# Fiducial Reference Measurements for Ground-Based DOAS Air-Quality Observations


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## Deliverable D1.4:

## Validation Report (VR)

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# Content

# Acronyms and abbreviations

Acronyms and abbreviated terms that are specific for this document can be found below.

| | |
|---|---|
| BIRA-IASB | Royal Belgian Institute for Space Aeronomy |
| DOAS | Differential Optical Absorption Spectroscopy |
| DOFS | Number of Degrees of Freedom for Signal |
| DSCD | Differential Slant Column Density |
| EVDC | ESA Validation Data Centre |
| FRM$_4$DOAS | Fiducial Reference Measurements for Ground-Based DOAS Air-Quality Observations |
| GB | Ground-based |
| LUT | Look-up Table |
| NDACC | Network for the Detection of Atmospheric Composition Change |
| OEM | Optimal Estimation Method |
| PM | Progress Meeting |
| QA/QC | Quality Assurance/Quality Control |
| RMS | Root mean square |
| S5P | Sentinel-5 Precursor |
| SLIMCAT | Single Layer Isentropic Model of Chemistry And Transport |
| SCD | Slant Column Density |
| SNR | Signal-to-noise Ratio |
| SZA | Solar zenith angle |
| VCD | Vertical Column Density |
| WP | Work Package |

# References


[RD-1] FRM$_4$DOAS CCN02 deliverable D-21 'Operational Processing System Validation and Test Report document'; see https://frm4doas.aeronomie.be/ProjectDir/Deliverables/FRM4DOAS_CCN02_D21_Operational_Processing_System_and_Test_Report_document_v1.0_20200623.pdf

[RD-2] FRM$_4$DOAS-2.0 deliverable D-1.1 'Technical Note on Estimation of Uncertainty Methodology'

[RD-3] Hendrick, F., et al.: validation of the technique through correlative comparisons, Atmos. Chem. Phys., 4, 2091–2106, 2004, http://www.atmos-chem-phys.net/4/2091/2004/.

[RD-4] Verhoelst, T., et al.: Ground-based validation of the Copernicus Sentinel-5P TROPOMI $NO_2$ measurements with the NDACC ZSL-DOAS, MAX-DOAS and Pandonia global networks, Atmos. Meas. Tech., 14, 481–510, https://doi.org/10.5194/amt-14-481-2021, 2021.

# 1 Introduction

In this document, first validation and verification results of the consolidated stratospheric $NO_2$ profiling algorithm are presented. The different consolidation steps, which are extensively described in deliverables D-1.1 and D-1.5, are the following:

- Implementation of the extra-DSCD error approach
- Use of ±15-day averaged weighting functions, twilight $NO_2$ profile variation, and a priori profile
- Calculation and use of optimised $NO_2$ weighting function and profile diurnal variation LUTs based on new PSCBOX/SLIMCAT photochemical model run with slower $NO_2$ variation at twilight ($NO_2$ photolysis rate $jNO_2$ x 0.9)
- Implementation of a correction for the Earth's sphericity on the $NO_2$ weighting functions
- Revision of the uncertainty budget

The present verification/validation exercise includes an overall quality check of the retrieval results in terms of profile shape, information content, consistency of time-series, etc, and a comparison of the retrieved VCDs to co-located TROPOMI overpass data extracted by BIRA-IASB from the S5P $NO_2$ off-line product (versions OFFL 01.03.01 to 01.04.00). This satellite product is the stratospheric column modelled by the TM5 chemistry transport model but with assimilated TROPOMI total $NO_2$ SCD over pristine/remote areas to correct for model biases.

In the first version of this document, we focus on the consolidated retrievals at the Harestua and Bremen stations where high SNR research-grade DOAS instruments are in operation since many years and for which retrieved stratospheric $NO_2$ vertical profiles have a tendency to show unrealistic double peak patterns, as described in the $FRM_4$DOAS Phase I deliverable D-21 (see [RD-1]). The verification/validation exercise will be extended to lower SNR commercial instruments in a second version of the present report that will be delivered at PM5.

# 2 Overall quality check

Time-series of $NO_2$ VCDs at 90°SZA sunrise and sunset retrieved at the Harestua (year 2020) and Bremen (year 2019) stations using the current and consolidated versions of the profiling algorithm are presented in Figure 1. It should be reminded here that the current version of the profiling algorithm uses a measurement noise which corresponds to three times the DSCD DOAS fitting error. This empirical modification of the standard OEM-settings was done in order to minimize the number of retrieved profiles showing a double-peak pattern (see [RD-1]). This OEM settings change is not included in the consolidated algorithm which uses the $NO_2$ DSCD DOAS fit error directly or the extra-DSCD error when it applies (see [RD-2]) for the construction of the measurement noise matrix $S_\varepsilon$. Data sets without and with QA/QC flagging are plotted in Figure 1. The QA/QC flagging approach includes the following four checks:

- Relative RMS of the difference between measured and recalculated SCDs smaller than 20% (modified to 10% in the case of the Bremen consolidated product; see below)
- $1 \leq DOFS \leq 3$
- Retrieved concentration values strictly positive
- Retrieval flagged as bad if presence of a double peak pattern in the retrieved profile which is not present in the a priori profile

The percentages of retrievals successfully passing the QA/QC filtering for both stations and versions of the profiling algorithm are presented in Table 1.

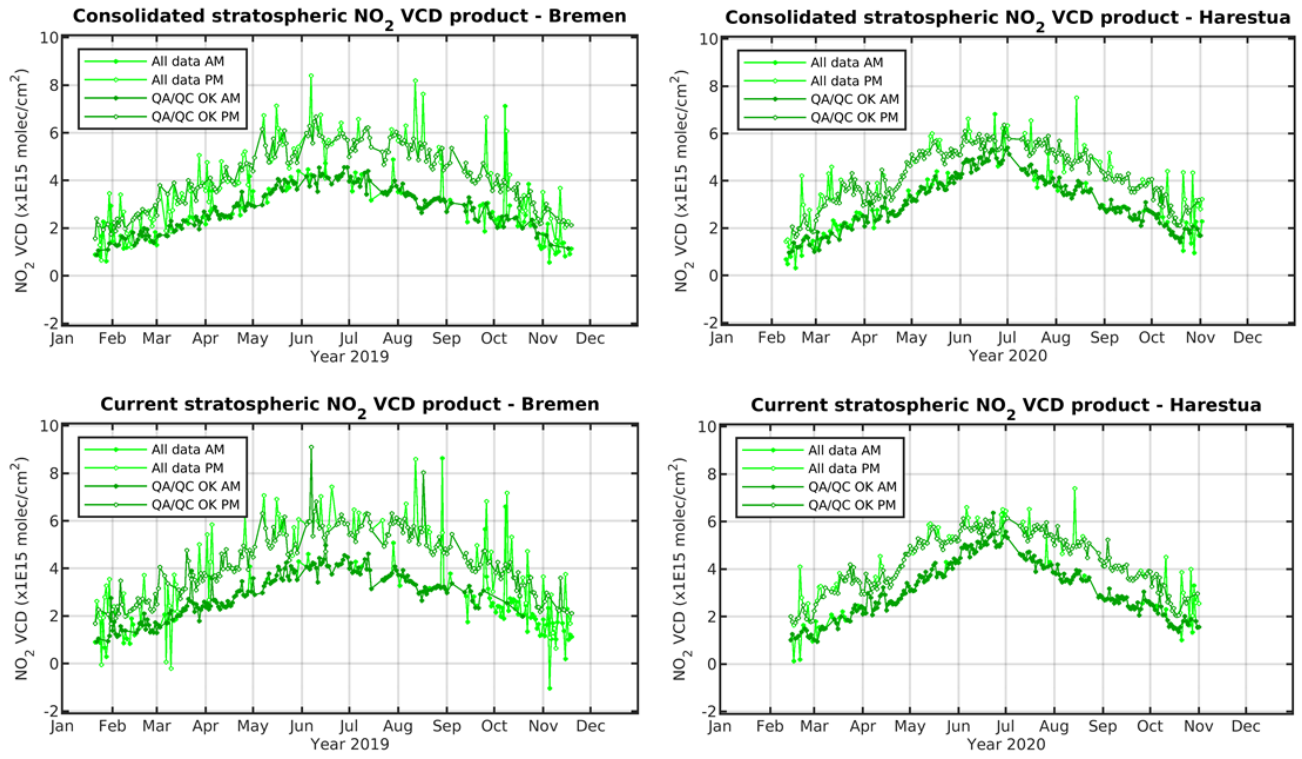


**Figure 1: $NO_2$ VCDs at 90°SZA sunrise and sunset retrieved from twilight zenith-sky measurements at the Bremen (year 2019; left plots) and Harestua (year 2020; right plots) stations. Upper and lower plots correspond to the consolidated and current retrieval results, respectively. Filled symbols are for AM, open symbols for PM. Dark green symbols are for data without errors or warnings (i.e. data that successfully pass all the QA/QC checks); light green points show all data without any QA/QC filtering. Retrieval is done only for days where the 75°-93°SZA range is covered by the measurements. Note the following gaps in the time-series: 02-08/07/2020 and 23-27/08/2020 for Harestua (due to too small number (≤5) of measurements in the 75°-93°SZA range) and 16-21/07/2019 and 05-11/09/2019 for Bremen (no measurement available).**

| Algorithm version | Bremen | | Harestua | |
|---|---|---|---|---|
| | AM | PM | AM | PM |
| Current | 69% | 75% | 88% | 80% |
| Consolidated | 67% | 65% | 78% | 80% |

**Table 1: Percentages of retrievals successfully passing the QA/QC filtering for both Bremen and Harestua stations and both current and consolidated versions of the algorithm.**

It can be seen from Figure 1 that at both stations the consolidated $NO_2$ VCD time-series show very similar seasonality and AM/PM separation as the current product. At the Bremen station, the scatter of the data points is significantly smaller for the consolidated than for the current VCDs. In particular, most of the high $NO_2$ column values corresponding to large tropospheric $NO_2$ contamination events remaining after QA/QC filtering in the current product time-series (especially the sunset one) are not present anymore in the consolidated data product. The examination of the retrieval results shows that this feature is due to the use of a more strict criterion for the QA/QC check on RMS in urban conditions (10% instead of 20%; see above) but also to the effects of the different consolidation steps, in particular the application of the extra-DSCD error approach, which significantly improves retrieval results in the case of low to moderate tropospheric $NO_2$ contamination (see [RD-3]). It is also remarkable to see that, even with a more strict QA/QC criterion on RMS, the different consolidation steps make

that a significantly larger number of valid (i.e. without any error or warning) $NO_2$ profiles and corresponding VCDs can be retrieved in the morning during the September-November period in the consolidated product.

In the case of Harestua, consolidated and current data sets are more similar, except the fact there are less valid morning retrievals in the consolidated data (78% instead of 88% for the current data product; see Table 1). This feature is mostly due to remaining profiles with a double-peak pattern which are filtered out by the QA/QC flagging. In the current product, this double-peak pattern is much less present due to the artificial increase of the random uncertainty (DOAS fit error x 3) used for the construction of the measurement noise matrix. Table 1 also indicates that for the consolidated product at both stations, the percentage of retrievals successfully passing the QA/QC filtering is similar for both sunrise and sunset conditions while larger AM/PM differences are obtained for the current product.

Bremen and Harestua consolidated profiles are presented in Figure 2. As can be seen, the $NO_2$ layer is located in the 15-35km altitude range with a maximum concentration around 25km of altitude. The concentration maximum also shows the expected seasonality, with higher values in summer. There are more gaps in the Bremen profile time-series than for the remote site of Harestua. It is due to days with moderate to large tropospheric contamination events that are frequently observed in Bremen and for which retrievals cannot be further improved through the application of the extra-DSCD error approach (and which are therefore filtered out by the QA/QC checks). An example of retrieval for such a day is shown in Figure 3.

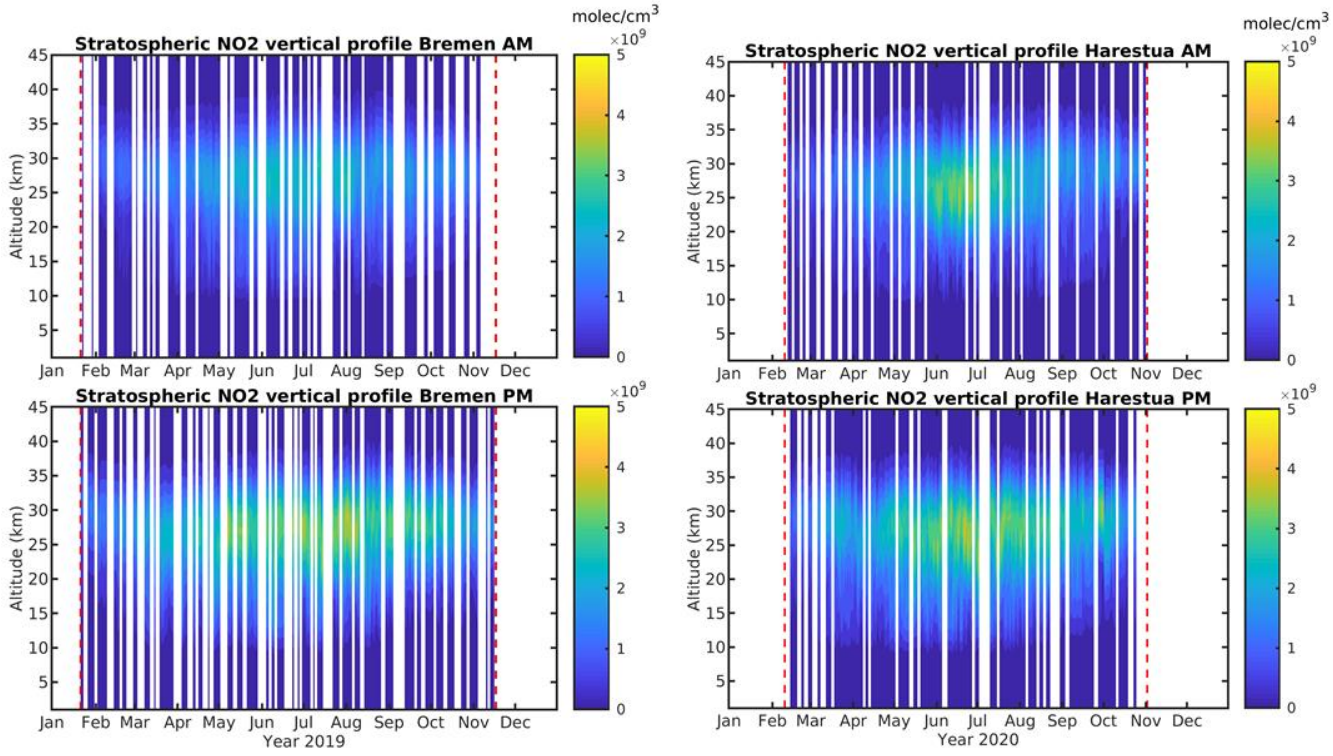


**Figure 2: Time-series of 90°SZA sunrise and sunset (lower and upper plots, respectively) $NO_2$ vertical profiles retrieved at the Bremen (year 2019; left plots) and Harestua (year 2020; right plots) stations using the consolidated profiling algorithm. Only the vertical profiles corresponding to retrievals that successfully pass the QA/QC filtering are shown here. Red dashed lines indicates the period of the year where measurements cover the 75°-93°SZA range. As for Figure 1, note the following gaps in the time-series which are not due to retrieval error or warning: 02-08/07/2020 and 23-27/08/2020 for Harestua (due to too small number (≤5) of measurements in the 75°-93°SZA range) and 16-21/07/2019 and 05-11/09/2019 for Bremen (no measurement available).**

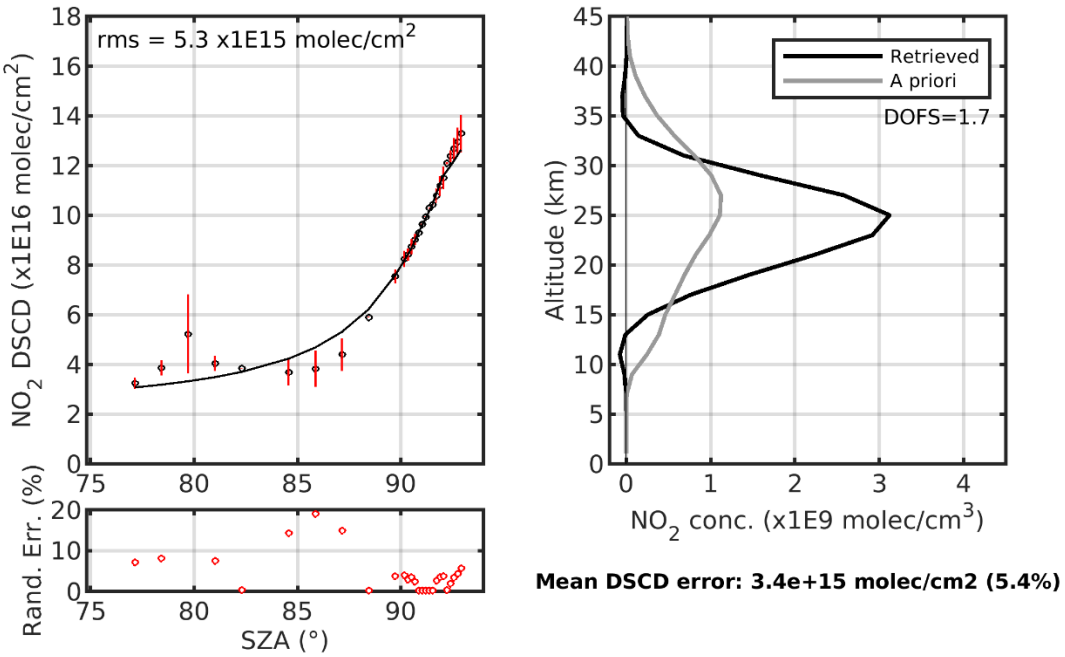


**Figure 3: Example of retrieval at the Bremen station for a day (03/04/2019 sunset) with large tropospheric $NO_2$ contamination during twilight. For this day, despite the application of the extra-DSCD error approach (see red error bars in the left upper plot), the retrieved profile is rejected by the QA/QC filtering (too high RMS and negative concentration values).**

Consolidated retrieval results have been also assessed in terms of information content. Figure 4 shows typical examples of averaging kernels for the consolidated product at both stations. The averaging kernels between 13 km and 35km are reasonably sharply peaked at their nominal altitude. 13–35 km is therefore the altitude range where the measurements give significant information about the vertical distribution of $NO_2$, in accordance with [RD-3]. Mean DOFS values and corresponding standard deviations are of 2.1 ± 0.5 and 2.6 ± 0.4 for the Bremen (year 2019) and Harestua (year 2020) stations, respectively.

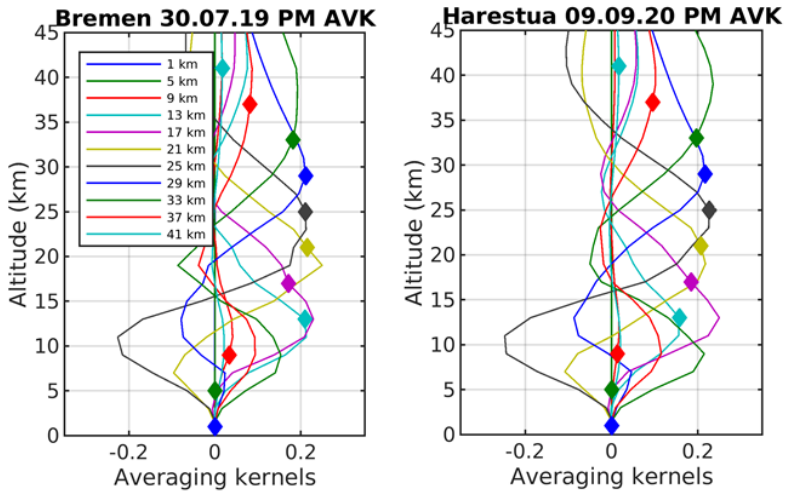


**Figure 4: Typical examples of averaging kernels for the Bremen (left plot) and Harestua (right plot) consolidated retrievals at sunset. Similar averaging kernels are obtained for the morning retrievals. Plain diamonds indicate the altitude at which each averaging kernel should peak in an ideal case.**

# 3 Comparison to TROPOMI satellite data

As already discussed in the FRM$_4$DOAS Phase I deliverable D-21, proper validation of the retrieved stratospheric $NO_2$ columns is made difficult since no other long-term reference measurements are available. Therefore, as in FRM$_4$DOAS Phase I, the retrieved $NO_2$ vertical columns are compared to a satellite-based product, which is in the present case the TROPOMI stratospheric $NO_2$ columns extracted by BIRA-IASB from the S5P $NO_2$ off-line product (versions OFFL 01.03.01 to 01.04.00). As noted in the Introduction, this product is actually a stratospheric column modelled with the TM5 model but with the TROPOMI data over clean regions assimilated for correcting for model biases.

Since the diurnal variation of stratospheric $NO_2$ is large, and (1) ground-based retrievals are representative of twilight conditions, and (2) TROPOMI overpass is around 13:30 local time, a photochemical correction should be applied to either ground-based or satellite data in order to perform comparison in the same $NO_2$ photochemical regime. Here, the NORS $NO_2$ photochemical correction tool based on PSCBOX/SLIMCAT model simulations (see [RD-4]) is applied to the TROPOMI data to transfer the column values to what is expected at the time/SZA of the ground-based twilight columns (90°SZA sunrise and sunset). Since the NORS photochemical correction tool and the ground-based retrievals are based on different PSCBOX/SLIMCAT model runs (standard run and run with $jNO_2$ x 0.9 (see [RD-1]), respectively), a correction is applied to the conversion factor extracted from the NORS tool in order to have consistent $NO_2$ photochemistry in both profile retrieval and NORS tool. Based on model output comparison, this correction is found to be on average 1.02 ± 0.07 and 0.99 ± 0.07 for the Bremen (year 2019) and Harestua (year 2020) stations, respectively.

The ground-based versus satellite $NO_2$ VCD comparison results are shown in Figure 4 and mean bias values and corresponding standard deviations are reported in Table 2 for both consolidated and current products. As can be seen, a good agreement is obtained between the consolidated stratospheric $NO_2$ VCDs and the TROPOMI data, in terms of absolute column values, AM/PM separation, and seasonal variation. As already highlighted in [RD-1], mean bias is smaller at sunrise than at sunset at both stations. At the Bremen site but also to a lesser extent at Harestua, the positive PM bias seems to be larger during the second half of the year (from August on). Although the mean biases are not statistically significant (and also within the uncertainty of the NORS conversion factor which can reach 10-15% in the February-April and October-November periods at both stations), these features, which are observed for both consolidated and current products, suggest a possible remaining misrepresentation of the $NO_2$ photochemistry in the TM5 model and/or in the NORS photochemical correction tool.

Table 2 also shows that, although again not statistically significant, sunrise absolute biases with respect to TROPOMI are a bit larger for the consolidated than for the current product, while at sunset, the opposite feature is obtained. The standard deviations on the mean biases are also found to be systematically smaller for the consolidated than for the current product, further indicating a smaller scatter in the VCDs derived from the consolidated profile retrievals (see also Section 2).

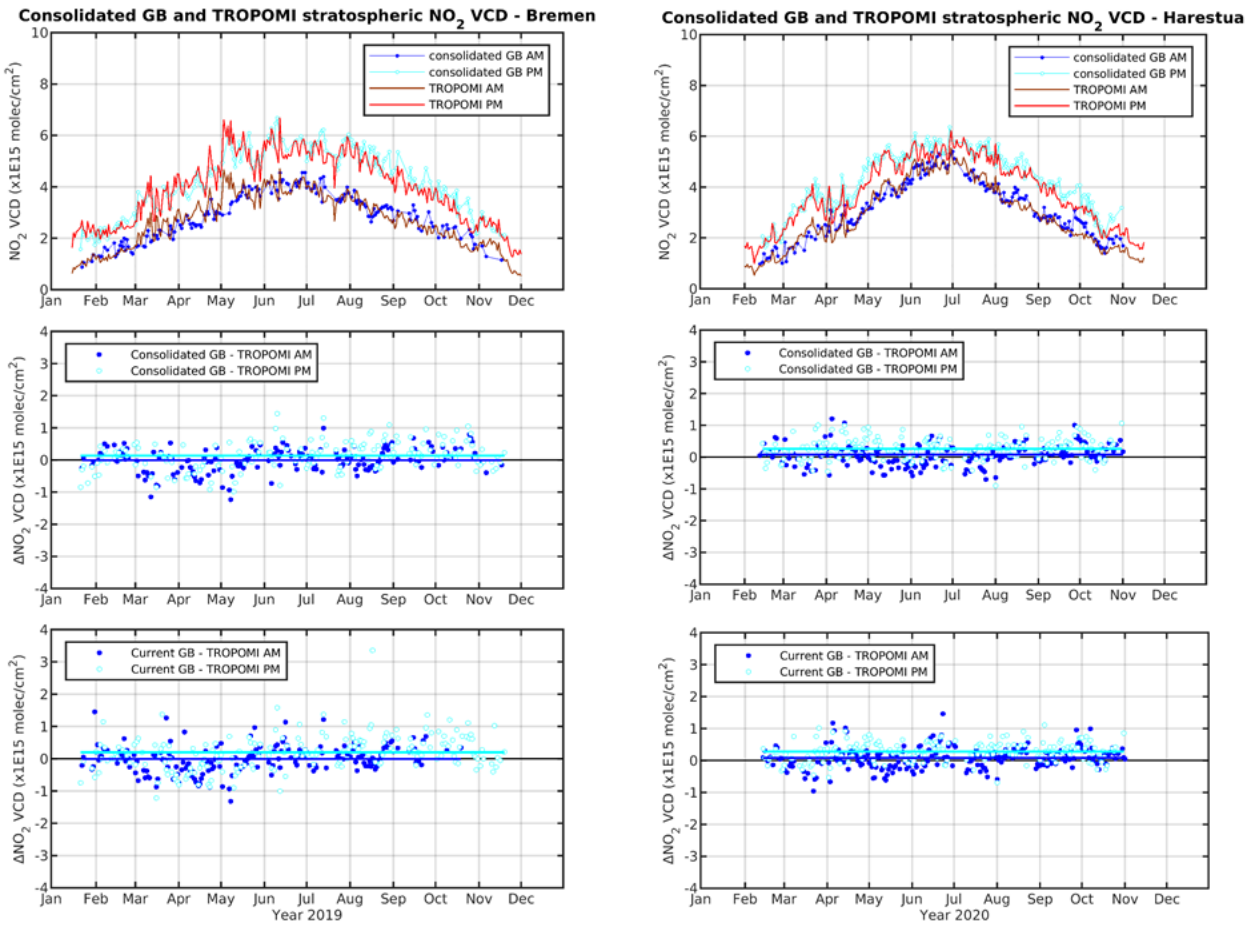


**Figure 4: Comparison between the consolidated AM and PM $NO_2$ stratospheric columns retrieved at the Bremen and Harestua stations and the TROPOMI stratospheric $NO_2$ off-line overpass product extracted at BIRA-IASB. The satellite VCDs are photochemically corrected to match the SZA corresponding to the ground-based retrievals (90° SZA sunrise and sunset). Absolute differences GB – TROPOMI $NO_2$ VCD for the consolidated and current products appear in the middle and lower plots, respectively. In those difference plots, thick solid lines indicate mean bias values.**

| Algorithm version | Bremen | | Harestua | |
|---|---|---|---|---|
| | AM | PM | AM | PM |
| Current | -0.02±4.19 | 1.97±5.83 | 0.33±4.13 | 3.82±5.79 |
| Consolidated | -0.05±3.67 | 1.31±4.41 | 0.81±3.29 | 2.58±3.25 |

**Table 2: Mean GB-TROPOMI absolute biases and corresponding standard deviations (both in x$10^{14}$ molec/cm$^2$ units) for consolidated and current products at the Bremen and Harestua stations.**

# 4 Conclusions

Overall this first validation and verification exercise of the consolidated stratospheric $NO_2$ product shows that both vertical columns and profiles from research-grade high SNR instruments operated in remote and moderate pollution conditions (Harestua and Bremen sites) have now a sufficient level of maturity for future submission on the NDACC and EVDC databases. It is worth noting that this good level of maturity is obtained using, for the construction of the measurement noise matrix, the $NO_2$ DSCD DOAS fit error directly or the extra-DSCD error when it applies, i.e. without any empirical change of the DOAS fit error as in the current product. The quality improvement (in particular the larger number of valid profiles without double-peak pattern) with respect to the

current product is found to be mostly due to the application of the extra-DSCD error approach and a new $NO_2$ photochemistry, as well as more strict QA/QC criterion on retrieval fit RMS in the case of urban site.

In a second version of this report, the verification/validation exercise will be extended to a selection of $FRM_4$DOAS stations where lower SNR commercial instruments are operated. This updated version is expected to be delivered around the PM5 meeting (January 2023).