



First characterization and validation of FORLI-HNO₃ vertical profiles retrieved from IASI/Metop

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Abstract. Knowing the spatial and seasonal distributions of nitric acid (HNO₃) around the globe is of great interest and allows us to comprehend the processes regulating stratospheric ozone, especially in the polar regions. Due to its unprecedented spatial and temporal sampling, the nadir-viewing Infrared Atmospheric Sounding Interferometer (IASI) is capable of sounding the atmosphere twice a day globally, with good spectral resolution and low noise. With the Fast Optimal Retrievals on Layers for IASI (FORLI) algorithm, we are retrieving, in near real time, columns as well as vertical profiles of several atmospheric species, among which is HNO₃. We present in this paper the first characterization of the FORLI-HNO₃ profile products, in terms of vertical sensitivity and error budgets. We show that the sensitivity of IASI to HNO₃ is highest in the lower stratosphere (10–20 km), where the largest amounts of HNO₃ are found, but that the vertical sensitivity of IASI only allows one level of information on the profile (degrees of freedom for signal, DOFS; ~ 1). The sensitivity near the surface is negligible in most cases, and for this reason, a partial column (5–35 km) is used for the analyses. Both vertical profiles and partial columns are compared to FTIR ground-based measurements from the Network for the Detection of Atmospheric Composition Change (NDACC) to characterize the accuracy and precision of the FORLI-HNO₃ product. The profile valida-

tion is conducted through the smoothing of the raw FTIR profiles by the IASI averaging kernels and gives good results, with a slight overestimation of IASI measurements in the upper troposphere/lower stratosphere (UTLS) at the six chosen stations (Thule, Kiruna, Jungfraujoch, Izaña, Lauder and Arrival Heights). The validation of the partial columns (5–35 km) is also conclusive with a mean correlation of 0.93 between IASI and the FTIR measurements. An initial survey of the HNO₃ spatial and seasonal variabilities obtained from IASI measurements for a 1-year (2011) data set shows that the expected latitudinal gradient of concentrations from low to high latitudes and the large seasonal variability in polar regions (cycle amplitude around 30 % of the seasonal signal, peak to peak) are well represented by IASI data.

1 Introduction

Nitric acid is the main form of oxidized nitrogen, in both the stratosphere and the troposphere, and constitutes the principal chemical sink/reservoir for NO_x (≡ NO+NO₂; Austin et al., 1986; Crutzen, 1979; Wespes et al., 2009). Being directly coupled to NO_x, HNO₃ impacts the ozone (O₃) budgets in the two layers (e.g. Neuman et al., 2001).

In the troposphere, the main sources of NO_x are fossil fuel combustion and biomass burning (~70%). Natural sources exist, such as lightning and microbial activity in soils, but their contribution to the total tropospheric NO_x is smaller than the anthropogenic one, especially in industrialized areas (Cooper et al., 2014; Kasibhatla et al., 1993; Logan, 1983; Wespes et al., 2007). The distribution of the NO_x sources directly influences that of HNO₃, which in the troposphere has a residence time of a few days to several weeks, depending on the latitudes (Logan et al., 1981; Wespes et al., 2007).

In the stratosphere, the main source of NO_x is nitrous oxide (N₂O) which is emitted at the surface by a variety of sources, including agricultural activities (Chipperfield, 2009; McElroy et al., 1976) and is then transported to the stratosphere, where it photodissociates or reacts with O (¹D) to form two NO molecules (Fischer et al., 1997; Muller, 2011; Portmann et al., 2012). The formed NO_x catalyse stratospheric ozone destruction through several cycles (Mohanakumar, 2008; Solomon, 1999). Apart from being an important reservoir species for NO_x, HNO₃ is a key species for the formation of polar stratospheric clouds (PSCs, type I) during the polar winter (Höpfner et al., 2006; Lambert et al., 2012; Tabazadeh et al., 2000). PSCs, which develop at very low temperatures (195 K) and are composed mainly of HNO₃, sulphuric acid and ice (Drdla and Müller, 2010; Lowe and MacKenzie, 2008), allow heterogeneous reactions and lead to the activation of chlorinated compounds in the gas phase, which in turn induce the subsequent mass destruction of ozone in the low to middle stratosphere of the polar regions in mid-spring (von Clarmann, 2013; Wegner et al., 2012). The process is amplified by the denitrification accompanying the sedimentation of the HNO₃-rich particles at the end of winter, which prevents the reformation of chlorine nitrate, one of the stable chlorine reservoirs (Gobbi et al., 1991; Solomon, 1999). In a denitrified stratosphere, most often observable in the Antarctic due to lower temperatures, very low HNO₃ concentrations are observed inside the polar vortex and a high concentration collar remains at the edge of the vortex (Santee et al., 1999, 2004, 2005; Staehelin et al., 2001; Wespes et al., 2009).

Note that the sedimentation is not the main sink for stratospheric HNO₃ at a broader scale; the principal degradation pathways are oxidation with the hydroxyl radical and photodissociation (Austin et al., 1986).

HNO₃ has been measured by a variety of instruments since its first observation from infrared solar absorption spectra in 1968 (Murcray et al., 1968). Ground-based instruments (Fiorucci et al., 2013; Rinsland et al., 1991; Wood et al., 2004) as well as sounding instruments on board balloons or aircrafts (Jucks et al., 1999; Neuman et al., 2001) or embarked on satellites (Austin et al., 1986; Orsolini et al., 2009; Wespes et al., 2007) or aboard the space shuttle (Rinsland et al., 1996) have all contributed to the characterization of the HNO₃ distributions throughout the lower atmosphere. One of the most complete data sets has been acquired by the

Microwave Limb Sounder (MLS) first on the Upper Atmosphere Research Satellite (UARS) from 1991 to 1998, then on the AURA satellite from 2004. It has allowed detailed analyses of seasonal and interannual variations (Santee et al., 1999, 2004) but at a coarse horizontal resolution due to the viewing mode. The vertical resolution of MLS ranges between 3 and 5 km, and the instruments probes the entire altitude range from the ground to 90 km. However, the HNO₃ measurements are considered reliable only in a narrow altitude range between 11 and 30 km, where the precision on the retrieved volume mixing ratio is 0.6–0.7 ppbv (Santee et al., 2007). HNO₃ distributions have also been obtained by the MIPAS instrument on ENVISAT, in the range 14–43 km with a sampling of 3–4 km and a reported accuracy of 0.2–0.6 ppbv (Piccolo and Dudhia, 2007; Vigouroux et al., 2007), and by the ACE-FTS on board SCISAT with even better precision (3%) between 10 and 37 km (Wang et al., 2007). Measurements from the SMR instrument on the ODIN satellite made at high vertical resolution (1.5–2 km) but with a precision of only 1.0 ppbv over the altitude range 18–45 km (Urban et al., 2009; Wang et al., 2007) have not been used much so far for geophysical analyses.

The Infrared Atmospheric Sounding Interferometer (IASI) on the MetOp satellite series operates in a different geometry (nadir) to all aforementioned instruments, and monitors HNO₃ using spectral information from its ν_5 and $2\nu_9$ vibrational bands. The IASI measurements have a limited vertical resolution because of the integrated view of the atmospheric column but they are made at exceptional spatial and temporal sampling. Specifically, as detailed in Sect. 2, IASI provides global measurements with a particularly good spatial and temporal sampling of the polar regions at all seasons. Other key features of IASI for HNO₃ are that the instrument provides simultaneous measurements of O₃ and other trace gases, allowing for the coupled HNO₃-O₃ cycles to be studied, and that it will operate on a long-term basis (2007–2022), allowing the identification and monitoring of trends. The potential of using the HNO₃ measurements of IASI was first shown by Wespes et al. (2009) using a 2-year data set. Although important conclusions and perspectives for the capability of IASI to sound HNO₃ were drawn from this study, the FORLI algorithm at that time only allowed for total column retrievals, and it was not possible to do a rigorous validation study due to the absence of archived data from ground-based FTIR measurements. Moreover, the total column retrieval combined with its maximum sensitivity in the stratosphere was shown to largely mask the potential of IASI to sound HNO₃ in lower layers. After this study, the Fast Optimal Retrieval on Layers for IASI (FORLI) software was adapted to allow retrieval of HNO₃ vertical profiles from IASI (Hurtmans et al., 2012). A full 8-year data set of global profiles is now available (2008–2015) but has not yet been used for extensive analysis (a subset was used in Cooper et al., 2014 to constrain lightning NO_x emissions in models). The product characterization and validation are also still lacking. This

paper uses a full year (2011) of HNO₃ profiles retrieved from IASI on Metop-A to do the following:

- fully characterize the HNO₃ retrieved concentrations in terms of vertical sensitivity and errors (Sect. 3) on the profiles and partial columns,
- validate the profiles and columns using correlative data from the NDACC FTIR network, which are also detailed here (Sects. 4 and 5),
- provide an overview of how the product can be used to analyse spatial and temporal variability (Sect. 6).

2 IASI measurements

2.1 IASI instrument

The first IASI instrument (IASI-A) was launched in 2006 on the Metop-A platform in a polar orbit (Clerbaux et al., 2009; Hilton et al., 2012). It is still operating nominally at the time of writing, in parallel with IASI-B that was launched on Metop-B in 2012. IASI is a nadir-viewing infrared Fourier transform spectrometer measuring the radiation emitted by the Earth's surface and the atmosphere in the 645–2760 cm⁻¹ spectral range (August et al., 2012; Clerbaux et al., 2009). The spectral resolution is 0.5 cm⁻¹ after apodization over the entire spectral range (Cayla, 2001; Hilton et al., 2012). The apodized radiometric noise is low, around 0.2 K in the atmospheric window of interest to this work, which includes the $\nu_5 + 2\nu_9$ band of HNO₃ (860–900 cm⁻¹), mostly suitable for the retrievals, as described in Wespes et al. (2007, 2009). IASI collects 120 views every 8 s along the 2200 km swath across to the satellite track and in this way provides global coverage twice a day (Clerbaux et al., 2009), with one overpass in the morning and one in the evening, at 09:30 Equator-crossing time. The spatial resolution varies from 113 km² at nadir to 400 km² at the end of the swath.

Note that, in addition to HNO₃, IASI measures a series of greenhouse gases: carbon dioxide (CO₂, Crevoisier et al., 2009) and methane (CH₄, Crevoisier et al., 2013). Also measured are reactive trace gases: carbon monoxide (CO, George et al., 2009), O₃ (Boynard et al., 2016; Wespes et al., 2016) and ammonia (NH₃, Van Damme et al., 2014). Together, they provide an extensive monitoring of the atmospheric system.

2.2 Retrieval method and settings

The IASI data are processed every day in near real time at ULB, by the FORLI algorithm which relies on a fast radiative transfer and on a retrieval methodology based on the optimal estimation method (OEM, Rodgers, 2000) to solve the inverse problem in the retrieval (Hurtmans et al., 2012). FORLI provides twice-daily vertical distributions of three species, namely O₃, CO and HNO₃. The FORLI methods have already been largely described (Hurtmans et al., 2012) so only

a brief reminder will be presented here, focusing on the retrieval parameters for HNO₃.

The forward model can be written in a generic way, as

$$Y = \mathbf{F}(x, \mathbf{b}) + \eta \quad (1)$$

where Y is the measurement vector (the IASI calibrated and apodized radiances in our case), x is the retrieved state vector, \mathbf{b} includes all parameters influencing the measurement, and η is the measurement noise. \mathbf{F} is the forward function, which describes the complete physics of the measurement (Hurtmans et al., 2012; Rodgers, 2000).

The inverse problem consists of finding a state vector \hat{x} approximating the true state vector x , in accordance with the measurement Y and with a prior knowledge of the state of the atmosphere, characterized by an a priori profile x_a and the corresponding variance–covariance matrix \mathbf{S}_a . The solution of the above equation for a linear problem is expressed as

$$\hat{x} = x_a + \left(K^T S_\epsilon^{-1} K + \mathbf{S}_a^{-1} \right)^{-1} K^T S_\epsilon^{-1} (y - K x_a), \quad (2)$$

where K is the Jacobian of the forward model F , and S_ϵ is the measurement error covariance. For a non-linear problem such as ours, the solution is found iteratively. The optimal estimation provides a very appropriate framework for characterizing the retrieved profiles in terms of vertical sensitivity (analysed with the averaging kernel functions) and errors. The way those quantities are calculated are described in Hurtmans et al. (2012) and are not repeated here. FORLI-HNO₃ in its latest version (v.20140922) provides profiles on 41 layers (from surface up to 40 km). The retrieval parameters, adapted from Wespes et al. (2009) and Hurtmans et al. (2012), are detailed in Table 1. The spectral range for the retrieval of HNO₃ profiles is 860–900 cm⁻¹ (see Fig. 2 in Wespes et al., 2009), in which only water vapour significantly interferes. Water vapour is adjusted as a column to improve the spectral fits in the range selected for the HNO₃ retrievals. The uncertainty on the water vapour column induces only small errors on the retrieved HNO₃ concentrations. The a priori profile (x_a) is defined as the mean of a combination of daily profiles from the LMDz-INCA chemistry transport model (from the ground up to 15.6 km) and of all profiles obtained from ACE-FTS (from 6 to 60 km). The resulting mean profile is constant over time and does not depend on latitude or longitude; i.e. the same a priori profile is used for all observations around the globe. A variance–covariance matrix from the ensemble of profiles is then calculated (\mathbf{S}_a) and yields high variability in the boundary layer (170 %) and in the UTLS region (80 %) and lower variability in the troposphere and the stratosphere (50 % and 20 %, respectively). The uncorrelated noise varies around the value of 2.10⁻⁸ W/(cm² cm⁻¹ sr). The FORLI-HNO₃ retrieval performances in terms of root mean square (rms) and bias values of the spectral residuals calculated after the retrievals, of retrieval total errors, and of degree of freedom for signal

Table 1. Retrieval settings used for the retrieval of HNO₃ concentration profiles, using the FORLI-HNO₃ software, and updated from Wespes et al. (2009). From first to last row: spectral range, a priori profile (x_a), a priori covariance matrix (S_a), uncorrelated noise (σ_ϵ) and state vector elements.

Retrieval spectral range	860–900 cm ⁻¹
x_a	LMDz-INCA (ground–15.6 km), ACE-FTS (6–60 km)
S_a	0–5 km: 170 %; 5–10 km: 50 %; 10–20 km: 80 %; 20–41 km: 20 %
σ_ϵ	2.10^{-8} W (cm ² cm ⁻¹ sr)
State vector	Surface temperature, HNO ₃ profile, water vapour column

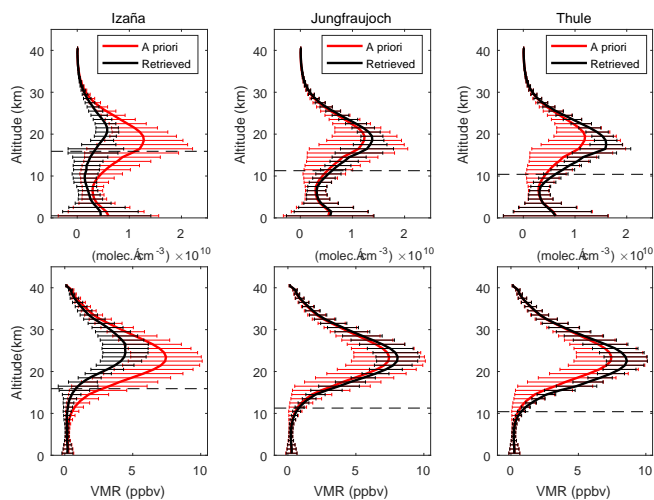


Figure 1. Example of IASI HNO₃ vertical profiles for July at three locations in the Northern Hemisphere: Izaña (28.3° N, 16.5° W), Jungfraujoch (46.6° N, 8.2° E) and Thule (76.5° N, 69.0° W). The a priori profile and a priori 1σ variation (horizontal bars) are represented in red, and the retrieved profile and its error are in black. The concentrations are expressed in molecular density, i.e. molec cm⁻³ (top panels), and in volume mixing ratio (ppbv, bottom panels). The black dashed line is the altitude of the tropopause, calculated as the lapse-rate tropopause.

(DOFS calculated as the trace of the averaging kernel matrix – DOFS = trace(A)) are detailed in Hurtmans et al. (2012). Identically to Wespes et al. (2009), a posteriori filtering of the data has been performed to remove some strongly biased HNO₃ observations. For instance, only HNO₃ observations with a good spectral fit (rms of the spectral residual lower than 3.10^{-8} W/(cm²cm⁻¹sr)) have been analysed. Additional quality flags rejecting biased or sloped residuals, suspect averaging kernels and maximum number of iterations exceeded are also applied. Cloud contaminated IASI scenes are also filtered out, based on cloud information from the Eumetcast operational processing (fractional cloud cover below 25 %).

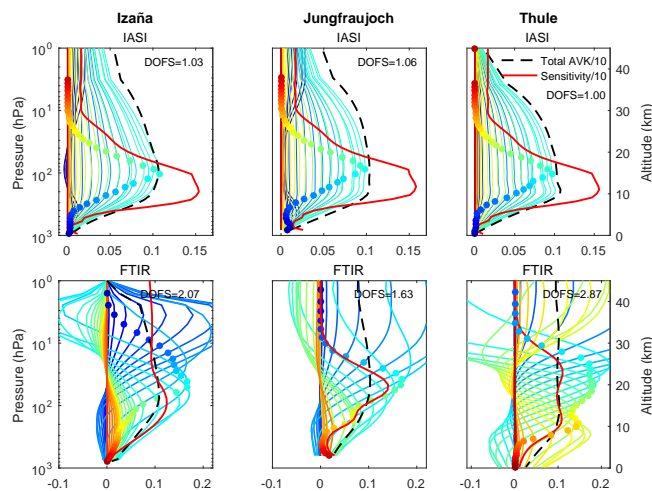


Figure 2. For three typical latitudes in July: Izaña (tropical, left), Jungfraujoch (midlatitude, middle) and Thule (polar, right): (top) IASI and (bottom) FTIR averaging kernels for HNO₃ expressed in column units (molec cm⁻²). The DOFS values are specified on each graph, and the total column averaging kernel is represented by the black dashed line. The red line is the sensitivity (see text for details) and the coloured dots represent the altitude of each kernel.

3 Characterization of FORLI-HNO₃ profiles and columns

Figure 1 displays typical FORLI-HNO₃ retrieved profiles at tropical latitudes (Izaña), midlatitudes (Jungfraujoch) and polar latitudes (Thule) in July as well as the a priori profile. It can be seen that the tropospheric concentrations are small and remain close to the a priori for all latitudes. Only Izaña stands out in this respect, with the retrieved concentrations 30 % smaller than those of the a priori profile. The stratospheric concentrations are much higher, especially between 15 and 25 km altitude, and the better sensitivity of the instrument at these altitudes (discussed next) allows for significant departure from the a priori profile. For these three example profiles, maximum values range between less than 5 ppbv at Izaña and 9.5 ppbv at Thule. This latitudinal difference is in fact a persistent and well-documented feature (e.g. Santee et al., 2007, 1999; Wespes et al., 2007), which is mostly associated with reduced HNO₃ photodissociation in the polar regions, mainly in winter.

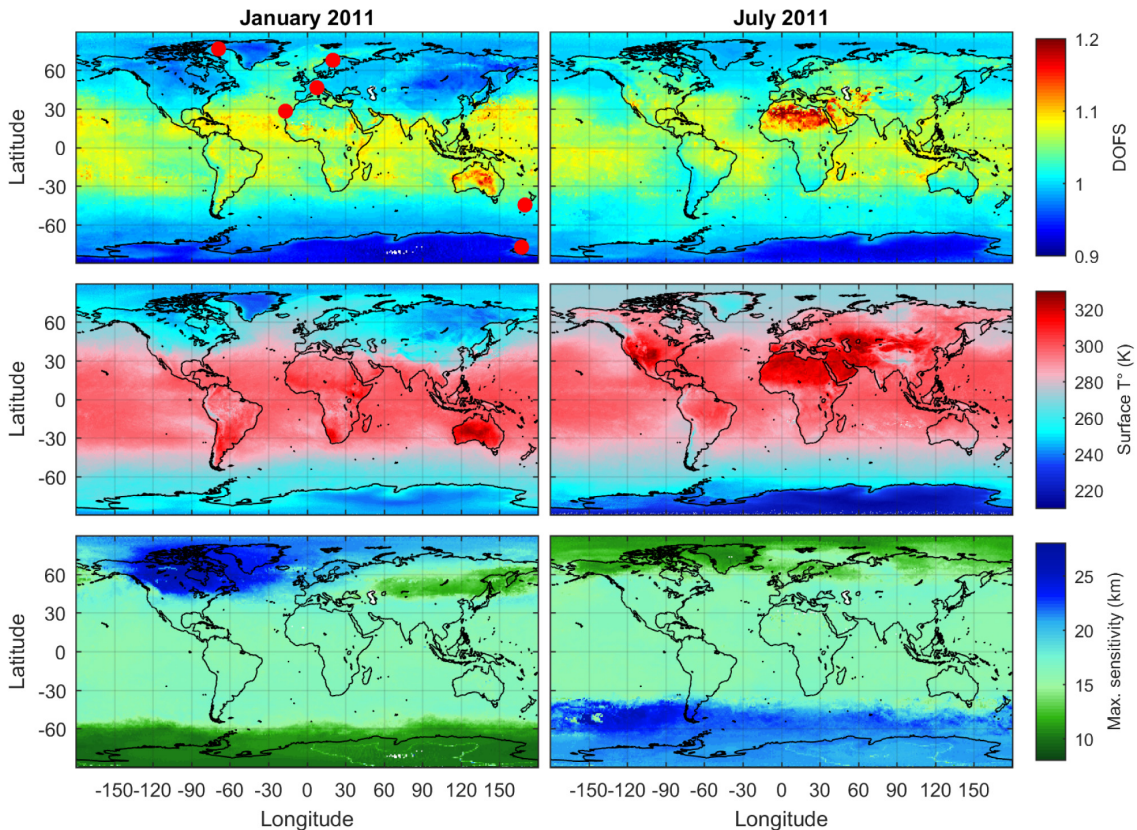


Figure 3. For January (left) and July (right) 2011. Global distribution of the DOFS for IASI HNO₃ total columns (top). The red dots on the left are the locations of the stations used for the validation, from north to south: Thule, Kiruna, Jungfraujoch, Izaña, Lauder, Arrival Heights. Global distribution of surface temperatures (in K) (middle). Global distribution of the altitude of maximum sensitivity (km) of IASI instrument, in the sense of the total averaging kernel (bottom).

The averaging kernels, presented in Fig. 2 (top panels) for the same three locations as in Fig. 1, allow characterizing the sensitivity of IASI to the HNO₃ profile, within the general FORLI framework. We find that the averaging kernels show similar shapes whatever the latitude and cover the whole range of altitudes from the surface to the upper stratosphere. The limited amount of vertical information is well seen from the overlap between the individual layer kernels. In addition, the quasi-absence of sensitivity in the lower troposphere below 5 km is obvious, with absolute values of the averaging kernels close to zero. This confirms the conclusion from Wespes et al. (2009) that the IASI instrument does not carry several pieces of vertical information for HNO₃. From the averaging kernels, we can also conclude that the maximum sensitivity to HNO₃ is at around 15 km, slightly higher (18 km) at tropical latitudes in comparison to polar latitudes (13 km). This translates to a maximum sensitivity in the upper troposphere/lower stratosphere (UTLS) at equatorial latitudes, and in the low to middle stratosphere at polar latitudes, which corresponds generally to the altitude of highest concentrations. Also represented in Fig. 2 is the IASI (and FTIR, in bottom panels) so-called “sensitivity” (red curves).

The sensitivity at altitude i is calculated as the sum of the elements of the corresponding averaging kernel, $\sum_j A_{ij}$ (with \mathbf{A} the averaging kernels matrix) and represents the fraction of the retrieval that comes from the measurement rather than from the a priori profile (Vigouroux et al., 2007). As opposed to this sensitivity, the total averaging kernel (dashed black lines) is calculated as $\sum_i A_{ij}$ and represents the contribution of each level to the sensitivity at a given altitude i .

In order to have a global vision of the results, Fig. 3 shows the global distributions of the degrees of freedom for signal (DOFS, top panels) separately for January (left) and July (right) 2011. These represent the number of independent pieces of information in the measurements and give an estimation of the vertical sensitivity of the retrievals. On average, all DOFS values range between 0.9 and 1.2, further indicating that only one level of information can be extracted from the IASI data for HNO₃. However, there are some latitudinal differences, with the DOFS being generally larger in the intertropical belt, with values around 1.1 or slightly more (e.g. in the deserts during the summer) due to larger surface temperatures inducing a better signal-to-noise ratio, in comparison to the midlatitudes and polar latitudes, where

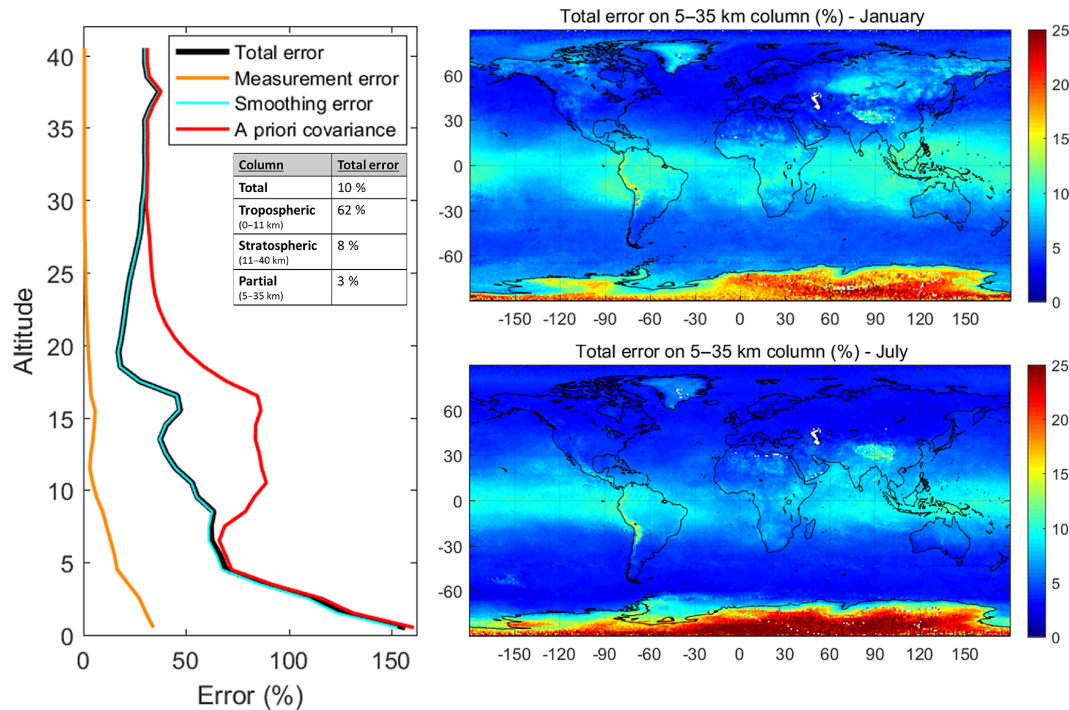


Figure 4. Error profiles for FORLI-HNO₃ showed in % (left). The total retrieval error is in black, the measurement error in orange and the smoothing error in light blue. The a priori variance (square root of the diagonal elements of \mathbf{S}_a) is in red. Also shown in the table is the total error on different partial columns (tropopause height taken as the lapse-rate tropopause for tropospheric and stratospheric columns). Spatial distribution of total retrieval error (%) (right) on the 5–35 km column for January (top) and July (bottom).

the DOFS is mostly around 0.9. However, it should be noted that the larger values of DOFS, particularly the ones found in the deserts, might also be, at least partly, attributed to the misrepresentation of the emissivity of these surfaces (Hurtmans et al., 2012). Indeed, even though we also find high surface temperatures (see Fig. 3, middle panels) in most of the intertropical regions of the globe, they do not necessarily induce such a large DOFS value. The lowermost panels in Fig. 3 depict the altitude of maximum sensitivity of IASI in January (left) and July (right). We show that the altitude of maximum sensitivity is invariant at equatorial and tropical latitudes, whereas it varies with season at midlatitudes and polar latitudes. As expected, the variations of the altitude of maximum sensitivity with the seasons follow the maximum HNO₃ concentrations (see below).

The optimal estimation method also enables characterizing the retrieved profiles in terms of error profiles. The total error on the retrieved profile can be divided into three components (Hurtmans et al., 2012; Rodgers, 2000):

- the smoothing error, due to the consideration that the retrieved profile is an estimation of a state smoothed by the averaging kernel, rather than an estimate of the true state,
- the error on the model parameters, due to fixed parameters in the direct model, e.g. surface emissivity, temper-

ature profile. This error is not taken into account in the routine processing of the error matrix in FORLI,

- the error due to the radiometric noise, i.e. the measurement error.

The contributions of the different error sources are presented in Fig. 4. This plot shows that the smoothing error is by far the main source of retrieval error over the entire altitude range (Wespes et al., 2007). We find, in agreement with the low values of the averaging kernels, that the total retrieval error in the low troposphere reproduces the a priori covariance, meaning that no information on HNO₃ profile is obtained from the IASI measurement at these altitudes. The total error decreases with increasing altitude, reaching minimum values of about 20 % around 20 km, where the sensitivity is highest. Comparing it to the a priori covariance, the precision is in fact increased mainly between 5 and 25 km, and especially around 14 km where the reduction of error reaches almost 50 %. Above 30 km, the gain of information is again minimal. The measurement error is a minor source of error; it reaches a maximum of 30 % in the boundary layer and quickly becomes negligible above 10 km. The error on the profile translates to a total retrieval error in the range of 5 to 50 % depending on latitude, with a mean value of 10 %. When calculated for various partial columns (see box in Fig. 4, left), it clearly appears that the tropospheric column

carries the largest error (62 %), whereas the error is lower for the total (10 %) or the stratospheric (8 %) column. Following the analysis of the error profiles in Fig. 4 (left), a column ranging from 5 to 35 km can be considered to be the one carrying most of the retrieved information; it is characterized by a total retrieval error of 3 % on a global average and the DOFS is the same as for the total column (ranging from 0.9 to 1.2).

Spatially, we find that the total error is larger at tropical latitudes, with values around 10–15 % (Fig. 4, right), mainly due to the higher concentrations of water vapour, which has absorption lines that interfere under large humidity with the ones of HNO₃ in the spectral region used for the inversion (Hurtmans et al., 2012; Wespes et al., 2009). The midlatitudes and polar latitudes are characterized by much lower total retrieval errors, with maximum values of about 3 % for the 5 to 35 km column. This corresponds to a reduction by a factor of 30 compared to the prior uncertainty defined by S_a (90 %). The very large errors found in Antarctica are most probably due to a misrepresentation of the surface emissivity above cold regions and to a very poor sensitivity above such cold regions (Hurtmans et al., 2012).

4 Validation methodology

The IASI derived HNO₃ profiles/columns are compared here with reference profiles/columns retrieved from measurements made by ground-based infrared Fourier transform spectrometers (FTIR) for the sake of validation. Note that the FTIR HNO₃ profiles have been used to validate other satellite data sets before (Vigouroux et al., 2007; Wang et al., 2007; Wolff et al., 2008; Wood et al., 2002).

4.1 FTIR stations and instrument

For our study, six stations routinely operating FTIR instruments, which are all part of the Network for the Detection of Atmospheric Composition Change (NDACC, <http://www.ndacc.org>) and span a large range of latitudes, were selected for the validation: Thule (76.5° N, 69° W), Kiruna (67.8° N, 20.4° E), Jungfraujoch (46.6° N, 8.0° E), Izaña (28.3° N, 16.5° E), Lauder (45.0° S, 169.7° E) and Arrival Heights (77.8° S, 166.7° E). The location of each station is displayed in Fig. 3 (red dots, upper left panel) and details on the operating instrument and retrieval algorithms are given in Table 2. The FTIRs provide data year round for all six stations, except at high latitudes (Thule and Arrival Heights in our case), where the lack of light prevents solar measurements during winter.

All instruments are Bruker spectrometers (120M for Thule and Arrival Heights, 120HR for Jungfraujoch and Lauder and 125HR for Kiruna and Izaña). The algorithms used for the retrieval of HNO₃ profiles are PROFFIT (Hase et al., 2004) for Kiruna and Izaña, SFIT2 (Pougatchev et al., 1995; Rins-

land et al., 1998) for Thule and Jungfraujoch and SFIT4 (Pougatchev et al., 1995) for Lauder and Arrival Heights. An updated Lauder and Arrival Heights HNO₃ data set was used in this study and the updates are detailed hereafter. The Lauder and Arrival Heights retrievals implemented SFIT4, closely adhering to the prescribed NDACC IRWG HNO₃ retrieval strategy (see http://www.acom.ucar.edu/irwg/IRWG_Uniform_RP_Summary-3.pdf), with the following particularities: at both sites the spectral resolution is 0.0035 cm⁻¹ and pressure and temperature profiles (ZPT) were obtained from NCEP. Using LINEFIT (Hase et al., 1999) to diagnose the instrument lineshape (ILS), an ideal ILS is assumed at Lauder while a parameterized linear ILS from 1.0 at ZPD to 0.95 (max OPD) is used in Arrival Heights retrievals. A single beam channelling fit is also implemented in the Arrival Heights retrievals. The signal-to-noise ratio (SNR) is calculated per spectrum and yields typical values of 180 and 195 for Lauder and Arrival Heights, respectively.

The three algorithms (PROFFIT, SFIT2 and SFIT4) use the optimal estimation method (OEM) developed by Rodgers (2000), which facilitates the comparison with IASI. All stations use microwindows in the region of 866–875.2 cm⁻¹ for the retrieval of HNO₃ profiles and the DOFS range between 1.9 ± 0.5 (Jungfraujoch) and 3.1 ± 0.4 (Thule). The a priori profiles are described individually at each station, independent of seasonality. It should be noted that, due to the lower degrees of freedom in the Lauder and Arrival Heights retrievals, there were numerical artefacts in the smoothing operation between the IASI and the FTIR ground-based measurements (see Sect. 4.2). To reduce these artefacts, a smoothed IASI a priori profile was used as the a priori in the ground-based retrievals in this study. The associated ground-based retrieval a priori covariance matrices (S_a) were also constructed from a smoothed IASI covariance data set. Spectroscopic line parameters were all taken from the HITRAN 2008 database (Rothman et al., 2009). Note that IASI retrievals use spectroscopic line parameters taken from the HITRAN 2004 database (Rothman et al., 2005). The update consists mainly of an improvement of the line positions and intensities (Flaud et al., 2006; Gomez et al., 2009; Rothman et al., 2009) and the differences it might induce should be kept in mind when analysing the comparison between the two instruments. Additional differences between the two instruments might also come from the uncertainty of the FTIR measurements themselves, which is dominated by the temperature and the spectroscopy information in the retrieval.

4.2 Co-location criteria and comparison method

The validation is performed for the year 2011 of IASI data. For the spatial co-location, the line of sight of the FTIR measurement is calculated, as well as the point along that line where the sensitivity is highest (i.e. where the total averaging kernel (see Fig. 2, black dashed line) reaches a maximum). A large “box” in which IASI measurements might be

Table 2. NDACC stations selected for the HNO₃ validation and their location, coordinates and altitude (in metres above sea level). The instrument and retrieval code for the retrieval of the data are specified for each station, as well as the microwindows and DOFS for total columns. References for further details are listed in the first column.

Station (References)	Location	Coordinates	Altitude (m a.s.l.)	Instrument	Retrieval code	Microwindows (cm ⁻¹)	DOFS
Thule (Hannigan et al., 2009)	Greenland	76.5° N, 69° W	225	Bruker 120M	SFIT2	867.5–870.0	3.1 ± 0.4
Kiruna (Blumenstock et al., 2006)	Sweden	67.8° N, 20.4° E	419	Bruker 125HR	PROFFIT9	867.0–869.6 872.8–875.2	3.0 ± 0.4
Jungfrauoch (Mahieu et al., 1997; Zander et al., 2008)	Switzerland	46.6° N, 8.0° E	3580	Bruker 120HR	SFIT2	868.5–870.0 872.25–874.0	1.9 ± 0.5
Izaña (García et al., 2012; Schneider et al., 2005)	Canary Islands	28.3° N, 16.5° W	2367	Bruker 125HR	PROFFIT9	867.0–869.6 872.8–875.2	2.3 ± 0.3
Lauder	New Zealand	45.0° S, 169.7° E	370	Bruker 120HR	SFIT4	867.05–870.0 872.25–874.0	2.1 ± 0.3
Arrival Heights	Ross Island, Antarctica	77.8° S, 166.7° E	200	Bruker 120M	SFIT4	867.05–870.0 872.25–874.0	1.9 ± 0.4

considered was defined for each station (approximately 10° of latitude and 15° of longitude around each station), but it is the location of the maximum sensitivity along the line of sight that determines the reference for the co-location with IASI measurements. The co-location criteria chosen is such that the IASI measurements should be within 0.5° in latitude and 1° in longitude from the FTIR reference point.

The co-location in time has been chosen after several tests (not shown) as ≤ 12 h. If more than one IASI measurement was satisfying these criteria, then all IASI retrieved profiles inside that spatial and temporal window were averaged. Each pair (FTIR, co-located IASI) undergoes the validation steps described below and in Rodgers and Connor (2003).

The raw profiles retrieved from IASI and FTIR cannot be compared adequately because of the difference in vertical sensitivity (Rodgers and Connor, 2003). To illustrate this, Fig. 2 depicts both IASI and FTIR typical averaging kernels (top and bottom panels, respectively) as well as the IASI and FTIR so-called “sensitivities” (red curves, previously explained in Sect. 3). We find that the FTIR instrument provides better vertical resolution, with each averaging kernel maximum close to its corresponding layer, and a total DOFS within the known values (see Table 2) for these examples. The averaging kernel associated with the total column (Fig. 2, black dashed lines) shows a maximum around 200 hPa for both instruments at all latitudes. Looking at the sensitivity of the two instruments (red lines), two maxima reaching 1 appear in the Thule FTIR example; one around 200 hPa (same as IASI) and one around 20 hPa, indicating that the measurement is specifically sensitive to variations in HNO₃ concentrations in those two regions of the atmosphere. On the other hand, the IASI maximum sensitivity largely ex-

ceeds the value of 1 around 200 hPa at all latitudes, indicating that the instrument might be oversensitive to HNO₃ concentrations in that region of the atmosphere (Vigouroux et al., 2007), and that it might overcompensate the lack of sensitivity in other regions of the atmosphere, yielding large HNO₃ concentrations.

In order to compare an FTIR-IASI profile pair and to reduce the smoothing uncertainties on the comparison, we use the method by Rodgers and Connor (2003). First we insert the IASI a priori in the FTIR profile using

$$x_{fi} = x_f + (\mathbf{A}_f - I)(x_{af} - x_{ai}), \quad (3)$$

where x_{fi} is the FTIR profile aligned with the IASI a priori x_{ai} , x_f is the raw FTIR profile, x_{af} the a priori FTIR profile, and \mathbf{A}_f is the FTIR averaging kernel matrix.

Next, this aligned FTIR profile is interpolated to the IASI altitude grid and the standard smoothing equation is applied, using the IASI averaging kernel and a priori:

$$x_s = x_{ai} + \mathbf{A}_I (x_{fr} - x_{ai}), \quad (4)$$

where x_s is the smoothed version of x_f , x_{fr} is the regridded FTIR profile and \mathbf{A}_I is the IASI averaging kernels matrix. A final step is to average, for a given FTIR profile, all corresponding IASI and smoothed FTIR profiles. This way, FTIR measurements with a high number of co-locations do not influence the statistics.

The comparison is carried out next for the profiles (Sect. 5.1) or partial columns (5–35 km; Sect. 5.2). For the discussion, we rely on the relative difference between the quantities retrieved from IASI and the corresponding ones from the smoothed FTIR data following:

$$x(\%) = \frac{\text{IASI} - \text{FTIR}}{\text{FTIR}} \times 100, \quad (5)$$

Table 3. For each station: minimum and maximum values of relative differences (%) between HNO₃ IASI profiles and FTIR smoothed profiles. The value between brackets is the altitude (km) of minimum (maximum) relative difference between profiles.

	Minimum (%) [altitude (km)]	Maximum (%) [altitude (km)]
Thule	0.4 [22]	12.5 [13]
Kiruna	−0.1 [24]	18.0 [13]
Jungfrauoch	0.1 [37]	25.8 [12]
Izaña	0.21 [2]	45.0 [13]
Lauder	0.7 [39]	37.2 [12]
Arrival Heights	0.3 [4]	1.8 [13]

with x being the relative difference. Standard deviations are also calculated as follows:

$$\sigma_x = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2}, \quad (6)$$

with N the number of observations, x_i the difference between IASI and FTIR values for the i th observation and \bar{x} the mean of the differences for all measurements. This allows for the characterization of the variability of the data set.

5 Validation results

5.1 Vertical profiles

The comparison of the HNO₃ mean vertical profiles retrieved from IASI and the FTIRs for each station is presented in Fig. 5, with the six panels on the left showing the comparison between IASI profile (red) and the raw (black) and smoothed (green) FTIR profiles, as well as IASI and FTIR a priori profiles (dashed red and dashed black lines). The right panel shows the mean relative differences (%) between IASI and the smoothed FTIR profile for each station. For all stations, the raw FTIR profile is largely different from the IASI profile, and this difference remains after regridding on the IASI retrieved levels (not shown). The smoothing of the FTIR profile with IASI averaging kernels brings the two profiles much closer together, with differences generally below 50% at all altitudes and maximum differences in the upper troposphere/lower stratosphere between 300 and 50 hPa. At the higher latitudes, the differences in the profiles are always below 20%. The statistics of the comparison between profiles is summarized in Table 3. Overall, the troposphere and higher stratosphere record lower values of relative difference between IASI and the smoothed FTIR profile. However, this is in most part related to the low vertical sensitivity in these regions of the atmosphere, forcing the retrieval to rely mostly on the a priori information, i.e. the same information after the smoothing of the FTIR profiles with IASI

a priori information. As indicated in Table 3 and as can be seen in Fig. 5 (right), at all stations, the maximum values for the relative differences with the smoothed profile are located in the low stratosphere (around 13 km altitude), where the sensitivity of IASI to the measurement is largest (see Fig. 2, top panels). These differences are always positive, suggesting an overestimation of the IASI concentrations in that region of the atmosphere, compared to the FTIR data, and they vary with latitude (from 1.8% at Arrival Heights to 37.2% at Lauder). Important differences between IASI and the FTIR are also found in the boundary layer, especially in Kiruna (−11.8%), Jungfrauoch (19.7%) and Arrival Heights (45.7%) and probably do not reveal a real difference, but rather an artefact, due to the regridding, with potentially a different altitude taken as ground level in both instruments. It should be noted that an overestimation of IASI measurements compared to ground-based measurements in the upper troposphere/lower stratosphere has also been found for O₃ vertical profiles (Antón et al., 2011; Dufour et al., 2012; Gazeaux et al., 2013). While some hypotheses have been brought forward by Dufour et al. (2012), the exact reason for that particular feature of FORLI for both HNO₃ and O₃ retrievals is not clear. The loose constraint applied to the retrieval at these altitudes, combined with a lack of vertical sensitivity, could be one reason for the overestimation in the UTLS, as it might be that the UTLS concentrations are overestimated to compensate for lower values in the rest of the profile (Dufour et al., 2012). A more in-depth analysis would, however, be needed to assess this matter in more details.

5.2 Partial columns

HNO₃ partial columns from 5 to 35 km have then been compared in a similar way as the profiles. We recall here that the choice of this partial column is made in order to consider only the range of altitudes where both instruments are sensitive (see discussion in Sect. 3 and comparison of averaging kernels in Fig. 2), getting rid of the low troposphere and the high stratosphere. The results for the 2011 time series are displayed in Fig. 6. For each station, the top panel shows the comparison between raw (black) and smoothed (green) FTIR and IASI partial columns (red). Each grey point represents a daily mean of all IASI observations recorded in the area around the FTIR station (the predefined “box” around each station, see Sect. 4.2.), with a 3σ confidence interval around each grey point. The entire time evolution of the columns from IASI is displayed in grey. It shows the exceptional temporal sampling and especially the usefulness of IASI measurements in the winter months at high latitude. The IASI a priori is also represented (grey dashed line) for each station. Note that the slight temporal variability of the IASI a priori is due to its representation in column units, making it dependent on the air column at the time of measurement. The possibility of investigating chemical and physical processes from these time series is briefly explored in Sect. 6. The bottom panels

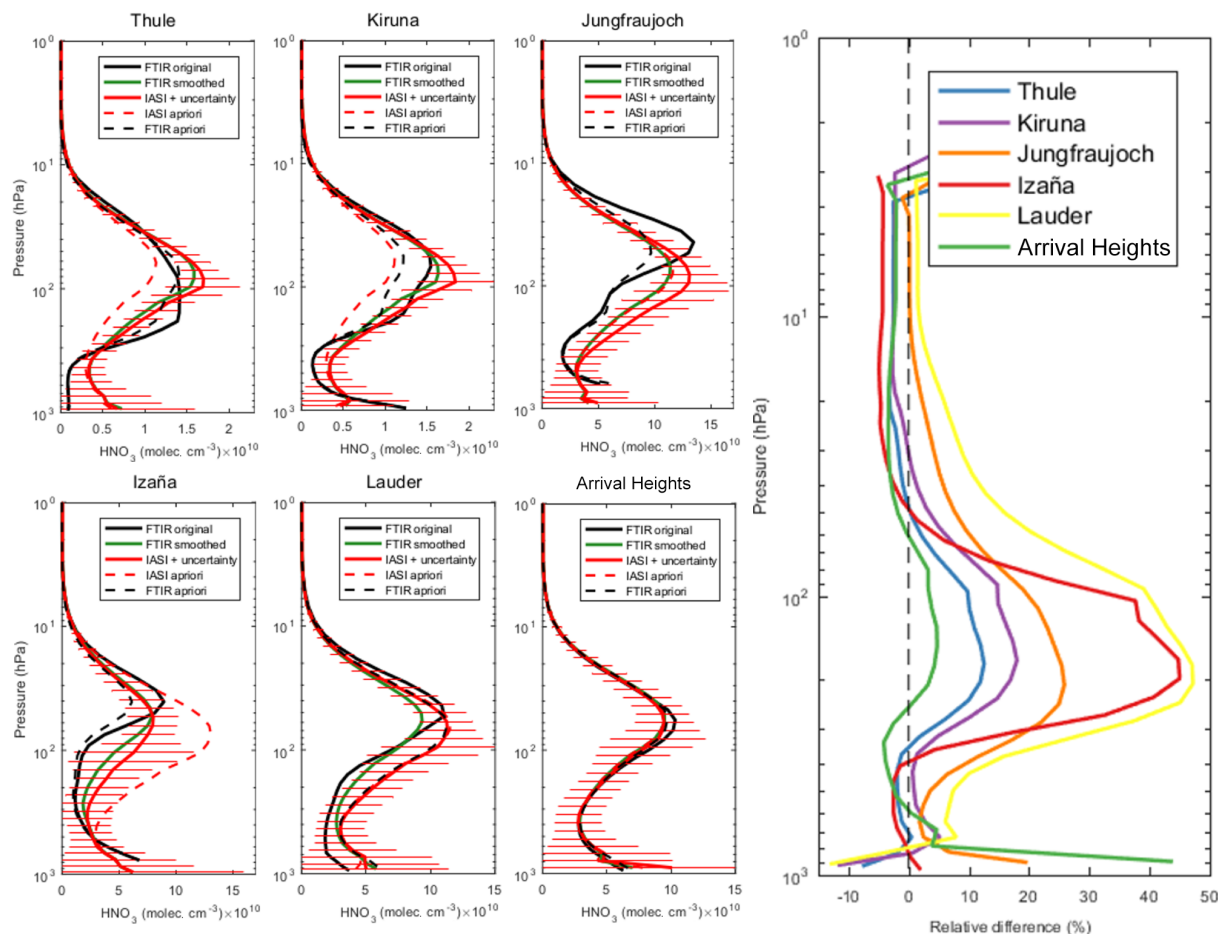


Figure 5. On the left are IASI (red), raw FTIR (black) and regridded and smoothed FTIR mean profiles (green). Also shown are the IASI and FTIR a priori profiles (red and black dashed lines, respectively). On the right, relative differences between the IASI and the FTIR smoothed profiles for each station are shown.

in Fig. 6 show the relative differences between the different data sets. The statistics of the comparison are provided in Table 4. For all stations and all measurements, we find that the FTIR column values are within the IASI total retrieval error range (see red error bars), with mean values of HNO₃ partial columns very similar between the two instruments (see Table 4, columns 4 and 5). Considering the smoothed columns, IASI is always positively biased, with bias values between 4.0 % in Thule and 16.3 % in Lauder, and with an overall bias (all stations together) of 10.5 % (Table 4). The smoothing of the FTIR data is particularly efficient for the comparison with IASI observations at Izaña, where the bias decreases from 21.3 to 9.2 % from the unsmoothed to the smoothed FTIR. Being the station with the largest difference between the FTIR and the IASI a priori profiles (see Fig. 5), Izaña is a good example of the influence of the a priori profiles on the retrievals. Indeed, with initially very different a priori profiles and limited vertical sensitivities yielding large relative differences between the two data sets (see Fig. 6, black dots), the

smoothing of the FTIR data set largely decreases the mean bias (green dots).

Looking at all stations, the standard deviation of the differences is larger than the bias at Thule, Kiruna, Izaña and Arrival Heights, suggesting that the bias is non-significant compared to the variability (Kerzenmacher et al., 2012). The reason for the different behaviour for Jungfraujoch and Lauder midlatitude stations is unclear at this point but, seeing that the biases at both stations are within the uncertainty range of both IASI and the FTIRs, this behaviour is not of great concern.

Figure 7 summarizes the results from the partial column validation by showing (top) the correlation between IASI and FTIR data, for all stations and (bottom) the relative differences in the columns. The stations are identified by a different colour. We find that the overall correlation coefficient reaches 0.93 (the correlation coefficients for each station are specified in Table 4, last column), showing that IASI captures the dynamic range of variability for the column, which

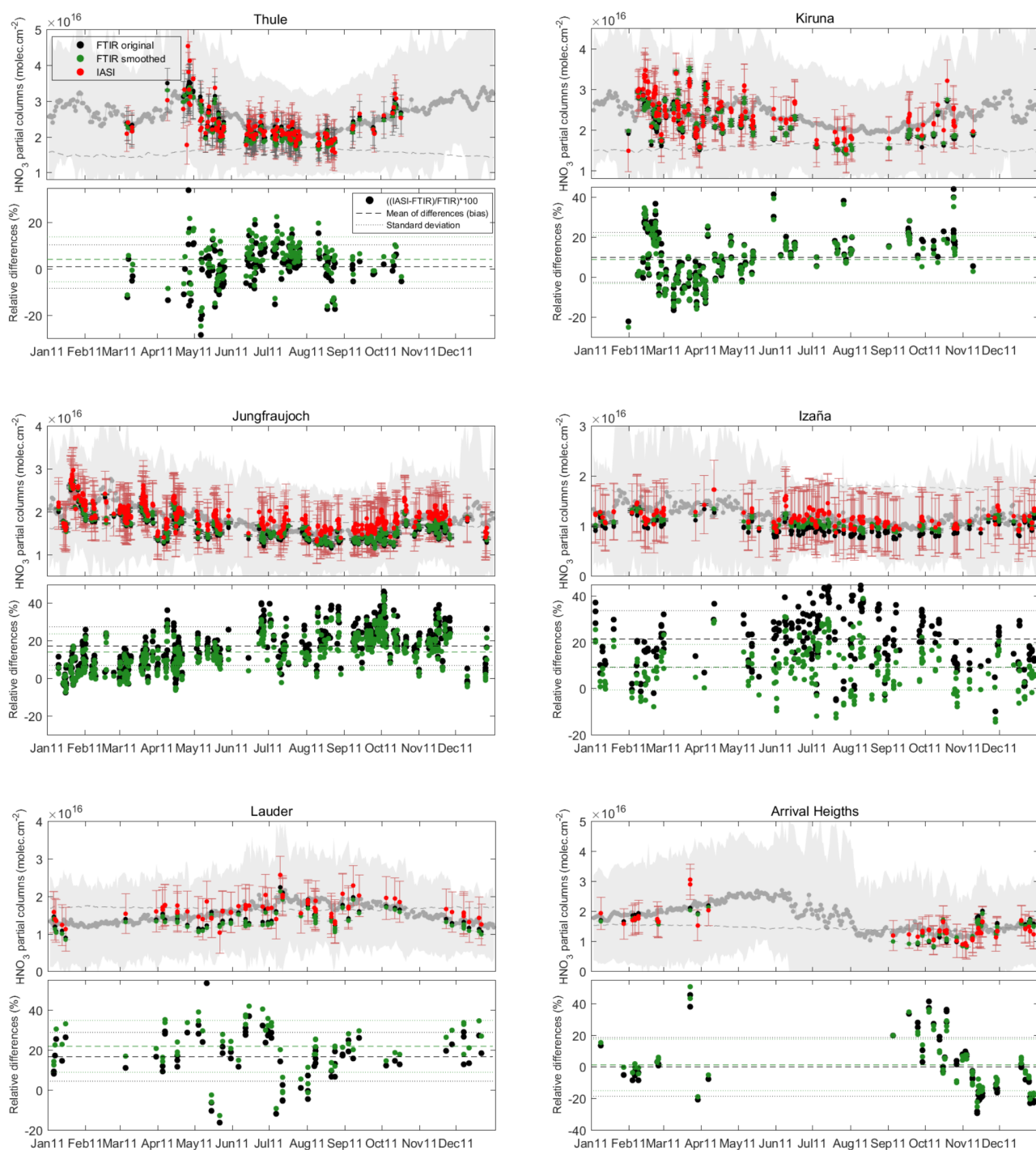


Figure 6. Comparison of the IASI and the corresponding FTIR partial (5–35 km) columns (top panels): the red dots are IASI derived partial columns, the black dots refer to the raw FTIR data and the green dots to the smoothed FTIR. The vertical error bars represent the retrieval total error for each instrument. Also represented (light grey) is the IASI data set averaged over a small region around the FTIR location (see text for details) and the standard deviation for each data point (grey shaded areas). The IASI a priori partial column is represented by the dashed grey line. Relative differences (dots), bias (dashed line) and standard deviation (dotted lines) between the two data sets for each station (bottom panels): in black, the difference between IASI and the raw FTIR data, in green, the difference between IASI and the smoothed FTIR data.

Table 4. For each station, mean of relative differences (bias) in %, calculated following Eq. (5) for smoothed FTIR partial columns, standard deviation of differences between IASI and smoothed FTIR, mean values for both data sets, number of comparison pairs and correlation coefficient between IASI and smoothed FTIR.

Stations	Bias (%) smoothed FTIR	SD (%)	Mean IASI (molec cm ⁻²)	Mean FTIR (molec cm ⁻²)	# pairs pairs	R
Thule	4.0	9.7	$2.3 \times 10^{16} \pm 0.5$	$2.2 \times 10^{16} \pm 0.4$	151	0.84
Kiruna	8.6	11.9	$2.4 \times 10^{16} \pm 0.4$	$2.2 \times 10^{16} \pm 0.4$	206	0.81
Jungfrauoch	13.9	9.6	$1.9 \times 10^{16} \pm 0.3$	$1.7 \times 10^{16} \pm 0.3$	583	0.91
Izaña	9.2	9.8	$1.1 \times 10^{16} \pm 0.2$	$1.1 \times 10^{16} \pm 0.1$	256	0.74
Lauder	16.3	11.9	$1.7 \times 10^{16} \pm 0.3$	$1.4 \times 10^{16} \pm 0.3$	80	0.81
Arrival Heights	-0.8	15.9	$1.4 \times 10^{16} \pm 0.4$	$1.4 \times 10^{16} \pm 0.3$	75	0.78
All stations	10.5	11.5			1351	0.93

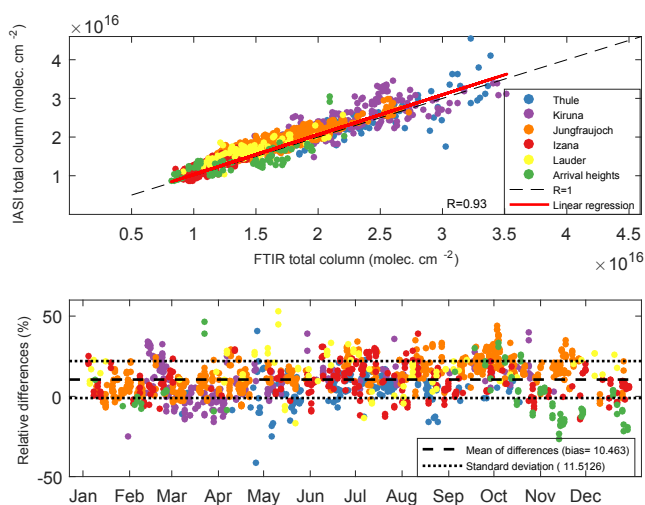


Figure 7. Comparison of the smoothed FTIR and IASI partial (5–35 km) columns for all stations considered, for the year 2011 (top). Also shown is the correlation coefficient value. Time series of the relative differences between IASI and FTIR total columns (calculated as $((\text{IASI}-\text{FTIR})/\text{FTIR}) \times 100$; %) (bottom). Also shown are the bias and standard deviation when considering all stations together (black dashed and dotted lines).

varies between 0.9×10^{16} and 4.5×10^{16} molec cm⁻², very well. This high correlation coefficient must, however, be considered cautiously, because of the influence of the remaining a priori information, albeit moderately since the least sensitive regions have been removed by considering the 5–35 km partial column. The relative differences clearly illustrate the positive bias of IASI described above, but also that the bias does not show any particular seasonality.

6 Spatial and temporal variability

6.1 Variability at NDACC stations

In Thule, IASI HNO₃ columns (red dots on Fig. 6) range between 1.6×10^{16} in summer and 4.5×10^{16} molec cm⁻² in spring. The amplitude of the seasonal cycle thus amounts to 3.0×10^{16} molec cm⁻². The annual cycle is consistent with the known variability of stratospheric polar latitudes (Wespes et al., 2009). The comparison of the seasonality with the FTIR is not possible at Thule since the FTIR instrument, which operates with solar light, does not provide data before March and after October.

In Kiruna, IASI partial columns range between around 1.5×10^{16} and 3.5×10^{16} molec cm⁻². The winter months (February to April, approximately) are characterized by higher columns, whereas the summer columns are lower (July and August), giving a seasonal amplitude of 2×10^{16} molec cm⁻². Due to the relatively high latitude of the station, January and December data are also missing in the FTIR record. With the available data, we find good agreement for seasonality between IASI and the FTIR, but with a time-dependent bias, especially a significant positive bias of IASI ($\sim 30\%$) for several days around mid-February and a low bias around -20% throughout March.

At Jungfrauoch and Izaña, IASI partial columns are lower than at higher latitudes, ranging between around 1.3×10^{16} and 3.0×10^{16} molec cm⁻² for Jungfrauoch and 0.9×10^{16} and 1.7×10^{16} molec cm⁻² for Izaña. The amplitude of the seasonal cycle is thus much weaker than at higher latitudes (1.7×10^{16} molec cm⁻² at Jungfrauoch and 0.9×10^{16} molec cm⁻² at Izaña), with only slightly higher concentrations observed in January and February at Jungfrauoch.

In the Southern Hemisphere, at Lauder, IASI partial columns range between 1.0×10^{16} and 2.6×10^{16} molec cm⁻² with slightly higher values recorded during the local winter and spring (August–September, mainly). The annual cycle amplitude reaches

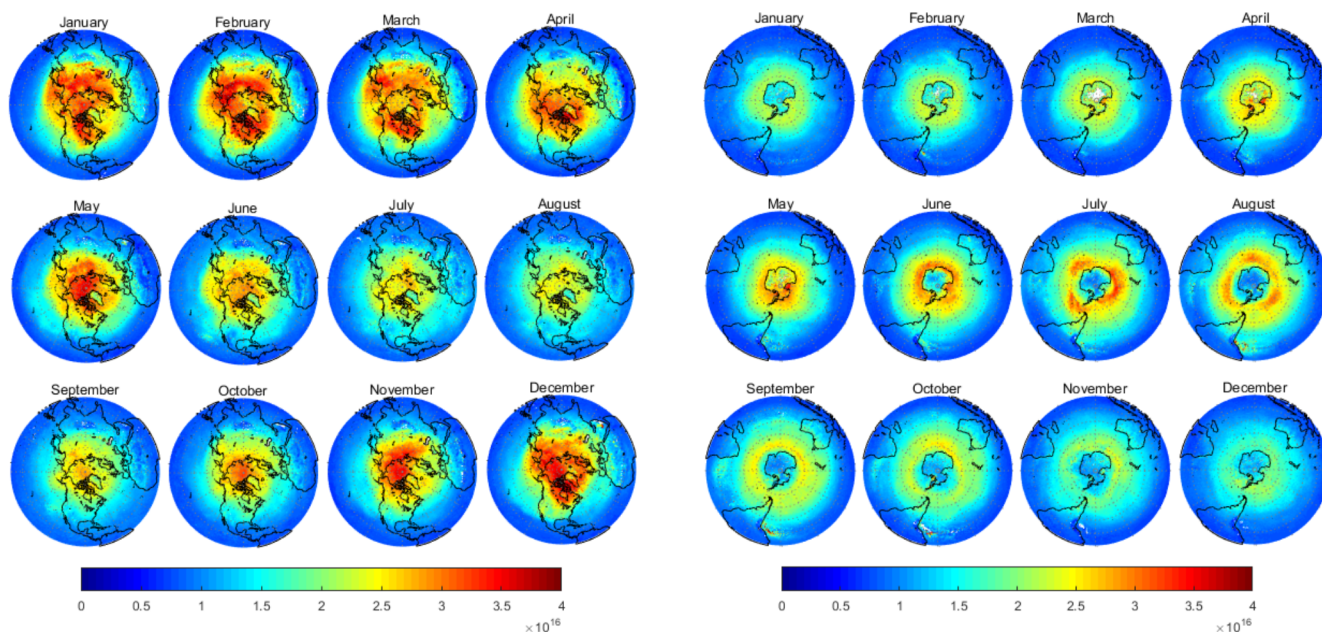


Figure 8. Monthly global distributions of IASI HNO₃ total columns in 2011 in the Northern Hemisphere (left) and the Southern Hemisphere (right). Columns are expressed in molec cm⁻².

1.5×10^{16} molec cm⁻² and well reflects the small annual cycle usually recorded for southern midlatitudes.

As for Arrival Heights, columns range between 0.9×10^{16} and 3.1×10^{16} molec cm⁻², and the day-to-day variability caused by the variability of the vortex itself is well seen in the data (see, for example, the three data points in April). Due to its very southern location and the absence of solar light over a long period of time, the FTIR instrument does not take any measurements from April to September. Given the low amount of FTIR data, it is quite difficult to establish any clear seasonality about HNO₃ columns. The complete IASI data set (grey dots in Fig. 6) can be used to assess the seasonal cycles at all stations. It is thus particularly helpful for polar regions (Thule and Arrival Heights) where the dynamics during winter are important. Hence, we find lower concentrations than expected at Thule from January to April (consistent with the few FTIR data available in March) and a strong decrease in HNO₃ concentrations in June at Arrival Heights, which are discussed below. Another important feature highlighted by the complete IASI data set is the large spatial variability recorded at high latitudes. Indeed, with each grey data point representing a daily mean of all IASI observations in a quite large box around the station, and the red dots being the closest IASI observation to the FTIR reference point for the comparison (see Sect. 4.2. for details), the difference between the two shows the spatial variability that can exist within a defined region. Such a feature can be observed at Arrival Heights, Thule and Kiruna, whereas other stations located closer to midlatitudes (Lauder, Izaña and Jungfraujoch) show little-to-no spatial variability. The

daily variability is also highlighted in Fig. 6, with the grey shaded areas representing the standard deviation (3σ) of the daily mean IASI observations. This variability includes the spatial variation of HNO₃ inside the selected boxes around the FTIR stations and the daily variation captured by the IASI daytime and nighttime measurements. It is particularly interesting in the midlatitude and high latitude stations, especially in winter (January–April for Thule, July–September for Arrival Heights), where it is much larger than the error values ($\sim 1.7 \times 10^{16}$ molecules cm⁻² for the daily variations vs. $\sim 0.5 \times 10^{16}$ molecules cm⁻² for the total error – red vertical error bars), and thus proves that the IASI instrument captures a real daily variability of HNO₃ partial columns at these latitudes. This is mainly linked to the rapid zonal transport of air masses induced by the development of the polar vortex in these regions (Wespes et al., 2009). Regarding the tropical latitudes, the daily variability should be considered more cautiously, since it is of the same magnitude as the retrieval error. Though not in the scope of the present study, the question of day and night variability needs to be further investigated.

6.2 Global variability

Beyond assessing the validity of HNO₃ locally, IASI offers the potential of global analysis due to its sampling. Monthly global distributions of the HNO₃ total columns in 2011, calculated from the FORLI-HNO₃ retrieved vertical profiles are shown in Fig. 8 for the Northern (left) and Southern (right) hemispheres. On the other hand, Fig. 9 depicts mean daily HNO₃ concentrations time series for nine latitudinal bands of

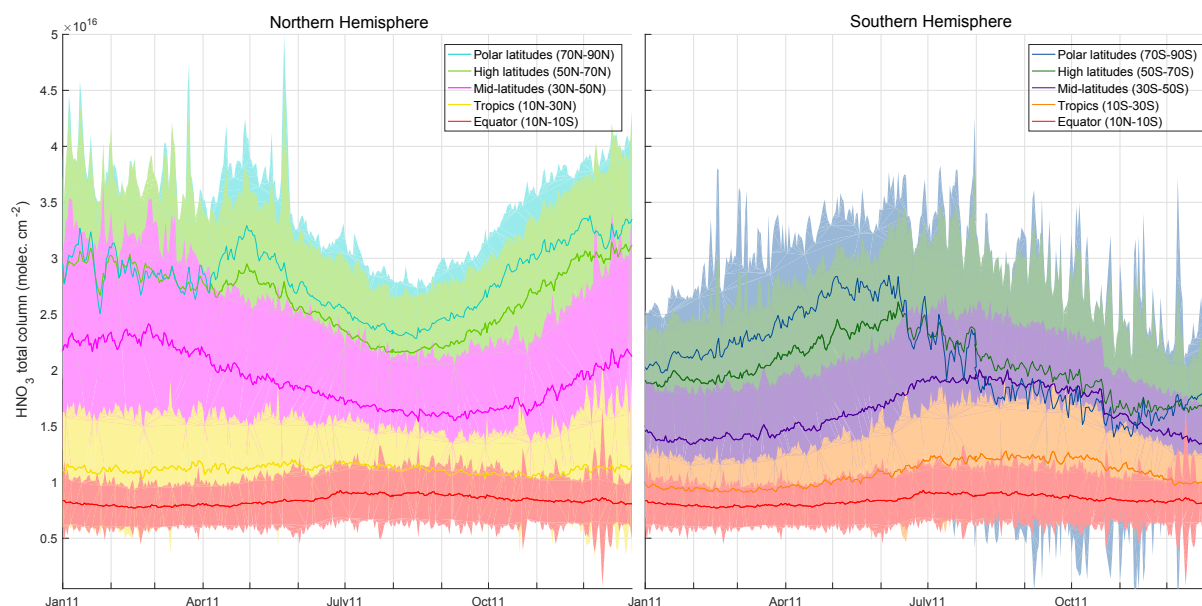


Figure 9. Seasonal variability (daily mean) and daily variability (shading, calculated as the standard deviation of the daily mean) of the total column for nine latitudinal bands of 20°, each shown with a different colour.

20° each (Northern Hemisphere on the left, Southern Hemisphere on the right). From these two figures, we show that the general spatial features with lower columns at tropical latitudes and higher columns at polar latitudes are clearly seen, especially during the winter.

The tropical regions show very low column values (around 1.0×10^{16} molec cm⁻²) all year round. Identically to the HNO₃ total column product (Wespes et al., 2009), no seasonality is observed (average amplitude of only 2.3×10^{15} molec cm⁻² for the Equator and both Tropics), nor any particular spatial pattern, as can be seen from Figs. 8 and 9. The midlatitudes and polar latitudes in both hemispheres record higher concentrations, especially during the winter, with maximum values of up to 4.5×10^{16} molec cm⁻² (Arctic). The build-up of high HNO₃ concentrations starts at the beginning of winter (October) and lasts until April–May, where the longer days enhance photodissociation. In the Southern Hemisphere, the concentrations also increase at the beginning of winter (April), but decrease rapidly (within 1 month) (see June on the right of Fig. 8 and the dark blue line on the right of Fig. 9) with the denitrification process happening during winter. Due to the denitrification, only a high concentration collar remains at the vortex edge, while the concentrations inside the polar vortex drop to as low as 1.0×10^{16} molec cm⁻². The phenomenon is very obvious in the Antarctic in July and August but, albeit moderately, also in the Arctic in January (see left panel of Fig. 9, light blue curve). Note that in the Arctic this is not a recurring annual feature. In 2011, it was caused by the exceptional stratospheric conditions during winter, which also led to a strong Arctic ozone depletion. This denitrifica-

tion was documented before in Manney et al. (2011) based on MLS limb observations.

With these fluctuations, the polar regions record not only the highest columns but also the largest cycle amplitudes, which are around 1.0×10^{16} and 1.4×10^{16} molec cm⁻² for North and South poles, respectively, with low columns in the summer and high columns in the winter.

In addition to the seasonal cycles, significant daily variability represented by the coloured shaded areas in Fig. 9 (calculated as 1σ of the daily IASI measurements) can be revealed due to the IASI sampling, especially at high latitudes during the denitrification periods. This daily variability has already been reported by Wespes et al. (2009). The main reason behind the day-to-day variability at high latitude is the variability of the vortex itself.

7 Conclusions and perspectives

In this paper we have characterized, validated and analysed the first results of the FORLI-HNO₃ vertical profile data set retrieved from IASI/MetOp. The profiles are retrieved on a 41 km altitude grid twice a day, globally. A 8-year record is now available on request and an implementation in the EU-METSAT IASI-Level 2 Product Processing Facility (August et al., 2012) is foreseen. One year (2011) of data has been investigated here but we expect the results and conclusions to be valid for other years of IASI data as well. The only particularity of the year 2011 is the exceptional denitrification that happened in the Arctic, which IASI was shown to capture well.

We have shown that IASI has a maximum sensitivity to the HNO₃ profile in the stratosphere, around 10–20 km altitude and that the vertical sensitivity of the instrument typically allows the retrieval of a single piece of information on the profile (DOFS varying from 0.9 to 1.2). The altitude of maximum sensitivity corresponds to the region of the atmosphere with the highest concentrations. The averaging kernels and error profiles showed that most of the available information in the IASI measurements originates from the altitude range between 5 and 35 km altitude. In terms of the corresponding partial column (5–35 km), the total retrieval error was calculated to be around 3 % at high latitudes, where water vapour does not interfere with HNO₃ absorption lines, increasing to 10–15 % at equatorial latitudes.

The validation was conducted by comparing the IASI retrieved HNO₃ profiles or partial columns to those retrieved from ground-based FTIR measurements made at six different stations spread around the globe at representative latitudes, namely Thule, Kiruna, Jungfraujoch, Izaña, Lauder and Arrival Heights. We found good general agreement between IASI and the smoothed FTIR profiles, but with an over-estimation of IASI data compared to FTIR measurements (10.5 % positive bias). In most cases, the differences were not found to be significant compared to the variability. The correlation between the two data sets is high for all stations (0.93 for all stations together), demonstrating the capability of IASI to capture the spatial and temporal patterns of the HNO₃ variability. However, as was shown by the comparison at Izaña, the influence of the a priori profile on the validation can be quite large, and the application of a common a priori profile to both measurements largely improves the comparison. The difference in the a priori profiles could also explain in part the differences found at other stations (Lauder, for example). It should also be noted that the differences observed between the two data sets can also be attributed, at least partly, to the difference in the spectral region used by each instrument, the different line parameters (HITRAN 2004 for IASI and HITRAN 2008 for FTIR) and codes used for the retrievals and the errors of each instrument. While no seasonality was observed in the biases, it could be interesting to conduct a similar study on a larger timescale to account for any potential trend in the bias.

IASI data allows remarkable monitoring of year-round HNO₃ concentrations. The global distribution acquired with IASI showed, for instance, a clear latitudinal gradient, with low and relatively constant concentrations at tropical latitudes, and much higher and very variable concentrations at midlatitudes and polar latitudes. The daily variability also highlighted by the IASI data set can be further investigated due to the capability of the IASI sounder to monitor the atmosphere at both day and night time.

The polar processes, including the strong denitrification in the Antarctic, are well monitored with IASI, both spatially and temporally. Overall, the results presented here are extremely encouraging with regard to the use of the HNO₃

data set from IASI to investigate stratospheric processes on local-to-global scales, with particular interest for the polar regions. The long time series that are available from IASI, which will span more than 15 years and be extended with the IASI-NG instrument on EPS-SG (Clerbaux and Crevoisier, 2013; Crevoisier et al., 2014), will be important for monitoring longer-term changes in stratospheric composition and its link to climate.

8 Data availability

The ground-based FTIR data used here are available from NDACC database (<ftp://ftp.cpc.ncep.noaa.gov/ndacc/station/>), except Lauder and Arrival Heights, which can be requested upon demand. The IASI data are available upon request.

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References

- Antón, M., Loyola, D., Clerbaux, C., López, M., Vilaplana, J. M., Bañón, M., and Alados-Arboledas, L.: Validation of the MetOp-A total ozone data from GOME-2 and IASI using reference ground-based measurements at the Iberian Peninsula, *Remote Sens. Environ.*, 115, 1380–1386, doi:10.1016/j.rse.2011.01.018, 2011.

- August, T., Klaes, D., Schlüssel, P., Hultberg, T., Crapeau, M., Ariaga, A., and Calbet, X.: IASI on Metop-A: Operational Level 2 retrievals after five years in orbit, *J. Quant. Spectrosc. Ra.*, 13, 1340–1371, doi:10.1016/j.jqsrt.2012.02.028, 2012.
- Austin, J., Garcia, R. R., Russell, J. M., Solomon, S., and Tuck, A. F.: On the Atmospheric Photochemistry of Nitric Acid, *J. Geophys. Res.*, 91, 5477–5485, doi:10.1029/JD091iD05p05477, 1986.
- Blumenstock, T., Kopp, G., Hase, F., Hochschild, G., Mikuteit, S., Raffalski, U., and Ruhnke, R.: Observation of unusual chlorine activation by ground-based infrared and microwave spectroscopy in the late Arctic winter 2000/01, *Atmos. Chem. Phys.*, 6, 897–905, doi:10.5194/acp-6-897-2006, 2006.
- Boynard, A., Hurtmans, D., Koukouli, M. E., Goutail, F., Bureau, J., Safieddine, S., Lerot, C., Hadji-Lazaro, J., Wespes, C., Pommereau, J.-P., Pazmino, A., Zyrichidou, I., Balis, D., Barbe, A., Mikhailenko, S. N., Loyola, D., Valks, P., Van Roozendaal, M., Coheur, P.-F., and Clerbaux, C.: Seven years of IASI ozone retrievals from FORLI: validation with independent total column and vertical profile measurements, *Atmos. Meas. Tech.*, 9, 4327–4353, doi:10.5194/amt-9-4327-2016, 2016.
- Cayla, F.-R.: L'interféromètre IASI: Un nouveau sondeur satellitaire à haute résolution, *La Météorologie*, 8, 23–39, 2001.
- Chipperfield, M.: Atmospheric science: Nitrous oxide delays ozone recovery, *Nat. Geosci.*, 2, 742–743, doi:10.1038/ngeo678, 2009.
- Clerbaux, C. and Crevoisier, C.: New Directions: Infrared remote sensing of the troposphere from satellite: Less, but better, *Atmos. Environ.*, 72, 24–26, doi:10.1016/j.atmosenv.2013.01.057, 2013.
- Clerbaux, C., Boynard, A., Clarisse, L., George, M., Hadji-Lazaro, J., Herbin, H., Hurtmans, D., Pommier, M., Razavi, A., Turquety, S., Wespes, C., and Coheur, P.-F.: Monitoring of atmospheric composition using the thermal infrared IASI/MetOp sounder, *Atmos. Chem. Phys.*, 9, 6041–6054, doi:10.5194/acp-9-6041-2009, 2009.
- Cooper, M., Martin, R. V., Wespes, C., Coheur, P.-F., Clerbaux, C., and Murray, L. T.: Tropospheric nitric acid columns from the IASI satellite instrument interpreted with a chemical transport model: Implications for parametrizations of nitric oxide production by lightning, *J. Geophys. Res.*, 119, 68–79, doi:10.1002/2014JD021907, 2014.
- Crevoisier, C., Chédin, A., Matsueda, H., Machida, T., Armante, R., and Scott, N. A.: First year of upper tropospheric integrated content of CO₂ from IASI hyperspectral infrared observations, *Atmos. Chem. Phys.*, 9, 4797–4810, doi:10.5194/acp-9-4797-2009, 2009.
- Crevoisier, C., Nobileau, D., Armante, R., Crépeau, L., Machida, T., Sawa, Y., Matsueda, H., Schuck, T., Thonat, T., Pernin, J., Scott, N. A., and Chédin, A.: The 2007–2011 evolution of tropical methane in the mid-troposphere as seen from space by MetOp-A/IASI, *Atmos. Chem. Phys.*, 13, 4279–4289, doi:10.5194/acp-13-4279-2013, 2013.
- Crevoisier, C., Clerbaux, C., Guidard, V., Phulpin, T., Armante, R., Barret, B., Camy-Peyret, C., Chaboureaud, J.-P., Coheur, P.-F., Crépeau, L., Dufour, G., Labonnote, L., Lavanant, L., Hadji-Lazaro, J., Herbin, H., Jacquinet-Husson, N., Payan, S., Péquignot, E., Pierangelo, C., Sellitto, P., and Stubenrauch, C.: Towards IASI-New Generation (IASI-NG): impact of improved spectral resolution and radiometric noise on the retrieval of thermodynamic, chemistry and climate variables, *Atmos. Meas. Tech.*, 7, 4367–4385, doi:10.5194/amt-7-4367-2014, 2014.
- Crutzen, P. J.: The Role of NO and NO₂ in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Planet. Sc.*, 7, 443–472, doi:10.1146/annurev.ea.07.050179.002303, 1979.
- Drdla, K. and Müller, R.: Temperature thresholds for polar stratospheric ozone loss, *Atmos. Chem. Phys. Discuss.*, 10, 28687–28720, doi:10.5194/acpd-10-28687-2010, 2010.
- Dufour, G., Eremenko, M., Griesfeller, A., Barret, B., LeFlochmoën, E., Clerbaux, C., Hadji-Lazaro, J., Coheur, P.-F., and Hurtmans, D.: Validation of three different scientific ozone products retrieved from IASI spectra using ozonesondes, *Atmos. Meas. Tech.*, 5, 611–630, doi:10.5194/amt-5-611-2012, 2012.
- Fiorucci, I., Muscari, G., Froidevaux, L., and Santee, M. L.: Ground-based stratospheric O₃ and HNO₃ measurements at Thule, Greenland: an intercomparison with Aura MLS observations, *Atmos. Meas. Tech.*, 6, 2441–2453, doi:10.5194/amt-6-2441-2013, 2013.
- Fischer, H., Waibel, A. E., Welling, M., Wienhold, F. G., Zenker, T., Crutzen, P. J., and Siegmund, P. C.: Observations of high concentration of total reactive nitrogen (NO_y) and nitric acid (HNO₃) in the lower Arctic stratosphere during the Stratosphere-Troposphere Experiment by Aircraft Measurements (STREAM) II campaign in February 1995, *J. Geophys. Res.*, 102, 23559, doi:10.1029/97JD02012, 1997.
- Flaud, J.-M., Brizzi, G., Carlotti, M., Perrin, A., and Ridolfi, M.: MIPAS database: Validation of HNO₃ line parameters using MIPAS satellite measurements, *Atmos. Chem. Phys.*, 6, 5037–5048, doi:10.5194/acp-6-5037-2006, 2006.
- García, O. E., Schneider, M., Redondas, A., González, Y., Hase, F., Blumenstock, T., and Sepúlveda, E.: Investigating the long-term evolution of subtropical ozone profiles applying ground-based FTIR spectrometry, *Atmos. Meas. Tech.*, 5, 2917–2931, doi:10.5194/amt-5-2917-2012, 2012.
- Gazeaux, J., Clerbaux, C., George, M., Hadji-Lazaro, J., Kuttippurath, J., Coheur, P.-F., Hurtmans, D., Deshler, T., Kovilakam, M., Campbell, P., Guidard, V., Rabier, F., and Thépaut, J.-N.: Intercomparison of polar ozone profiles by IASI/MetOp sounder with 2010 Concordiasi ozonesonde observations, *Atmos. Meas. Tech.*, 6, 613–620, doi:10.5194/amt-6-613-2013, 2013.
- George, M., Clerbaux, C., Hurtmans, D., Turquety, S., Coheur, P.-F., Pommier, M., Hadji-Lazaro, J., Edwards, D. P., Worden, H., Luo, M., Rinsland, C., and McMillan, W.: Carbon monoxide distributions from the IASI/METOP mission: evaluation with other space-borne remote sensors, *Atmos. Chem. Phys.*, 9, 8317–8330, doi:10.5194/acp-9-8317-2009, 2009.
- Gobbi, G. P., Deshler, T., Adriani, A., and Hofmann, D. J.: Evidence for denitrification in the 1990 Antarctic spring stratosphere: I, Lidar and temperature measurements, *Geophys. Res. Lett.*, 18, 1995–1998, doi:10.1029/91GL02310, 1991.
- Gomez, L., Tran, H., Perrin, A., Gamache, R. R., Laraia, A., Orphal, J., and Hartmann, J. M.: Some improvements of the HNO₃ spectroscopic parameters in the spectral region from 600 to 950 cm⁻¹, *J. Quant. Spectrosc. Ra.*, 110, 675–686, doi:10.1016/j.jqsrt.2008.07.004, 2009.

- Hannigan, J. W., Coffey, M. T., and Goldman, A.: Semiautonomous FTS observation system for remote sensing of stratospheric and tropospheric gases, *J. Atmos. Ocean. Technol.*, 26, 1814–1828, doi:10.1175/2009JTECHA1230.1, 2009.
- Hase, F., Blumenstock, T., and Paton-Walsh, C.: Analysis of the instrumental line shape of high-resolution Fourier transform IR spectrometers with gas cell measurements and new retrieval software, *Appl. Optics*, 38, 3417–3422, doi:10.1364/AO.38.003417, 1999.
- Hase, F., Hannigan, J. W., Coffey, M. T., Goldman, A., Höpfner, M., Jones, N. B., and Wood, S. W.: Intercomparison of retrieval codes used for the analysis of high-resolution, ground-based FTIR measurements, *J. Quant. Spectrosc. Ra.*, 7, 25–52, doi:10.1016/j.jqsrt.2003.12.008, 2004.
- Hilton, F., Armante, R., August, T., Barnet, C., Bouchard, A., Camy-Peyret, C., and Zhou, D.: Hyperspectral Earth Observation from IASI: Five Years of Accomplishments, *B. Am. Meteorol. Soc.*, 93, 347–370, doi:10.1175/BAMS-D-11-00027.1, 2012.
- Höpfner, M., Luo, B. P., Massoli, P., Cairo, F., Spang, R., Snels, M., Di Donfrancesco, G., Stiller, G., von Clarmann, T., Fischer, H., and Biermann, U.: Spectroscopic evidence for NAT, STS, and ice in MIPAS infrared limb emission measurements of polar stratospheric clouds, *Atmos. Chem. Phys.*, 6, 1201–1219, doi:10.5194/acp-6-1201-2006, 2006.
- Hurtmans, D., Coheur, P.-F., Wespes, C., Clarisse, L., Scharf, O., Clerbaux, C., and Turquety, S.: FORLI radiative transfer and retrieval code for IASI, *J. Quant. Spectrosc. Ra.*, 113, 1391–1408, doi:10.1016/j.jqsrt.2012.02.036, 2012.
- Jucks, K. W., Johnson, D. G., Chance, K. V., Traub, W. A., and Salawitch, R. J.: Nitric acid in the middle stratosphere as a function of altitude and aerosol loading, *J. Geophys. Res.*, 104, 26715, doi:10.1029/1999JD900330, 1999.
- Kasibhatla, P. S., Levy II, H., and Moxim, W. J.: Global NO_x, HNO₃, PAN, and NO_y Distributions From Fossil Fuel Combustion Emissions: A Model Study, *J. Geophys. Res.*, 98, 7165–7180, doi:10.1029/92JD02845, 1993.
- Kerzenmacher, T., Dils, B., Kumps, N., Blumenstock, T., Clerbaux, C., Coheur, P.-F., Demoulin, P., García, O., George, M., Griffith, D. W. T., Hase, F., Hadji-Lazarou, J., Hurtmans, D., Jones, N., Mahieu, E., Notholt, J., Paton-Walsh, C., Raffalski, U., Ridder, T., Schneider, M., Servais, C., and De Mazière, M.: Validation of IASI FORLI carbon monoxide retrievals using FTIR data from NDACC, *Atmos. Meas. Tech.*, 5, 2751–2761, doi:10.5194/amt-5-2751-2012, 2012.
- Lambert, A., Santee, M. L., Wu, D. L., and Chae, J. H.: A-train CALIOP and MLS observations of early winter Antarctic polar stratospheric clouds and nitric acid in 2008, *Atmos. Chem. Phys.*, 12, 2899–2931, doi:10.5194/acp-12-2899-2012, 2012.
- Logan, J. A.: Nitrogen oxides in the troposphere: Global and Regional Budgets, *J. Geophys. Res.*, 8, 10785–10807, doi:10.1029/JC088iC15p10785, 1983.
- Logan, J. A., Prather, M. J., Wofsy, S. C., and Mc Elroy, M. B.: Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, 86, 7210–7254, doi:10.1029/JC086iC08p07210, 1981.
- Lowe, D. and MacKenzie, A. R.: Polar stratospheric cloud microphysics and chemistry, *J. Atmos. Sol.-Terr. Phy.*, 70, 13–40, doi:10.1016/j.jastp.2007.09.011, 2008.
- Mahieu, E., Zander, R., Delbouille, L., Demoulin, P., Roland, G., and Servais, C.: Observed trends in total vertical column abundances of atmospheric gases from IR solar spectra recorded at the Jungfraujoch, *J. Atmos. Chem.*, 2, 227–243, doi:10.1023/A:1005854926740, 1997.
- Manney, G. L., Santee, M. L., Rex, M., Livesey, N. J., Pitts, M. C., Veefkind, P., and Zinoviev, N. S.: Unprecedented Arctic ozone loss in 2011, *Nature*, 478, 469–475, doi:10.1038/nature10556, 2011.
- McElroy, M. B., Elkins, J. W., Wofsy, S. C., and Yung, Y. L.: Sources and sinks for atmospheric N₂O, *Rev. Geophys. Space Ge.*, 14, 143–150, doi:10.1029/RG014i002p00143, 1976.
- Mohanakumar, K.: *Stratosphere Troposphere Interactions – An Introduction*, Springer, Netherlands, doi:10.1007/978-1-4020-8217-7, 2008.
- Muller, R.: Stratospheric Ozone Depletion and Climate Change, *Roy. Soc. Ch.*, doi:10.1039/9781849733182, 2011.
- Murcray, D. G., Kyle, T. G., Murcray, F. H., and Williams, W. J.: Nitric Acid and Nitric Oxide in the Lower Stratosphere, *Nature*, 218, 78–79, doi:10.1038/218078a0, 1968.
- Neuman, J. A., Gao, R. S., Fahey, D. W., Holecek, J. C., Ridley, B. A., Walega, J. G., and Ray, E. A.: In situ measurements of HNO₃, NO_y, NO, and O₃ in the lower stratosphere and upper troposphere, *Atmos. Environ.*, 35, 5789–5797, doi:10.1016/S1352-2310(01)00354-5, 2001.
- Orsolini, Y. J., Urban, J., and Murtagh, D. P.: Nitric acid in the stratosphere based on Odin observations from 2001 to 2009 – Part 2: High-altitude polar enhancements, *Atmos. Chem. Phys.*, 9, 7045–7052, doi:10.5194/acp-9-7045-2009, 2009.
- Piccolo, C. and Dudhia, A.: Precision validation of MIPAS-Envisat products, *Atmos. Chem. Phys.*, 7, 1915–1923, doi:10.5194/acp-7-1915-2007, 2007.
- Portmann, R. W., Daniel, J. S., and Ravishankara, A. R.: Stratospheric ozone depletion due to nitrous oxide: influences of other gases, *Philos. T. R. Soc. Lond.*, 367, 1256–1264, doi:10.1098/rstb.2011.0377, 2012.
- Pougatchev, N. S., Connor, B. J., and Rinsland, C. P.: Infrared measurements of the ozone vertical distribution above Kitt Peak, *J. Geophys. Res.*, 100, 16689–16697, doi:10.1029/95JD01296, 1995.
- Rinsland, C. P., Zander, R., and Demoulin, P.: Ground-based infrared measurements of HNO₃ total column abundances: Long-term trend and variability, *J. Geophys. Res.*, 96, 9379–9389, doi:10.1029/91JD00609, 1991.
- Rinsland, C. P., Gunson, M. R., Salawitch, R. J., Michelsen, H. A., Zander, R., Newchurch, M. J., and Mahieu, E.: ATMOS/ATLAS-3 measurements of stratospheric chlorine and reactive nitrogen partitioning inside and outside the November 1994 Antarctic Vortex, *Geophys. Res. Lett.*, 23, 2365–2368, doi:10.1029/96GL01474, 1996.
- Rinsland, C. P., Jones, N. B., Connor, B. J., Logan, J. A., Pougatchev, N., Goldman, A., and Demoulin, P.: Northern and Southern Hemisphere Ground-Based Infrared Spectroscopic Measurements of Tropospheric Carbon Monoxide and Ethane, *J. Geophys. Res.*, 103, 28197–28217, doi:10.1029/98JD02515, 1998.

- Rodgers, C. D.: Inverse Methods for Atmospheric Sounding – Theory and Practice, Series on Atmospheric Oceanic and Planetary Physics, Vol. 2, World Scientific Publishing Co. Pte. Ltd, doi:10.1142/9789812813718, 2000.
- Rodgers, C. D. and Connor, B. J.: Intercomparison of remote sounding instruments, *J. Geophys. Res.*, 108, 4116, doi:10.1029/2002JD002299, 2003.
- Rothman, L. S., Jacquemart, D., Barbe, A., Benner, D. C., Birk, M., Brown, L. R., and Wagner, G.: The HITRAN 2004 molecular spectroscopic database, *J. Quant. Spectrosc. Ra.*, 96, 139–204, doi:10.1016/j.jqsrt.2004.10.008, 2005.
- Rothman, L. S., Gordon, I. E., Barbe, A., Benner, D. C., Bernath, P. F., Birk, M., and Vander Auwera, J.: The HITRAN 2008 molecular spectroscopic database, *J. Quant. Spectrosc. Ra.*, 110, 533–572, doi:10.1016/j.jqsrt.2009.02.013, 2009.
- Santee, M. L., Manney, G. L., Froidevaux, L., Read, W. G., and Waters, J. W.: Six years of UARS Microwave Limb Sounder HNO₃ observations?: Seasonal, interhemispheric, and interannual variations in the lower stratosphere, *J. Geophys. Res.*, 104, 8225–8246, doi:10.1029/1998JD100089, 1999.
- Santee, M. L., Manney, G. L., Livesey, N. J., and Read, W. G.: Three-dimensional structure and evolution of stratospheric HNO₃ based on UARS microwave limb sounder measurements, *J. Geophys. Res.-Atmos.*, 109, 1–19, doi:10.1029/2004JD004578, 2004.
- Santee, M. L., Manney, G. L., Livesey, N. J., Froidevaux, L., MacKenzie, I. A., Pumphrey, H. C., and Harwood, R. S.: Polar processing and development of the 2004 Antarctic ozone hole: First results from MLS on Aura, *Geophys. Res. Lett.*, 32, 1–4, doi:10.1029/2005GL022582, 2005.
- Santee, M. L., Lambert, A., Read, W. G., Livesey, N. J., Cofield, R. E., Cuddy, D. T., and Murtagh, D.: Validation of the Aura Microwave Limb Sounder HNO₃ measurements, *J. Geophys. Res.*, 112, 1–22, doi:10.1029/2007JD008721, 2007.
- Schneider, M., Blumenstock, T., Chipperfield, M. P., Hase, F., Kouker, W., Reddman, T., Ruhnke, R., Cuevas, E., and Fischer, H.: Subtropical trace gas profiles determined by ground-based FTIR spectroscopy at Izaña (28° N, 16° W): Five-year record, error analysis, and comparison with 3-D CTMs, *Atmos. Chem. Phys.*, 5, 153–167, doi:10.5194/acp-5-153-2005, 2005.
- Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, 37, 275–316, doi:10.1029/1999RG900008, 1999.
- Stahelin, J., Harris, N. R. P., Appenzeller, C., and Eberhard, J.: Ozone trends: A review, *Rev. Geophys.*, 39, 231–290, doi:10.1029/1999RG000059, 2001.
- Tabazadeh, A., Santee, M. L., Danilin, M., Pumphrey, H. C., Newman, P. A., Hamill, P. J., and Mergenthaler, J. L.: Quantifying Denitrification and its effects on Ozone recovery, *Science*, 288, 1407–1411, doi:10.1126/science.288.5470.1407, 2000.
- Urban, J., Pommier, M., Murtagh, D. P., Santee, M. L., and Orsolini, Y. J.: Nitric acid in the stratosphere based on Odin observations from 2001 to 2009 – Part 1: A global climatology, *Atmos. Chem. Phys.*, 9, 7031–7044, doi:10.5194/acp-9-7031-2009, 2009.
- Van Damme, M., Clarisse, L., Heald, C. L., Hurtmans, D., Ngadi, Y., Clerbaux, C., Dolman, A. J., Erisman, J. W., and Coheur, P. F.: Global distributions, time series and error characterization of atmospheric ammonia (NH₃) from IASI satellite observations, *Atmos. Chem. Phys.*, 14, 2905–2922, doi:10.5194/acp-14-2905-2014, 2014.
- Vigouroux, C., De Mazière, M., Errera, Q., Chabrillat, S., Mahieu, E., Duchatelet, P., Wood, S., Smale, D., Mikuteit, S., Blumenstock, T., Hase, F., and Jones, N.: Comparisons between ground-based FTIR and MIPAS N₂O and HNO₃ profiles before and after assimilation in BASCOE, *Atmos. Chem. Phys.*, 7, 377–396, doi:10.5194/acp-7-377-2007, 2007.
- von Clarmann, T.: Chlorine in the stratosphere, *Atmosfera*, 26, 415–458, doi:10.1038/353707a0, 2013.
- Wang, D. Y., Höpfner, M., Blom, C. E., Ward, W. E., Fischer, H., Blumenstock, T., Hase, F., Keim, C., Liu, G. Y., Mikuteit, S., Oelhaf, H., Wetzel, G., Cortesi, U., Mencaraglia, F., Bianchini, G., Redaelli, G., Pirre, M., Catoire, V., Huret, N., Vigouroux, C., De Mazière, M., Mahieu, E., Demoulin, P., Wood, S., Smale, D., Jones, N., Nakajima, H., Sugita, T., Urban, J., Murtagh, D., Boone, C. D., Bernath, P. F., Walker, K. A., Kuttippurath, J., Kleinböhl, A., Toon, G., and Piccolo, C.: Validation of MIPAS HNO₃ operational data, *Atmos. Chem. Phys.*, 7, 4905–4934, doi:10.5194/acp-7-4905-2007, 2007.
- Wegner, T., Groß, J.-U., von Hobe, M., Strohm, F., Suminska-Ebersoldt, O., Volk, C. M., Hösen, E., Mitev, V., Shur, G., and Müller, R.: Heterogeneous chlorine activation on stratospheric aerosols and clouds in the Arctic polar vortex, *Atmos. Chem. Phys.*, 12, 11095–11106, doi:10.5194/acp-12-11095-2012, 2012.
- Wespes, C., Hurtmans, D., Herbin, H., Barret, B., Turquety, S., Hadji-Lazaro, J., and Coheur, P. F.: First global distributions of nitric acid in the troposphere and the stratosphere derived from infrared satellite measurements, *J. Geophys. Res.-Atmos.*, 112, 1–10, doi:10.1029/2006JD008202, 2007.
- Wespes, C., Hurtmans, D., Clerbaux, C., Santee, M. L., Martin, R. V., and Coheur, P. F.: Global distributions of nitric acid from IASI/MetOP measurements, *Atmos. Chem. Phys.*, 9, 7949–7962, doi:10.5194/acp-9-7949-2009, 2009.
- Wespes, C., Hurtmans, D., Emmons, L. K., Safieddine, S., Clerbaux, C., Edwards, D. P., and Coheur, P.-F.: Ozone variability in the troposphere and the stratosphere from the first 6 years of IASI observations (2008–2013), *Atmos. Chem. Phys.*, 16, 5721–5743, doi:10.5194/acp-16-5721-2016, 2016.
- Wolff, M. A., Kerzenmacher, T., Strong, K., Walker, K. A., Toohey, M., Dupuy, E., Bernath, P. F., Boone, C. D., Brohede, S., Catoire, V., von Clarmann, T., Coffey, M., Daffer, W. H., De Mazière, M., Duchatelet, P., Glatthor, N., Griffith, D. W. T., Hannigan, J., Hase, F., Höpfner, M., Huret, N., Jones, N., Jucks, K., Kagawa, A., Kasai, Y., Kramer, I., Küllmann, H., Kuttippurath, J., Mahieu, E., Manney, G., McElroy, C. T., McLinden, C., Mébarki, Y., Mikuteit, S., Murtagh, D., Piccolo, C., Raspollini, P., Ridolfi, M., Ruhnke, R., Santee, M., Senten, C., Smale, D., Tétard, C., Urban, J., and Wood, S.: Validation of HNO₃, ClONO₂, and N₂O₅ from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS), *Atmos. Chem. Phys.*, 8, 3529–3562, doi:10.5194/acp-8-3529-2008, 2008.
- Wood, S. W., Bodeker, G. E., Boyd, I. S., Jones, N. B., Connor, B. J., Johnston, P. V., and Sasano, Y.: Validation of version 5.20 ILAS HNO₃, CH₄, N₂O, O₃, and NO₂ using ground-based measurements at Arrival Heights and Kiruna, *J. Geophys. Res.-Atmos.*, 107, 1–11, doi:10.1029/2001JD000581, 2002.

Wood, S. W., Batchelor, R. L., Goldman, A., Rinsland, C. P., Connor, B. J., Murcray, F. J., and Heuff, D. N.: Ground-based nitric acid measurements at Arrival Heights, Antarctica, using solar and lunar Fourier transform infrared observations, *J. Geophys. Res.-Atmos.*, 109, 1–9, doi:10.1029/2004JD004665, 2004.

Zander, R., Mahieu, E., Demoulin, P., Duchatelet, P., Roland, G., Servais, C., and Rinsland, C. P.: Our changing atmosphere: Evidence based on long-term infrared solar observations at the Jungfraujoch since 1950, *Sci. Total Environ.*, 391, 184–195, doi:10.1016/j.scitotenv.2007.10.018, 2008.