphere

					between 35-45 km). Only consistence between data series is checked.
OHP	Difference between datasets <5%	HALOE	Steinbrecht et al., 2009		This work is not to validate O ₃ measurements but to obtain a trend on temperature and ozone in the upper stratosphere between 35-45 km). Only consistence between data series is checked.
OHP	Difference between datasets <5%	GOMOS	Steinbrecht et al., 2009		This work is not to validate O ₃ measurements but to obtain a trend on temperature and ozone in the upper stratosphere between 35-45 km). Only consistence between data series is checked.
OHP	Difference between datasets <5%	SCIAMACHY	Steinbrecht et al., 2009		This work is not to validate O ₃ measurements but to obtain a trend on temperature and ozone in the upper stratosphere between 35-45 km). Only consistence between data series is checked.

Differential Absorption LIDAR (DIAL) systems provides vertical distribution of night-time ozone at altitudes comprised between about 10 and 45 km with a typical vertical resolution of 300 m to 3 km, depending on the altitude. Typical values for DIAL accuracies are 3-7% between 15 and 40 km height. Above 40 km due to the decrease of the signal/noise ratio, errors increase and a bias up to 10% may appear (Godin et al., 1999)

Discussion.

DIAL ozone vertical profiles have been used for validation or comparison with a variety of ozone satellite products.

Cortesi et al. 2007, used OHP DIAL (mid-latitude station) and Ny Alesund DIAL (high latitude station), for validation of MIPAS. The procedure of validation has been explained previously in the section dedicated to MWR, but some considerations have to be taken into account referring to the characteristics of DIAL instruments.

DIAL systems take measurements only during night-time, for this reason the collocation criterion takes matches within a 400 km with a time difference of 10 hours. DIAL validation period was from July 2002 to end of March 2004. The comparison was extended to vertical distribution of ozone number density between 8-15 km and 45-50 km.

The vertical profile analysis was made at each station by deriving vertically resolved statistics of the comparisons between MIPAS v4.61 ozone profiles and correlative data obtained at NDACC stations. To eliminate vertical smoothing differences, high

resolution correlative measurements were previously convolved with MIPAS AVKs and biased by the first guess profile as proposed by Rodgers and Connor (2003).

The total systematic error of the comparison was calculated as the sum of MIPAS systematic error and the systematic bias due to non-perfect collocation.

Results for the whole set of collocated pairs (for all stations, not only NORS ones): mean relative difference was lower than $\pm 5\%$ between 15 and 40 km (close to NORS product DIAL O₃ Profile) with slightly larger values of positive and negative bias outside this altitude range, +5% at mid-latitude and <7% at high latitude.

Good coincidence of median and mean of the differences in the lower and middle stratosphere shows the quality of the agreement in this region of the atmosphere.

Mid latitude and Tropical regions shows differences of 5%, between 20 and 40 km. Between 21 and 24 km range differences increase to 10%. Outside this range bias increases up to $\pm 5\%$.

High latitude MIPAS O₃ was low biased with respect to DIAL and differences always remain below 7% from 15 km to 40 km. Differences increase at the lowest tangent point of MIPAS at 12 km with a negative bias of -20%.

DIAL systems from Ny Alesund and OHP have also been used to validate ozone profiles of ACE-FTS and ACE-MAESTRO in **Dupuy et al., 2009**. This work includes the validation using MWR, previously analyzed in this report, and FTIR.

The period of validation was comprised between February 21st 2004 and August 31st 2006.

The coincidence criterion in this case was slightly more relaxed than in the previous work of Cortesi et al. (2007) due to the lower number of coincident measurements. To ensure statistical significance of the comparison, the selected criterion, was at least, three coincidences of DIAL measurements with ACE instrument to perform the comparison. Considered time difference was ± 12 h and spatial difference was 500 km around the station.

Satellite data used in this comparison have a vertical resolution ranging from 0.5 to 5 km. To account for DIAL higher vertical resolution, DIAL vertical profiles were first integrated to obtain partial columns calculated within layers centred at the ACE measurement grid levels. These partial columns were converted to VMR values attributed to the same tangent heights. The resulting profiles were then interpolated into satellite altitude grids (1 km for ACE-FTS, and 0,5 km for ACE-MAESTRO).

The comparison was carried out in three stages:

1. Individual coincident events were examined and quality of retrieval profiles was checked.
2. Time series of ACE and GB measurements and their relative differences were analyzed in time periods where homogeneous results were obtained.
3. Vertical structure of differences was investigated within the homogeneous time periods previously found by grouping stations where similar results were found.

The step (3) makes that no individual comparisons for each station were reported in this work, but a general conclusion about NDACC DIAL data used for this validation (Eureka, Ny-Alesund, Andoya, Hohenpeissenberg and OHP) was analyzed.

Mean relative differences between DIAL and ACE FTS in the altitude range 15-42 km were about $\pm 10\%$ whereas for ACE-MAESTRO between 15-37 km were -7%, down to

-18% below 15 km. Whereas positive mean relative differences were found in the range 37-41 km ($\sim+8\%$).

ACE FTS and ACE MAESTRO reproduce correctly the temporal variations of the ozone layer but no seasonal variation could be identified in the satellite time series due to the limited temporal sampling available.

The DIAL instrument of OHP was also used by **Brinksma et al., (2006)** as a part of the geophysical validation of SCIAMACHY limb ozone profiles. The objective of this work was to validate the IFE algorithm v1.61. The period of comparison was extended over Jan, March, May, Sept and Nov 2004.

Collocation criterion considered in this work was a maximum distance of 1000 km around the station. For night-time measurements the temporal criterion was 20h.

SCIAMACHY-IFE profiles were found to be lower than DIAL ones by about 3% between 16-40 km. Average difference profile has a zigzag shape with maximum around 31 km and minimum around 40, 20 and 27 km: because of the air volumes sampled by SCIAMACHY at different tangent heights were not exactly vertically aligned.

A very detailed comparison of DIAL ozone time series at OHP with various ozone records derived from various satellite instruments has been performed by **Nair et al., (2011)**.

The comparison was made using data from 1985 to 2009. The satellite instruments taken into account in this work were SAGEII, SBUV/2 HALOE, MLS and GOMOS.

All measurements were chosen according to quality criteria based on quality flags or previous studies developed for every satellite instrument. To avoid aerosol contamination from the Mount Pinatubo eruption, data below 25 km were excluded from DIAL observation during the period 1991-1993.

Comparison periods depend on the time overlap between DIAL and other instruments. Spatial criterion in this work was $\pm 2.5^\circ$ latitude and $\pm 5^\circ$ longitude and temporal criterion was ± 12 h. These criteria were more relaxed for the occultation instruments SAGE II, HALOE and GOMOS due to their lower sampling, allowing a greater extension on the longitudinal interval for spatial collocation. However, spatial criterion was tightened for AURA-MLS due to the largest number of collocated measurements.

In order to compare different products it is necessary to make some transformations, taking into account that the altitude grid varies for each instrument and that ozone units from some instruments have to be converted to number density.

When the vertical resolution of the satellite measurements was similar to the DIAL resolution, as is the case of SAGE II, HALOE and GOMOS, satellite and DIAL profiles were interpolated to 1 km grid.

HALOE VMR ozone values were converted to number density by using temperature and pressure data from HALOE. The same procedure was used to convert MLS ozone data taking geopotential altitudes as geometric ones. For both sensors of MLS, the comparison was performed in the lower resolution vertical grid, degrading DIAL measurements accordingly. In the comparison with SBUV(/2), DIAL data were first convolved using AVKs of the satellite instrument and later converted to DU. Then partial columns were added above each pressure level with respect to DIAL altitudes. The resulting values were interpolated to the pressure levels of SBUV(/2) and the adjacent layers were then subtracted to obtain partial ozone column in each layer.

The relative differences of the profiles for pairs of DIAL-satellite instrument were calculated for some selected altitudes of 18, 21, 25, 30, 35 and 40 km by averaging ozone to a range of ± 2 km of the profiles.

SAGE II was compared during the period 1985-2005. Monthly mean relative differences were found to be lower than 5% between 19-23 and 23-27 km, and 10% between 28-32 and 33-37 km. Differences increased over 10% at 16-20 and 38-42 km.

HALOE period of comparison was 1991-2005. The deviation was within 5% at all altitudes but for 16-20 km and 38-42 km it exceeds 10%.

SBUV/2 was coincident between 1985 and 2007. Excellent agreement of $\pm 4\%$ was observed at 23 km and 26 km, $\pm 5\%$ at 29 km and $\pm 10\%$ at 35 km.

UARS-MLS was validated during the period 1995-2000. The best agreement was found in the ranges of 23-27 km and 28-32 km with differences within $\pm 10\%$.

Aura-MLS was validated over 2005-2010. Differences were about $\pm 5\%$ at all altitudes except for altitude intervals 16-20 and 38-42 km where differences reached $\pm 10\%$.

GOMOS exhibits small variations at all altitudes during the period from 2002 to 2005. After 2005 GOMOS had problems in its detector (high noise) causing an increase in the differences.

During overlapping periods between DIAL and satellites, relative differences were almost the same for all datasets at 19-23 and 23-27 km ($\pm 5\%$), and at 28-32 and 33-37 km ($\pm 10\%$).

To set the ozone trends in the upper atmosphere **Steinbrecht et al., (2009)** considered OHP DIAL O₃ profile between 10 and 50 km, besides the NDACC MWR, as described in previous section, .

DIAL O₃ profiles were compared to GOMOS and Limb O₃ profiles of SCIAMACHY to obtain a consistent data series. The differences between datasets were found less than 5% for ozone.

Conclusions.

O₃-DIAL main characteristic is the high vertical resolution of their measurements.

Although the coincidence criteria have to be more relaxed than in the case of MWR to get statistical significance in the comparison, comparisons between satellite and DIAL profiles shows in general a good agreement in the stratosphere, with lower relative differences in the low-middle stratosphere than in upper stratosphere.

6.1.1.3. FTIR Stratospheric O₃ column

Ground-based high spectral resolution Fourier-transform solar absorption spectroscopy is a powerful remote sensing technique to retrieve information of both, total column and low resolution vertical distribution of various constituents of the atmosphere absorbing in the IR region of spectrum.

Table 6. Main results of the FTIR Stratospheric O₃ column comparison

NORS product	Station	Differences	Satellite	Reference	Comments
FTIR Stratospheric	Jungfraujoch	MRD (mean of relative differences) -3.5 ± 6.1	MIPAS	Cortesi et al., 2007	Comparison of partial integrated columns

column					
		MIPAS. No statistically significant bias.			
		Relative differences between 0 and -10% (debiased standard deviation 10%)	ACE-FTS	Dupuy et al., 2009	
		Relative differences between $\pm 10\%$	ACE-MAESTRO		
	Izaña	Relative differences of -2% to 10% (de-biased standard deviation 2%)	ACE-FTS	Dupuy et al., 2009	Comparison of partial integrated columns. MRD between 10 to 7% with de-biased standard deviation of 2%
		Relative differences between $\pm 5\%$.	ACE-MAESTRO		Mean relative differences between -9 and +2%. De-biased standard deviation of the MRD about 6%. Greater differences for high latitude stations.
		Analytical algorithm MRD - $2\% \pm 1.4\%$	IASI-analytical	Viatte et al., 2011	MRD does not exceed the estimated uncertainty
		Operational algorithm MRD - $5.2\% \pm 1.9\%$	IASI-operational		
		MRD - $2.4\% \pm 1.1\%$	GOME2		
		MRD - $0.5\% \pm 0.7\%$	OMI		
		La Réunion	Relative differences between -5 to 5%	ACE-FTS	Dupuy et al., 2009
	Relative differences between -10 to +5%		ACE-MAESTRO	Mean relative differences between -9 and +2%. De-biased standard deviation of the MRD about 6%. Greater differences for high latitude stations.	
	Relative differences between 6 and 41 km - $14 \pm 12\%$		ACE-FTS	Senten et al., 2008	Variation of observed differences larger than expected on the basis of random errors of the relative differences.
	Differences vary between 9 and 17%		HALOE		

Discussion

FTIR measurements from 68°N to 77.5°S NDACC stations were taken into consideration as part of MIPAS validation made by **Cortesi et al. (2007)**. From the Northern Hemisphere, the FTIR instrument from the Jungfraujoch station was used for this validation. The validation period was from July 2002 to April 2004.

FTIR measures solar absorption spectra taken at direct Sun and provides ozone columns as well as low resolution vertical profiles, using the Optimal Estimation Method of Rodgers and the inversion programs namely SFIT and PROFITT, cross validated by Hase et al. (2004). Quality control of GB data was applied according to NDACC guidelines. The retrieval process involved the choice of retrieval parameters that have been previously optimized for each station (spectral micro-windows, spectroscopic parameters, a priori information and model parameters). Spectroscopic database was common for all stations; in this work was HITRAN 2004 database.

For the comparison, pairs of coincident ozone profiles from MIPAS and FTIR were selected according to the collocation criteria of ± 3 h and 300 km with spatial separation evaluated at the MIPAS nominal tangent height of 21 km.

MIPAS profiles were degraded to the lower vertical resolution of FTIR measurements. In this work vertical profiles and ozone partial columns were validated. Comparison of vertical profiles is out of the scope of NORS but partial columns were obtained for Jungfraujoch in the pressure range of 2-214 hPa. In this range of pressure the FTIR sensitivity was reasonable (up to around 40 km) and contains the lowest altitudes valid for MIPAS (12 km).

For ozone partial columns, absolute differences between MIPAS and FTIR were calculated and divided by FTIR ozone partial column to obtain the relative differences.

For ozone partial columns at the Jungfraujoch station, the MRD were -3.5% with a standard deviation of 6.1%. The estimated random error of the relative difference of O₃ partial columns was around 6%, which was comparable to the standard deviation of the comparison for Jungfraujoch and there was no statistically significant bias.

The NDACC FTIR of Izaña and La Réunion stations were compared in **Dupuy et al. (2009)** to ACE-MAESTRO and ACE-FTS satellite instruments during the period comprised between February 21st 2004 and August 31st 2006.

As NDACC stations, the instruments from Izaña and La Réunion were under quality standard of NDACC FTIR group and use the retrieval methods and algorithms reported above.

In this study the coincidence criteria was ± 48 h and 1000 km for Jungfraujoch, ± 24 h and 1000 km for Izaña and ± 24 h, $\pm 10^\circ$ latitude and $\pm 15^\circ$ longitude for La Réunion.

ACE-FTS and ACE-MAESTRO profiles were interpolated to the FTIR retrieval grid and extended to the lowest retrieved altitude using FTIR a priori values. The resulting profiles were smoothed using FTIR AVKs and partial columns were calculated for a specific altitude for every NDACC station. The lower limit of the partial column was given by ACE-FTS and MAESTRO lowest measured altitude and the upper limit was determined by sensitivity of FTIR measurements according to Vigouroux et al., (2007). The lower limits were between 10-18 km and the upper limit varies in the range of 38-47 km depending on the station.

Relative differences in the ozone partial columns data series for ACE-FTS varies from 0 to -20% for Jungfraujoch, from -2% to 10% for Izaña and around $\pm 5\%$ for La Réunion.

The FTIR of Izaña station was used for the validation of different retrieval algorithms of IASI (Operational and Analytical) by **Viatte et al., (2011)**. In this study ozone partial columns were compared to GOME2 and OMI as well. The period of validation was from March to June 2009.

After passing a quality filter, data were referred to a precise location. Data from satellite were selected with a 2° latitude belt, between 27.5°-29.7°N for GOME-2, 27.7° and 29.7°N for OMI and 27.3-29.3°N for IASI. A very restrictive temporal criterion of 1h difference between the GB measurements and the satellite overpass was imposed. The mean relative differences found for the analytical algorithm of IASI were $-2\% \pm 1.4\%$ whereas for the operational one were $-5.2\% \pm 1.9\%$. For GOME 2 MRD were $-2.4\% \pm 1.1\%$ and for OMI $-0.5\% \pm 0.7\%$.

The IASI operational algorithm underestimates FTIR O₃ columns systematically. Differences exceed the estimated uncertainty of FTIR. The agreement of the IASI analytical algorithm, with OMI and GOME2 can be considered excellent.

The FTIR Stratospheric ozone from La Réunion was compared to ACE-FTS, HALOE in **Senten et al., 2008**.

The coincidence criteria for all comparison with satellite data was a maximum of 15° difference in longitude, 10° in latitude and a maximum of 24h time difference. The period of comparison was extended for four days between 20/08 and 6/10 2004.

The comparison were limited to partial columns (PC) defined by the altitude range where DOFS (degrees of freedom for signal) was about 1 and restricted to altitudes ranges where sensitivity of FTIR was greater than 50%.

The relative differences between FTIR and satellite have been defined as $2 * (PC_{sat} - PC_{FTIR}) / (PC_{sat} + PC_{FTIR})$, as none of the instruments was taken as reference. The random error associated with the relative differences has been calculated as combination of the random error of satellite and FTIR PCs.

During the period of the comparison there were only five overpasses of ACE-FTS above the station. Relative differences ranges between -14% and +12%, between ~6 km and ~47 km. In this comparison, the variation in the observed differences was larger than expected on the basis of the random errors of the relative differences, although in the range of high sensitivity, ACE-FTS and FTIR ozone profiles agree quite well.

Analogue to the ACE-FTS comparison, the smoothed HALOE profiles agreed fairly well with FTIR profiles. The differences between HALOE and GB FTIR O₃ PCs in the range of 10-47 km vary between 9% and 17% with HALOE profiles being smaller than GB ones.

Conclusions

FTIR is a very powerful technique that provides tropospheric and stratospheric columns of a wide range of atmospheric absorbers as well as their low resolution vertical profiles. Comparison of ozone partial columns shows a good consistency between satellite and GB data and confirms this kind of observations as an excellent tool to validate satellite-borne instrumentation.

No comparison of tropospheric ozone columns has been performed to our knowledge using FTIR data from NDACC/NORS FTIR instrumentation.

6.1.1.4. DOAS/MAXDOAS Stratospheric O₃ column.

In this section results for satellite stratospheric ozone column and DOAS stratospheric ozone column found in literature for NORS/NDACC stations will be discussed.

DOAS stratospheric ozone column from NORS/NDACC stations of Izaña and La Réunion have been used to validate satellite data, the results of these comparisons found in literature have been summarized in Table 7.

Table 7. Main results of the DOAS Stratospheric O₃ column comparison

NORS product	Station	Differences	Satellite	Reference	Comments
DOAS/MAXDOAS Stratospheric O ₃ column	Izaña	Agreement of 1.6% with standard deviation of 3%	GOME GOME-2	Gil-Ojeda et al., 2012	Comparison of total ozone column. Satellite is lower than DOAS by 1% considering that total ozone column below the observatory is 3%.
		Agreement of 1.1% with standard deviation of 3%	OMI		
		Agreement of 1.1% with standard deviation of 3%	SCIAMACHY		
		Agreement of 1.1% with standard deviation of 3%	TOMS V8		
	OHP	Maximum difference 4.7%	TOMS V8	Hendrick et al., 2011	Differences show a systematic seasonal variation with a summer maximum
		Maximum difference 1.2%	GOME		
		Maximum difference 2.8%	SCIA-TOSOMI		
		Maximum difference 3.1%	SCIA-OL3		
		Maximum difference 3.4%	OMI-TOMS		
		Maximum difference 2.0%	OMI-DOAS		
	La Réunion	Maximum difference 1.4%	TOMS V8	Pastel et al., 2013	Difference shows systematic seasonality, smaller with TOMS (EP) than with other satellites
		Maximum difference 3.5%	GOME		
		Maximum difference 1.8%	SCIA-TOSOMI		
		Maximum difference 2.6%	SCIA-OL3		
		Maximum difference 2.6%	OMI-TOMS		
		Maximum difference 1.8%	OMI-DOAS		
		Mean Bias and Standard 1.4%	TOMS(EP)-DOAS		
	Mean Bias and Standard -0.04%	OMI(DOAS)-DOAS			
	Mean Bias and	OMI(TOMS)-			

	Standard 0.47%	DOAS		
	Mean Bias and Standard 0.15%	GOME-DOAS		
	Mean Bias and Standard -0.24%	SCIAMACHY-DOAS		

DOAS instrumentation can obtain total ozone column twice at day with limited sensitivity to stratospheric temperature and cloud or aerosol coverage. Within the NDACC UV visible group a recommendation for improving and homogenizing the retrieval of total ozone columns from DOAS spectrometers has been developed and implemented in recent years.

NDACC recommendation addressed both DOAS retrieval parameters and the calculation of air mass factors necessary in order to obtain the total ozone columns.

To investigate the impact of the use of one of the most important improvements into NDACC recommendation, look up tables from TOMS V8 ozone profile climatology have been used in the calculation of AMF. **Hendrick et al. (2011)** performed an extensive comparison of NDACC/SAOZ instrumentation from 8 stations with satellite measurements from TOMS (from NASA GSFC database), GOME (operational ESA GDP4 level 2), SCIAMACHY-TOSOMI (from ESA-KNMI TEMIS site), SCIAMACHY-OL3 (offline version 3) OMI-TOMS and OMI-DOAS (both last available from NASA AVDC site).

The period of comparison was from 1989 to 2009, avoiding the period where the perturbation due to Pinatubo eruption becomes important for DOAS instruments (October 1991-October 1992). Two NORS stations were involved in the comparison exercise; OHP and La Réunion.

Spatial collocation criterion was 300 km radius around the stations.

A significant better agreement was observed after applying new recommendations but systematic seasonal differences still remain between SAOZ and satellite instruments. The results of the comparison are displayed in Table 7. The observed systematic seasonal differences can be attributed to temperature and SZA dependencies in satellite retrievals. The effect of the temperature dependence was more evident for TOMS and OMI-TOMS retrieval because of their spectral range. This effect was also present with a smaller amplitude in GOME and both SCIAMACHY retrievals, but was not observed in OMI-DOAS retrievals.

The SZA dependency was particularly large for SCIAMACHY-TOSOMI and it was also present in SCIAMACHY OL3, OMI-TOMS and OMI-DOAS retrievals. As DOAS measurements were carried out at SZA of 90° during the whole year, this discrepancy must be attributed to satellite retrievals.

Gil-Ojeda et al. (2012) performed a comparison similar to those carried out for FTIR instrumentation by Viatte et al (2011) at Izaña station but focused on DOAS instrumentation. The period for comparison was from 1998-2012 and involved the following nadir satellite-borne instruments; TOMS-v8, OMI and SCIAMACHY.

Spatial coincidence criterion was fixed to data around 500 km of the station.

In this comparison the new recommendation from NDACC has been also tested, finding that the seasonality previously observed when compared to Brewer instrument was reduced to less than 1%.

Zenith sky measurements performed at Izaña station can be considered representative of stratosphere only and due to the fact that the ozone retrieval was carried out in the visible range, no dependence with temperature was observed.

Comparison with TOMS-v8, OMI and SCIAMACHY shows an excellent agreement better than 1%, differences were slightly larger for GOME2 (1.6%) and OMI (1.1%) with a standard deviation of 3%.

However, satellite results should show a difference of -1% with DOAS considering that 3% of the total ozone column is below the station.

Pastel et al., 2013 studied a long series of ozone and NO₂ total columns over Bauru (Brazil) and La Reunion Island since 1995 and 1993 respectively. The Mean O₃ total column is about 270 DU with a season cycle of about 30-40DU with a maximum in spring. Ground-based O₃ data have been compared to satellite data available over the same period. Systematic biases of less than 1.04% are observed between DOAS and satellites and results also show systematic seasonality of up to 3.9%. The mean bias between satellites and DOAS instrument are mainly due to the different treatment of the longitudinal ozone variations in the retrievals and the sensitivity of the measurements to tropospheric ozone. Other sources of uncertainty come from errors in the absorption cross-sections.

6.2. NO₂ products

The objective of this section is to improve our knowledge about NO₂ and the remote sensing techniques used to measure it. The NO₂ products taken into account are the following:

- DOAS/ MAXDOAS Stratospheric NO₂ column
- DOAS Tropospheric NO₂ column
- DOAS Stratospheric NO₂ profile
- FTIR Stratospheric NO₂ column
- MAXDOAS LT NO₂ Profile (NO₂ low tropospheric profile)

6.2.1. Consistency between Stratospheric NO₂ products and Satellite data.

In this section the validation of stratospheric NO₂ column data derived from OMI, GOME-2 and SCIAMACHY instruments will be presented. DOAS, MAXDOAS and FTIR ground-based instruments located at the Alps (Bern, Jungfrauoch and Haute Provence Observatory, OHP), Izaña, La Reunion and Ny-Alesund were considered for the validation (see Table 2). Therefore results from the papers including such validations will be presented in Table 8, together with the satellite instruments validated and the technique used for the validation.

Table 8. Papers used in the validation of the stratospheric NO₂

Papers	DOAS	FTIR	SCIAMACHY	GOME / GOME-2	OMI
Dirksen et al., 2011	x	x			x
Gil et al., 2008	x		x	x	
Hendrick et al., 2012	x	x	x	x	
Pastel et al., 2013	x		x	x	x

Pinardi et al., 2011	x		x	x	
Sussmann et al., 2005		x	x		

6.2.1.1. FTIR Stratospheric NO₂ column.

Table 9. Main results of the FTIR Stratospheric NO₂ column comparison

Product	Station	Difference	Sensor	Reference	Comments
FTIR NO ₂ Stratospheric total column	Izaña	Linear fit R-Square= 0.69 Slope= 1.26	DOAS	Dirksen et al., 2011	Low R-square due to Improper illumination of the DOAS sensor (it has already been corrected)
		6.8%	OMI		Over the SAOZ and NDACC stations, DOMINO exceeds ground - based stratospheric NO ₂
	Jungfrauoch	25.3%	OMI		Over the SAOZ and NDACC stations, DOMINO exceeds ground - based stratospheric NO ₂
	Zugspitze (and some other places)	0.83E+15		Sussmann et al., 2005	

6.2.1.2. DOAS/MAXDOAS Stratospheric NO₂ column

Table 10. Main results of the DOAS/MAXDOAS Stratospheric NO₂ column comparison

Product	Station	Difference	Sensor	Reference	Comments
DOAS / MAXDOAS NO ₂ Stratospheric total column	Izaña	15-20%	FTIR	Dirksen et al., 2011	Due to inaccuracies in, e.g., the assumed profile, air mass factor... In good agreement with other studies (De Maziere et al., 1998, Kerzenmacher et al., 2008).
		29.1%	OMI	Dirksen et al., 2011	Over the SAOZ and NDACC stations, DOMINO exceeds ground - based stratospheric NO ₂
		1.1% Standard dev: 2.2x10 ¹⁴ molec/cm ²	SCIAMACHY	Gil et al., 2008	SCIAMACHY overestimates the Stratospheric NO ₂ in comparison to DOAS
		-9.4%	GOME		GOME

		Standard dev: 3.0×10^{14} molec/cm ²			underestimates the Stratospheric NO ₂ in comparison to DOAS	
		See Table 15	GOME-2	Pinardi et al., 2011	Small negative bias of GOME-2 relative to NDACC&UVVIS observations	
	Jungfraujoch	15-20%	FTIR	Dirksen et al., 2011	"Old FTIR products" were used in that study. The newest ones were used in Hendrick et al 2012. Due to inaccuracies in, e.g., the assumed profile, air mass factor... In good agreement with other studies (De Maziere et al., 1998, Kerzenmacher et al., 2008).	
		21%	OMI		Over the SAOZ and NDACC stations, DOMINO exceeds ground - based stratospheric NO ₂	
		7.8±8.2%	FTIR	Hendrick et al., 2012	In general, FTIR measurements lower than SAOZ	
		1.9±11.5%	SCIAMACHY		Satellite minus SAOZ relative differences	
		0.9±8.8%	GOME		Satellite minus SAOZ relative differences	
		2.3±11.6%	GOME-2		Satellite minus SAOZ relative differences	
		See Table 15	GOME-2	Pinardi et al., 2011		
		La Reunion	-1.3%	OMI	Dirksen et al., 2011	Over the SAOZ and NDACC stations, DOMINO exceeds ground - based stratospheric NO ₂
			19.1%	GOME V1.0 IUP	Pastel et al., 2013	(Sat-GB)/GB
	-5.8%		GOME GDP4 ESA	Pinardi et al., 2011	Small negative bias of GOME-2 relative to NDACC&UVVIS	
	-4.1%		SCIAMACHY V2.0 IUP			

		0.3%	OMI DOAS V3		observations
		See Table 15	GOME-2		
		See Table 15	GOME-2	Pinardi et al., 2011	
	Ny Alesund	-27.5%	OMI	Celarier et al., 2008	OMI-SAOZ
	OHP	-1.5%	OMI	Dirksen et al., 2011	Over the SAOZ and NDACC stations, DOMINO exceeds ground - based stratospheric NO ₂
		See Table 15	GOME-2	Pinardi et al., 2011	

6.2.1.3. Remarks

Accuracies and uncertainties should be well known in order to perform reliable comparison and to understand the possible differences among the data sets. Errors and uncertainties are presented and documented in different ways depending on the paper. An overview of such errors and uncertainties is summarized next. Detailed explanation of the origin of the errors is not included.

Accuracies and uncertainties depend on (1) errors in the retrieval, (2) uncertainty in NO₂ cross-sections and spectroscopic line parameters, and (3) uncertainty in the reference content and AMF calculations.

Methodology and algorithms:

Nowadays most of the products from DOAS/MAXDOAS and FTIR instruments from NDACC (Network for the Detection of Atmospheric Composition Change) stations are computed following the NDACC recommendations (<http://www.ndsc.ncep.noaa.gov/>) in their algorithms. Some studies did not have the NDACC recommendations included yet when the paper was written which can be a source of uncertainty in the results. The NDACC station operators are continuously revising and updating their algorithms to avoid such issue.

Satellite instrument products are obtained from different algorithms depending on the group. For more information please check Table 11, Table 12 and Table 13

Table 11. Wavelength, algorithm and cross sections used by the SCIAMACHY algorithms

Papers	Wavelength (nm)	Algorithm	Cross Sections
Gil et al., 2008	425-450 nm	University of Bremen (Richter et al., 2005a, Richter et al., 2005b)	Bogumil et al. (2003) at 243K
Hendrick et al., 2012	426.5–451.5 nm	TM4NO2A v1.10, KNMI/BIRA TEMIS NO ₂ algorithm (Boersma et al., 2004, 2007; Dirksen et al., 2011)	NO ₂ , ozone, water vapour, the Ring effect, and a third order polynomial for the residual broadband features due to Rayleigh and Mie scattering are taken into account. NO ₂ cross-sections at 220K from

			Vandaele et al. (1998)
Pastel et al., 2013	425-450 nm	University of Bremen V2.0 (Richter et al. 2004).	Bogumil et al. (2003) at 243K
Sussmann et al., 2005	425-450 nm	University of Bremen (UB1.5) (Richter et al. 2004).	Bogumil et al. (2003) at 243K

Table 12. Wavelength, algorithm and cross sections used by the GOME-2 algorithms

Papers	Wavelength (nm)	Algorithm	Cross Sections
Gil et al., 2008	425-450nm	University of Bremen (Richter et al., 2005a, Richter et al., 2005b)	NO ₂ cross-sections of (Burrows et al., 1998) at 241K
Hendrick et al., 2012	425-450nm	TM4NO2A v1.10, KNMI/BIRA TEMIS NO ₂ algorithm (Boersma et al., 2004, 2007; Dirksen et al., 2011)	NO ₂ , ozone, water vapor, the Ring effect, and a third order polynomial for the residual broadband features due to Rayleigh and Mie scattering are taken into account. NO ₂ cross-sections at 220K from Vandaele et al. (1998)
Pastel et al., 2013	425-450nm	University of Bremen V1.0 and the ESA GOME Data Processor GDP4	Bogumil et al. (2003) at 243K
Pinardi et al., 2011	425-445 nm	DLR algorithm with version 4.3 and 4.4 of the GOME Data Processor (GDP) (see TN-DLR-ATBD 2011 and TN-DLR-PUM 2010)	TN-DLR-ATBD 2011 and TN-DLR-PUM 2010

Table 13. Wavelength, algorithm and cross sections used by the OMI algorithms

Papers	Wavelength (nm)	Algorithm	Cross Sections
Dirksen et al., 2011	405-465nm	Dutch OMI NO ₂ retrieval (DOMINO) Boersma et al.(2007) and Standard Product retrieval from NASA GSFC	NO ₂ , ozone, and water vapour, the Ring effect and a third order polynomial that describes the background of the reflectance spectrum. The NO ₂ cross section spectrum for 220 K is taken from Vandaele et al. [1998].
Pastel et al., 2013	405-465 nm	NASA V3 (Boersma et al., 2002)	Vandaele et al., 1998 at 220 k

Results

Satellite data are usually validated against ground-based data. In the case of the remote sensing of gases from the ground, with DOAS and FTIR instruments, many uncertainties should be taken into consideration, as it has been already reported in many papers (Sussmann et al., 1997 and Sussmann 1999, Hendrick et al., 2004, Gil et al., 2008, Ionov et al., 2008...). Therefore, caution is recommended when comparing satellite and ground-based measurements.

All the authors take into account the photochemical behaviour of the NO₂. To carry out the comparison, NO₂ products have been corrected to the same solar zenith angle (SZA) by means of box models or with empirical models.

Even though open issues remain, ground-based measurements are considered the truth in order to validate satellite products. It is important, therefore, to know how they compare to each other. Dirksen et al., 2011 (results of the “old FTIR products”, the newest ones were used in Hendrick et al 2012) over Jungfraujoch and Izaña found that FTIR and DOAS/MAXDOAS data are mutually consistent only within 15-20%. After the improvement of the FTIR algorithms, Hendrick et al., 2012 found that the consistency of FTIR and DOAS/MAXDOAS data is within 8±8 % over Jungfraujoch. Those results depend on the season, which is consistent with results presented in other papers. Table 9 and Table 10 show the main results obtained in the papers.

For the validations of SCIAMACHY stratospheric NO₂ with DOAS/MAXDOAS and FTIR instruments, papers present differences of satellite minus ground-based results of about 1-14% in Sussmann et al., 2005 over Zugspitze with FTIR, Gil et al., 2008 over Izaña with DOAS, Hendrick et al., 2012 over Jungfraujoch with both DOAS and FTIR and Pastel et al., 2013 over La Reunion with DOAS instruments. For GOME validation, Gil et al., 2008 over Izaña and Hendrick et al., 2012 over Jungfraujoch found differences of up to 10%.

For GOME-2 Pinardi et al., 2011 and Hendrick et al., 2012 both over Jungfraujoch found differences of about 2±12%. Over La Reunion, Pastel et al., 2013 reports a MRD of 19% and -5.8% for the University of Bremen and the ESA algorithms respectively. Validation of GOME-2 over other stations such as OHP, Izaña and La Reunion are shown in Pinardi et al., 2011 (see Table 15).

In the validation of OMI results, three papers have been considered. Celarier et al., 2008 uses the NASA algorithm to derive the stratospheric NO₂ and reports a disagreement of about 14% over OHP and La Reunion. Dirksen et al., 2011 found a difference of about 13% with the DOMINO algorithm over Jungfraujoch and Izaña. The best results are presented by Pastel et al., 2013 over La Reunion with a MRD of 0.28 %

In Appendix I, a brief abstract of each paper can be found.

Table 14. Main results of the Stratospheric NO₂ column comparison

Papers	FTIR vs DOAS	SCIAMACHY vs DOAS	SCIAMACHY vs FTIR	GOME / GOME-2 vs DOAS	GOME / GOME-2 vs FTIR	OMI vs DOAS	OMI vs FTIR
Dirksen et al., 2011	15-20%					IZAÑA: 29.1% JUNGFRAUJOCH: 21% OHP: -1.5% REUNION: -1.3%	IZAÑA: 6.8% JUNGFRAUJOCH: 25.3%
Gil et al., 2008		IZAÑA: 1.1% (Standard dev 2.2×10^{14} molec/cm ²)		IZAÑA: 9.4% (Standard dev 3.0×10^{14} molec/cm ²)			
Hendrick et al., 2012	7.8±8.2%	JUNGFRAUJOCH: 1.9±11.5%		JUNGFRAUJOCH: 0.9±8.8% GOME 2.3±11.6% GOME-2			
Pastel et al., 2013		LA REUNION : 4.1%		LA REUNION : 19.1% IUP V.10 -5.8% ESA GDP4		LA REUNION : 0.28%	
Pinardi et al., 2011				See Table 15			
Sussmann et al., 2005			ZUGSPITZE: 7-10%				

Table 15. Results from Pinardi et al., 2011, Table 3.1

Table 3.1 – Statistical summary of absolute differences in NO₂ total column data between GOME-2 GDP 4.3/4.4 and contributing NDACC/UVVIS stations: range of monthly median difference, global median difference, and standard deviation (all in 10¹⁴ molecule/cm²)

Station	Location	Institute	Latitude	Longitude	Range of monthly mean difference	Global mean difference	Global standard deviation
Ny-Ålesund	Spitsbergen	IUP/U.Bremen	78.91° N	11.93° E	-5 / +5	-1	4
Thule	Greenland	DMI	76.51° N	68.76° W	+1 / +6	+4	3
Scoresbysund	Greenland	CNRS/DMI	70.48° N	21.97° W	+4 / +5	-2	3
Kiruna	Sweden	NIWA	67.84° N	21.06° E	-5 / +4	0	3
Sodankylä	Finland	CNRS/FMI	67.37° N	26.67° E	-5 / +3	-3	4
Zhigansk	Eastern Siberia	CNRS/CAO	66.72° N	123.40° E	-3 / +1	-1	2
Harestua	Norway	BIRA-IASB	60.22° N	10.75° E	-3 / +9	+2	6
Bremen	Germany	IUP/UBremen	53.11° N	8.86° E	-7 / +9	+3	8
Jungfraujoch	Switzerland	BIRA-IASB	46.55° N	7.98° E	+3 / +10	+5	5
Moshiri	Japan	STEL/U.Tokyo	44.40° N	142.30° E	-3 / +3	-2	4
OHP	France	CNRS/LATMOS	43.94° N	5.71° E	-6 / +1	-3	5
Issyk-Kul	Kyrgyzstan	KSNU	42.63° N	76.98° E	-8 / +2	-1	5
Izaña	Tenerife	INTA	28.29° N	16.49° W	-7 / 0	-3	4
Mauna Loa	Hawaii	NIWA	19.54° N	155.58° W	-10 / -3	-7	3
Mérida	Venezuela	IUP/U.Bremen	8.60° N	71.14° W	-3 / +3	-1	3
Saint Denis	Reunion Isl.	CNRS/U.Reunion	21.07° S	55.48° E	-7 / 0	-3	3
Bauru	Brazil	CNRS/UNESP	22.35° S	49.03° W	-1 / +3	-5	9
Lauder	New Zealand	NIWA	45.03° N	169.68° E	-14 / -3	-7	4
Kerguelen	Indian Ocean	CNRS	49.36° S	70.26° E	-10 / -5	-7	3
Macquarie	Australia	NIWA	54.50° S	158.96° E	-19 / -5	-10	5
Marambio	Antarctica	INTA	64.23° S	56.72° W	-6 / +3	-3	5
Dumont d'Urville	Antarctica	CNRS	66.67° S	140.00° E	-5 / +2	-3	3
Rothera	Antarctica	BAS-NERC	67.57° S	68.13° W	-6 / -1	-4	3
Arrival Heights	Antarctica	NIWA	77.82° S	166.66° E	-5 / +2	-2	2
Belgrano	Antarctica	INTA	77.87° S	34.63° W	-6 / 0	-4	3

Discussion

The algorithms used to compute stratospheric NO₂, their accuracies, and results of the comparison are shown in previous sections and in Appendix I. As it has been already presented, many uncertainties are involved in this kind of measurements. Many authors have been working in this problem. Next, we present a summary of the considerations extracted from the literature that have to be taken into account to perform reliable comparisons:

1. Differences in the measurement technique and the uncertainty associated to each instrument and algorithm (selected cross sections, line parameters and their dependence with temperature, the AMF calculations including the models and assumptions used to compute them, the a priori assumed NO₂ profile...).
2. The vertical smoothing errors are studied by means of the averaging kernels. It has been taken into account in the following studies: Hendrick et al., 2012 and Dirksen et al., 2011 based on previous studies of Eskes and Boersma, 2003. Sussmann et al., 2005 explain that the accurate determination of the total NO₂ column from SCIAMACHY depends heavily on a priori assumptions on the vertical VMR profile, which is not available from the measurements and therefore, introduces significant biases. For the comparison of FTIR and SCIAMACHY, a perfect agreement could not be expected due to the different averaging kernels. The kernels indicate that both FTIR

- and SCIAMACHY retrievals perform with a significant underestimation of the tropospheric column, but are able to properly monitor changes in the stratospheric part.
3. The horizontal smoothing error is related to satellites and the size of their images and pixels. All the studied papers used a mean value of the retrieved stratospheric NO₂ around the station where the comparison is carried out. Depending on the considered satellite instrument the horizontal average involves 200, 400 or up to 500 km around the station. For the stratospheric NO₂ this effect is not as relevant as for the tropospheric NO₂.
 4. Different effective air mass. This effect should be taken into account when comparing DOAS instruments with other instruments. DOAS measurements are performed pointing to the zenith at twilight. The effective NO₂ mass measured by the instrument is located about 200-300 km to the east of the station for the sunrise and to the west for the sunset. Therefore, the effective solar zenith angle at the effective air mass is about 3° lower than the SZA at the station. This effect has only been considered in:
 - a. Adams et al., 2012 is one of the few papers that mentioned this effect. They observed that DOAS instruments sample a NO₂ layer located at about 30 km height with an SZA that is up to 3° smaller than the SZA at the instrument. This causes the underestimation of NO₂ concentrations, particularly for measurements taken at large SZAs in the spring and fall.
 - b. Celarier et al., 2008 makes reference to this effect but do not take it into account when processing the data.
 - c. Gil et al., 2008 say that the maximum sensitivity of ground-based zenith instrumentation at dawn occurs some 200 km in the direction towards sunrise. They comment that while this difference must be considered at high latitudes where NO₂ zonal gradients can be significant in winter due to asymmetry of the polar vortex (Solomon et al., 1994), its contribution at tropical regions is within the error bars and has not been taken into account in this work.
 5. Diurnal variation: All the studied papers take into account the photochemical behaviour of the NO₂ and perform corrections to locate all the measurements at the same time.
 - a. Gil et al., 2008: SLIMCAT 3D CTM (Denis et al., 2005)
 - b. Dirksen et al., 2011 : A chemical box model [Denis et al., 2005; Ionov et al., 2008], based on chemistry from the SLIMCAT 3 - D CTM [Chipperfield et al., 1996]
 - c. Hendrick et al., 2012: SLIMCAT 3- D-CTM (Chipperfield et al., 2006)
 - d. Pastel et al., 2013: SLIMCAT 3D CTM (Chipperfield et al., 1999 and Denis et al., 2005)
 - e. Sussmann et al., 2005: there is no significant seasonal change of the daytime increasing rate of stratospheric NO₂ within the FTIR error bars.
 6. For studies at high latitude it is important to know where the Polar Vortex is located, as it have been presented by:
 - a. Adams et al., 2012 observed that ozone and NO₂ columns tend to be lower when the lower stratosphere (18–20 km) is inside the polar vortex
 - b. Dirksen et al., 2011 saw on March 9 that Sodankyla was skirted by the vortex edge and the warmer air mass with enhanced stratospheric NO₂ was located outside the vortex. Regarding the diurnal cycle, the region with low NO₂ increase rates coincides with the low NO₂ values inside the denoxified polar

vortex. The authors found high increase rates for the air outside the vortex, which is rich in reactive nitrogen.

7. Other considerations:

- a. Hendrick et al., 2012: Sensitivity tests have shown that the use of an aerosol extinction profile corresponding to volcanic conditions (i.e.: Pinatubo) has an impact of up to 10% on the retrieved stratospheric NO₂ columns. Ozone can also influence the abundance of NO₂ in the stratosphere since a decrease in ozone leads to an increase in NO₂ and vice versa

6.2.2. Consistency between Tropospheric NO₂ products and Satellite data

6.2.2.1. DOAS/MAXDOAS Tropospheric NO₂ column.

Table 16. Main results of the Tropospheric NO₂ column comparison

Product	Station	Difference	Sensor	Reference	Comments
DOAS/MAXDOAS NO ₂ tropospheric total column	OHP	8-20% Northern Hemisphere 10-25% Southern Hemisphere	GOME-2	Pinardi et al., 2011	(Sat-GB)/Sat
	DANDELIONS campaign	RMS difference: 3.9-5.4	OMI	Celarier et al., 2008	MAXDOAS vs satellite is largely dominated by the difference in their spatial and temporal averaging

In this section, the validation of tropospheric NO₂ column data derived from OMI and GOME-2 instruments will be presented. DOAS and MAXDOAS ground-based instruments located at the Alps (Jungfraujoch and Haute Provence Observatory, OHP), Izaña, La Reunion and Ny-Alesund are considered for the validation (see Table 2). Therefore, only results from the papers including such validations will be presented here.

Pinardi et al., 2011 validated GOME-2 data with OHP MAXDOAS. Celarier et al., 2008 is also included in this comparison because he presents a comparison of ground-based DOAS/MAXDOAS NO₂ measurements during the DANDELIONS campaigns (Brinksma et al., 2008) and uses ground-based data to validate OMI tropospheric NO₂ data. See Table 17.

Table 17. Papers for MAXDOAS Tropospheric NO₂ Column

Papers	DOAS	SCIAMACHY	GOME / GOME-2	OMI
Celarier et al., 2008	x			x
Pinardi et al., 2011	x	x	x	

6.2.2.2. Remarks

Accuracies and uncertainties should be well known in order to perform reliable comparisons and to understand the possible differences among the data sets. Errors and uncertainties are presented and documented in different ways depending on the paper. An overview of such errors and uncertainties are summarized next, however, a detailed explanation about the origin of the errors is not included. Accuracies and uncertainties depend on (1) errors in the retrieval,

(2) uncertainty in NO₂ cross-sections and (3) uncertainty in the reference content and AMF calculations.

Methodology of the algorithms

In Celarier et al., 2008, MAXDOAS instruments were operated in different ways depending on the owner institution (Brinksma et al., 2008, Russchenberg et al., 2005, Warner et al., 2004 or Wittrock et al., 2004). Nowadays, all NDACC stations are adopting the NDACC recommendations (<http://www.ndsc.ncep.noaa.gov/>) in their algorithms. As MAXDOAS instruments and data treatment procedures are different, instrument results were intercompared providing a very good agreement between the BIRA and Bremen data sets (correlation coefficients of 0.9 and slope of 1.1), and also between the BIRA and Heidelberg instruments (correlations between 0.82 and 0.91).

In Pinardi et al, 2011, tropospheric NO₂ GOME-2 data from June 2007 to March 2010 are validated by comparison with data from the MAXDOAS instrument located at OHP. MAXDOAS data are interpolated to GOME-2 overpass time. Only GOME-2 cloud free data within a 100 km radius above OHP are used. For more detail see Table 18.

Table 18. Wavelength, algorithm and cross sections used by OMI and GOME-2 to derive tropospheric NO₂ Column

Papers	Wavelength (nm)	Algorithm	Cross Sections
Celarier et al., 2008	415-465 nm	Spatial and regional overpass products (OVP) (Version 1.0) (http://avdc.gsfc.nasa.gov/Data/Aura/OMI/OMNO2/index.html). (Bucsela et al., 2006; Boersma et al., 2002; Wenig et al., 2007; Boersma et al., 2004	NO ₂ [Vandaele et al., 1998], O ₃ [Burrows et al., 1999a], and ring [Chance and Spurr, 1997]. These spectra were convolved with a model OMI instrument slit function prior to use in the fitting algorithm.
Pinardi et al., 2011	425-445 nm	DLR algorithm with version 4.3 and 4.4 of the GOME Data Processor (GDP) (see TN-DLR-ATBD 2011 and TN-DLR-PUM 2010)	TN-DLR-ATBD 2011 and TN-DLR-PUM 2010

Results

To perform an accurate validation, it is important to take into account the heterogeneity of the troposphere and the horizontal smoothing effect of the OMI and GOME-2 results. Ground instruments sample a single point while the OMI and GOME-2 NO₂ values are the average value of the area covered by the pixel (13×24 km² for OMI and 40×40 km² for GOME-2). This issue is one of the main problems related to tropospheric NO₂ satellite validation (Celarier et al., 2008). Even though, good agreement is generally seen between the OMI and ground-based data. OMI underestimates by 15% the NO₂ total tropospheric columns. Some study cases showed that results improved when the match up criteria is tightened, proving the importance of the horizontal smoothing effect. In Table 19 the results presented in Celarier et al 2008 (from Table 3 of this paper) are shown.

In Pinardi et al., 2011, the result of the comparison at OHP gives a correlation coefficient of about 0.67 and a slope of 0.8±0.04 for a linear regression fit. For the monthly mean values the relative differences are generally within ±50%.

Pinardi et al., 2011 carried out extra validations with different satellite products (GOME-2 GDP and TEMIS products and SCIAMACHY TEMIS product) around OHP and Beijing. The comparison gave good agreements in the seasonal variation but revealed bias of up to 50% probably due to the different assumptions on the tropospheric AMF.

Table 19. Summary of validation study results for OMI NO₂ data product (Celarier et al., 2008).

Instrument	Column	Group	OMI, rel. to GB	Remarks
SAOZ	Strat.	CNRS	+10%	As large as 50% in tropics.
MAX-DOAS	Trop.	BIRA, etc.	-15%	Large scatter in the data.
Brewer	Total	GSFC	-33%	Large <i>N</i> , large scatter.
MF-DOAS	Total	WSU	-19%	Very small <i>N</i> .
Pandora-1	Total	GSFC	-15%	Very small <i>N</i> .
DS-DOAS	Total	BIRA	-16%	Small <i>N</i> , large scatter.
FTUVS	Total	JPL	-23%	Small <i>N</i> , but good correlation.
Aircraft <i>in situ</i>	Trop.	UC Berkeley, GSFC	+10%	Large scatter.

Discussion

Differences in the measurement technique and the uncertainty associated to each instrument and algorithm (selected cross-sections and their dependence with the temperature, the AMF calculations and the models and assumptions used to compute them, the assumed a priori NO₂ profile...).

Smoothing error: the vertical smoothing errors are studied by means of the averaging kernels, not considered in the papers.

1. Smoothing error: the horizontal smoothing error is related to satellites and the size of their images and pixels. All the papers studied used a mean value of the retrieved stratospheric NO₂ around the station where the comparison is carried out. Depending on the considered paper, the horizontal average involves different regions around the station. Pinardi et al., 2011 considered 100 km around OHP with GOME-2. The effect of the horizontal smoothing on satellite data results in an increase of the retrieved tropospheric NO₂ when the station is located on a clean area and in a reduction, when the station is located on a polluted area skirted by rural areas. In order to investigate the effect of the horizontal smoothing in the comparison, Celarier et al., 2008 presented results of single MAXDOAS samples and the average of simultaneous measurements from three directions of MAXDOAS instrument. A significant improvement is observed in the comparison results when various directions are included. This proves that the smoothing effect should be taken into account when comparing satellite with ground-based data.
2. Different effective air mass. This effect should be taken into account when comparing DOAS/ MAX-DOAS instruments with other instruments. DOAS/MAXDOS measurements are performed pointing to a specific part of the atmosphere. The

- effective NO₂ mass measured by the GB instrument and satellite instrument may not agree. This issue must be taken into account but the correction of this effect is difficult.
3. Diurnal variation: In the troposphere the diurnal variation of the NO₂ concentrations depends more on the sources than on the photochemical behaviour.
 4. Other considerations: Celarier et al., 2008: The effect of the aerosols on retrievals and on most of the ground-based measurements has not been investigated. Aerosols can mask some of the tropospheric NO₂ introducing a bias in the results.

6.3.CO products

6.3.1. Consistency between tropospheric and stratospheric CO products and Satellite data

Table 20. Results of Kerzenmacher et al., 2012, therein Table 2.

Table 2. Results of the CO total column comparisons between IASI and the as-IASI-FTIR data. The mean and median differences and the 1- σ standard deviation are indicated in columns 2 to 4, the number of individual comparisons, of unique FTIR values and of unique IASI values in columns 5 to 7, the number of days in column 8, the correlations, R , between the individual column values in column 9 and the maximum temporal coincidence (hours and minutes), max Δt , in column 10.

FTIR station	Mean diff. [%]	Median diff. [%]	1-Std diff. [%]	# of pairs	# of FTIR	# of IASI	# of days	R	Max Δt
Ny-Alesund	-1.5	-3.3	15.3	4514	53	17	14	0.60	9h21'
Kiruna	1.3	-0.9	19.3	2519	66	34	42	0.60	11h43'
Bremen	10.8	9.3	13.7	952	40	14	20	0.32	9h16'
Jungfraujoch	2.3	2.0	12.5	5173	309	257	97	0.77	15h43'
Izaña	-2.4	-2.4	9.9	2466	109	81	67	0.73	13h39'
Wollongong	-4.5	-5.3	12.9	13402	611	244	77	0.77	16h27'

Kerzenmacher et al., 2012 presents the validation of the CO IASI total column data with ground-based NDACC Fourier transform infrared (FTIR) data at Ny-Alesund, Jungfraujoch and Izaña stations (see Table 21). No validation of IASI CO data with FTIR data was found over La Reunion. No other papers were found related to this validation.

Table 21. Papers for FTIR CO Column

Papers	FTIR	IASI	MOPITT
Kerzenmacher et al., 2012	x	x	

6.3.2. Remarks

Accuracies and uncertainties should be well known in order to perform reliable comparison and to understand the possible differences among the data sets. Errors and uncertainties are presented and documented in different ways depending on the paper. An overview of such errors and uncertainties are summarized next. A detailed explanation of the origin of the errors is not included. Accuracies and uncertainties depend on (1) errors in the retrieval, (2) uncertainty in the spectroscopic line parameters.

Methodology of the algorithm

Kerzenmacher et al., 2012 report on the validation of the IASI CO total column (CO-TC) from the FORLI retrieval version (20100815) using correlative CO profile products retrieved

from ground-based solar absorption FTIR. The period of time used in this evaluation is from January 1 to December 31, 2008.

Results

Results of Kerzenmacher et al., 2012 are presented in Table 20.

Discussion

A careful comparison between IASI and NDACC total columns is performed within the limits of the co-location criteria (100 km and 24 h of the centre of the IASI footprint) adjusting for:

1. Altitude differences. The FTIR profile has to be adjusted in partial column units in such a way that its total column corresponds to the IASI total columns with different ground level altitudes.
2. Smoothing of the FTIR data with the IASI CO averaging kernel. The altitude-corrected FTIR profiles (in partial column units) are smoothed with the total column averaging kernels of the IASI retrievals.

6.4. CH₄ Products

6.4.1. Consistency between tropospheric and stratospheric CH₄ products and Satellite data

Dils et al., 2006 presents the validation of the CH₄ SCIAMACHY total column data with ground-based NDACC FTIR data at Ny-Alesund, Jungfraujoch and Izaña stations. No validation of SCIAMACHY CH₄ data with FTIR data was found over La Reunion. No other papers were found related to this validation.

Table 22. Results from Dils et al., 2006 (therein Table 8.)

Table 8. Summary of statistical results of comparisons between SCIAMACHY and FTIR g-b data for (X)CH₄. Bias is the calculated weighted bias (in %) of the SCIAMACHY data relative to the 3rd order polynomial fit through the ground based FTIR data for (X)CH₄, using the small grid (SG=±2.5° LAT, ±5° LON) and large grid (LG=±2.5° LAT, ±10° LON) spatial collocation criteria (see Eq. 3). The indicated errors represent the weighted standard errors of the ensemble of individual weighted biases (see Eq. 5). *n* is the number of correlative individual SCIAMACHY data. σ_{scat} is the weighted percentage 1 σ standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit(see Eq. 8). *R* is the correlation coefficient between the monthly mean SCIAMACHY and FTIR data and *P* is the probability of no-correlation.

Algorithm → Station ↓		WFMD, SG XCH ₄ cor	WFMD, LG XCH ₄ cor	IMLM, SG CH ₄ v6.3	IMLM, LG CH ₄ v6.3	IMAP, SG XCH ₄ v1.1	IMAP, LG XCH ₄ v1.1
Ny Alesund	Bias	0.13±1.69	-1.26±1.16	/	/	0.09±0.16	0.04±0.11
	<i>n</i>	39	90	0	0	511	1105
(σ _{scat} FTIR=0.62) Kiruna	σ _{scat}	1.81	2.61	/	/	0.80	0.78
	Bias	-2.48±0.23	-2.07±0.17	-2.94±5.97	-2.63±4.42	-0.29±0.23	-0.004±0.16
(σ _{scat} FTIR=1.27) Harestua	<i>n</i>	2600	4486	16	27	458	819
	σ _{scat}	2.37	2.20	5.39	4.55	1.22	1.03
(σ _{scat} FTIR=1.12) Zugspitze	Bias	-2.50±0.27	-2.33±0.25	-4.94±6.22	-4.33±5.84	0.66±0.25	0.96±0.18
	<i>n</i>	1848	2186	19	21	393	682
(σ _{scat} FTIR=0.76) Jungfraujoch	σ _{scat}	2.44	2.35	9.71	9.59	1.12	1.10
	Bias	-2.02±0.21	-1.50±0.13	-2.42±0.97	-1.86±0.58	2.39±0.15	2.56±0.10
(σ _{scat} FTIR=0.71) Egbert	<i>n</i>	1529	3741	351	945	1063	2387
	σ _{scat}	1.67	1.19	6.65	6.49	1.01	1.18
(σ _{scat} FTIR=1.41) Toronto	Bias	-3.74±0.12	-3.21±0.08	-4.75±0.61	-4.62±0.41	0.24±0.09	0.23±0.06
	<i>n</i>	4247	8525	748	1585	2518	4837
(σ _{scat} FTIR=1.69) Izaña	σ _{scat}	1.28	1.31	5.13	4.65	1.09	1.23
	Bias	-4.56±0.13	-4.75±0.09	-5.58±0.78	-6.10±0.54	-2.21±0.14	-2.36±0.10
(σ _{scat} FTIR=0.55) Wollongong	<i>n</i>	3774	7516	426	923	1142	2379
	σ _{scat}	1.86	1.63	4.72	4.37	1.27	1.18
(σ _{scat} FTIR=1.56) Lauder	Bias	-3.19±0.14	-3.32±0.10	-4.24±0.82	-4.74±0.55	-1.55±0.16	-1.67±0.11
	<i>n</i>	3781	7426	428	960	1108	2315
(σ _{scat} FTIR=0.99) Arrival Heights	σ _{scat}	2.06	1.90	5.13	4.43	1.42	1.33
	Bias	-3.45±0.12	-5.19±0.08	-1.58±0.41	-2.29±0.15	-1.52±0.07	-1.51±0.04
(σ _{scat} FTIR=1.52) Global	<i>n</i>	852	4397	400	2275	1880	5929
	σ _{scat}	1.17	1.33	2.17	2.12	0.69	0.69
(σ _{scat} FTIR=1.15) Global	Bias	-3.99±0.26	-4.12±0.12	-3.40±0.35	-3.24±0.19	-0.63±0.17	-0.52±0.10
	<i>n</i>	484	1809	927	2474	798	2093
(σ _{scat} FTIR=1.15) Global	σ _{scat}	1.14	0.83	3.07	2.54	1.44	1.43
	Bias	-0.77±0.49	-0.77±0.49	0.24±2.58	0.24±2.58	3.08±0.27	3.18±0.22
(σ _{scat} FTIR=1.15) Global	<i>n</i>	426	426	41	41	257	393
	σ _{scat}	1.86	1.86	5.71	5.71	1.36	1.35
(σ _{scat} FTIR=1.15) Global	Bias	-1.19±1.99	-2.89±0.38	-4.61±4.71	-4.69±5.23	4.35±2.33	4.83±1.83
	<i>n</i>	41	1470	16	72	2	15
(σ _{scat} FTIR=1.15) Global	σ _{scat}	3.96	2.83	4.30	12.1	1.05	1.49
	Bias	-3.24±0.07	-3.28±0.05	-2.86±0.21	-2.83±0.10	-0.48±0.06	-0.62±0.04
(σ _{scat} FTIR=1.15) Global	<i>n</i>	19 621	42 072	3372	9323	10 130	22 954
	σ _{scat}	2.09	1.93	3.20	3.14	1.07	1.09
(σ _{scat} FTIR=1.15) Global	<i>R</i>	0.80	0.80	0.52	0.71	0.76	0.70
	<i>P</i>	1.79E-19	2.02E-21	2.45E-4	3.62E-9	1.15E-14	1.91E-12

Table 23. Papers for FTIR Tropospheric CH₄ Column

Papers	FTIR	SCIAMACHY	IASI	TANSO-FTS
Dils et al., 2006	x	X		

Methodology of the algorithm

Dils et al., 2006 validated SCIAMACHY CH₄ total column data from January to December 2003 by comparison with data of 11 ground-based FTIR spectrometers from the NDACC at the stations of Ny-Alesund, Jungfraujoch, Izaña. Satellite CH₄ total column data were computed with the WFM-DOAS version 0.5, IMLM version 6.3 and IMAP-DOAS algorithms. The first two algorithms use channel 8 (with a pixel size of 30×120 km²) while IMAP-DOAS uses channel 6 (with a pixel size of 30×60 km²) of SCIAMACHY.

Time series of the relative differences between the selected SCIAMACHY individual mean vmrs (X^{SCIA}) and the corresponding values from the 3rd order polynomial interpolation through

the normalised g-b FTIR daily network data (x_i^{PF}), i.e., $[(x_i^{SCIA} - x_i^{PF})/x_i^{PF}]$ have been made for all the different SCIAMACHY algorithms and target products.

Results

It must be noted that the differences between the algorithm parameters are considerable in the case of CH₄. The WFMD XCH₄ data products have been corrected to compensate for a clear solar zenith angle (SZA) dependence that became apparent during the course of this validation exercise.

Discussion

Due to the inherent different properties of FTIR and SCIAMACHY measurements, the validation is not straightforward and several issues must be resolved in order to perform a proper intercomparison. These issues are:

1. In order to increase the amount of available coincident data for the comparison, Dils et al., 2006 used a data set of values from a third order polynomial fit to the FTIR CH₄ measurements, rather than with the FTIR data themselves. It increases the amount of validated data but cannot reproduce specific high concentration events.
2. The precision and accuracy of the data are 7% for CO and CH₄ making use of conservative estimates for the accuracies considering the entire FTIR network.
3. Before making the comparisons, Dils et al., 2006 verified that the total column averaging kernels of both data products (GB FTIR and SCIAMACHY) are very similar, showing a sensitivity close to 1 from the ground to the stratosphere. The associated smoothing errors for both data sets are negligible compared to the observed differences between them. Therefore, they have compared the data products without taking the averaging kernels explicitly into account.
4. The ground station altitude plays a role because most molecules present larger concentrations in the lower troposphere. It is important to know the location of the ground observatory and the pixel mean altitude. Therefore, Dils et al, 2006 normalised the CH₄ total column data into mean volume mixing ratios (vmrs) by means of the ECMWF operational pressure data. They assumed that the volume mixing ratio of CH₄ is constant as a function of altitude. This assumption can induce an error of up to 3% over Jungfraujoch, Zugspitze and Izaña. To reduce the effect of this error CH₄ SCIAMACHY vmrs are multiplied by a profile correction factor.
5. In addition, the horizontal smoothing error is related to satellite pixel size. It is not possible to correct for this effect but it should be taken into account when comparing the data. The spatial collocation criteria include all SCIAMACHY pixels centred within $\pm 2.5^\circ$ latitude and $\pm 5^\circ$ or $\pm 10^\circ$ longitude of the FTIR ground-station coordinates.

7. Appendix I

[Celarier et al., 2008](#) found good agreement between the OMI and ground-based measurements, with OMI stratospheric NO₂ underestimated by about 14%. Typical correlations between OMI NO₂ and ground-based measurements are generally >0.6 . They mention that the part of the stratosphere sampled by the DOAS instrument is at some distance

from the measurement sites and that this effect should be taken into account. However, they used a match up criterion in which the ground site is within the OMI FOV. The RMS absolute (and relative) between ground-based SAOZ and OMI data is 0.96 (33.4%) with a correlation coefficient of 0.68 at OHP (Haute Provence Observatory), while over La Reunion the RMS absolute (and relative) is 0.54 (18.5%) and the correlation coefficient 0.71.

Dirksen et al., 2011: The overall accuracy of the stratospheric NO₂ vertical columns retrieved with ground-based UV-Vis instruments is about 21% [Ionov et al., 2008]. Dirksen et al., 2011 concluded that the FITR and DOAS techniques over Sodankyla, Jungfraujoch and Izaña are mutually consistent within 15–20% due to inaccuracies in, e.g., the assumed profile and air mass factor. Such inaccuracies cast some doubt on their usefulness as “ground-truthing” for satellite retrievals. This is consistent with accuracies previously reported in other studies. De Mazière et al. [1998] found a +5% offset between the ground-based FTIR and zenith sky measured vertical NO₂ columns at Jungfraujoch. Kerzenmacher et al. [2008] performed a comprehensive validation study of ACE-FTS versus ground-based FTIR and UV-Vis (SAOZ) instruments and found a +15% offset between the spaceborne FTIR and SAOZ techniques.

The agreement between OMI and ground-based stratospheric NO₂ is on average within 13%. This agreement is considered optimal, given the estimated accuracy of the ground-based techniques of 21% and the precision of the OMI retrievals of approximately 0.2×10^{15} molecules/cm². Over NDACC stations, DOMINO exceeds ground-based stratospheric NO₂ by $+0.23 \times 10^{15}$ molecules/cm² and the standard product of NASA/KNMI (SP) by $+0.06 \times 10^{15}$ molecules/cm². Therefore, DOMINO is on average approximately 0.2×10^{15} molecules/cm² higher than the standard product over these stations.

The early springtime stratospheric NO₂ columns correlate strongly with stratospheric (30–50 hPa) temperatures, due to the temperature dependence of the N₂O₅ photo-dissociation rate and of the NO_x partitioning.

For some parts of the orbit, discrepancies between DOMINO and the SP AMFs on the order of 5% are found with a notable increase around viewing zenith angles (VZA) of 45°. Investigation of the look-up tables of the DOMINO and SP revealed that the latter has reference points for VZA = 0°, 30°, 45° and 70°, indicating that the large discrepancy for VZAs between 45° and 70° is most likely due to interpolation errors in the SP look-up table.

Gil et al., 2008 obtained the climatological seasonal wave of NO₂ vertical column density by taking the mean for each day of all the years considered. Mean annual values are of 2.51×10^{15} and 3.79×10^{15} molecules/cm² for a.m. and p.m., respectively. Although strongly modulated by photochemistry through the number of sunlit hours in the stratosphere, a spring-autumn asymmetry occurs.

Maximum sensitivity of ground-based zenith instrumentation at dawn occurs some 200 km in the direction towards sunrise. While this difference must be considered at high latitudes where NO₂ zonal gradients can be significant in winter due to asymmetry of the polar vortex (Solomon et al., 1994), its contribution at tropical regions is within the error bars and has not been taken into account in this work.

When compared to the ground-based data, SCIAMACHY shows excellent agreement while GOME data reveal too low summer values and the annual maximum shifted towards spring. SCIAMACHY minus ground-based differences are 1.1% on average with a moderate standard deviation of 2.2×10^{14} molecules/cm². GOME yields lower values (-9.4%) and larger standard deviation 3.0×10^{14} molecules/cm². The satellite data should be slightly lower than the ground-based measurements as result of the photochemical change of NO₂ over the day.

However, this is not the case for SCIAMACHY while for GOME the underestimation is very strong. For SCIAMACHY, the most probable reason is the use of NO₂ cross-sections at 243 K instead of 220 K, which leads to a systematic overestimation of about 6% (2×10^{14} molecules/cm² in summer, 1.2×10^{14} molecules/cm² in winter). For GOME NO₂ columns, a spectral interference pattern induced by the diffuser plate used for irradiance measurements prevents the use of the solar measurements as reference (Richter and Burrows, 2002). In addition, the Burrows et al. cross-sections used for GOME show differences of up to 10% compared to the cross-sections used for the ground-based measurements which can introduce a corresponding scaling error.

Hendrick et al., 2012 show that FTIR NO₂ columns agree well with SAOZ columns with a bias of $-7.8 \pm 8.2\%$ on average over the 1990-2009 period. A good agreement is also found between satellite nadir and SAOZ data sets with mean relative differences of $+0.9 \pm 8.8\%$ (GOME), $+1.9 \pm 11.5\%$ (SCIAMACHY), and $+2.3 \pm 11.6\%$ (GOME-2).

The decline of stratospheric NO₂ of about 3% per decade, obtained from three independent measurement techniques, provides further evidence that, at least for northern mid-latitudes, the trend in stratospheric NO₂ does not necessarily reflect the evolution of N₂O, considered as the main source of NO_x in the stratosphere. The most reasonable explanation for this feature is a change in the NO_x partitioning in favour of NO, due to possible stratospheric cooling (Revell et al. (2012)) and the decline of chlorine content in the stratosphere, the latter being further confirmed by the observed decrease in ClONO₂ at the Jungfraujoch station.

Pastel et al., 2013 presents long series of ozone and NO₂ total column measured with two ground-based SAOZ UV-visible spectrometers over the NDACC stations located in Bauru (Brazil) and Reunion Island (Indian Ocean) since 1995 and 1993 respectively. Ground-based measurements have been compared with satellite data from EP-TOMS, GOME, SCIAMACHY and OMI instruments. The ozone SAOZ random error estimated by Hendrick et al., 2011 is 4.7% and the total accuracy is around 5.9%. While the total accuracy on the SAOZ NO₂ vertical column is estimated to be around 10-15% (Ionov et al., 2008).

Pinardi et al. 2011 present a validation of NO₂ products derived from GOME-2 measurements from January 2007 to December 2010 with correlative measurements from NDACC stations placed all over the world. The algorithm used to derive the product has been generated at DLR from MetOp-A GOME-2 measurements using the UPAS environment version 1.2, the level-0-to-1 v4.0/4.1 processor and the level-1-to-2 GDP v4.3/4.4 DOAS retrieval processor (see TN-DLR-ATBD 2011 and TN-DLR-PUM 2010). The percentage relative difference between GOME-2 and NDACC UV-VIS measurements varies with the season but it ranges from 8-20% in the Northern Hemisphere and from 10-25% in the Southern Hemisphere. For the tropical stations Izaña, Mauna Loa, and Reunion (Saint-Denis) the monthly mean agreement varies from 0 to $-7 \cdot 10^{14}$ molec/cm² and the standard deviation is about $3 \cdot 10^{14}$ molec.cm⁻².

Sussmann et al., 2005 obtained a day to-day scatter of 6.5% from SCIAMACHY columnar NO₂ data with a pollution-clearing criterion applied to a 200 km selection radius around Zugspitze and all resulting data averaged for each day. This agrees well to the FTIR result of 9.2% for the day-to-day scatter. Note that a perfect agreement could not be expected due to the different averaging kernels and different sampling geometries (Zugspitze point measurement versus SCIAMACHY 200 km selection radius). Clearly, the SCIAMACHY

columns show significantly higher values than FTIR throughout the full validation period. The difference ($colSCIA-col/FTIR$) is $0.83 \text{ E}+15 \text{ cm}^{-2}$ on average. Ny-Alesund agreement is of the order of a few $10^{14} \text{ molec/cm}^2$.

8. Appendix II: Tropospheric NO₂

Celarier et al., 2008. Very good agreement is found between the BIRA and Bremen data sets (correlation coefficients of 0.9 and slope of 1.1), and also between BIRA and the three Heidelberg telescopes (correlations between 0.82 and 0.91). The regression analyses of the OMI tropospheric NO₂ validation with MAXDOAS instruments show similar results with the BIRA and the Bremen data sets, the correlation coefficient between ground-based and satellite data was about 0.6. A lower correlation was obtained with the Heidelberg data when considering only the southwest direction measurements (closest to the viewing direction of both Bremen and BIRA instruments), possibly due to the smaller number of coincidences with this instrument, and also the shorter integration time used, which may increase the sensitivity to local inhomogeneities in the NO₂ field. These results significantly improved when Heidelberg measurements were carried out from three directions and the average value again compared with satellite data. This suggests that the scatter in MAXDOAS versus satellite comparisons is, indeed, largely dominated by the difference in their spatial and temporal averaging.

Pinardi et al. 2011 present a validation of NO₂ products derived from GOME-2 measurements from January 2007 to December 2010 with correlative measurements from OHP NDACC station. The algorithm used to derive the product has been generated at DLR from MetOp-A GOME-2 measurements using the UPAS environment version 1.2, the level-0-to-1 v4.0/4.1 processor and the level-1-to-2 GDP v4.3/4.4 DOAS retrieval processor (see TN-DLR-ATBD 2011 and TN-DLR-PUM 2010). Pollution episodes are well reproduced by GOME-2. The comparison of tropospheric NO₂ derived from GOME-2 and OHP MAXDOAS instrument gives a correlation coefficient of about 0.67 and a linear regression slope of 0.8. These results are in good agreement with previously published comparisons.

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