First validation of the TROPOMI/S5P stratospheric NO_2 measurements using a new harmonized data set from the FTIR ground-based network

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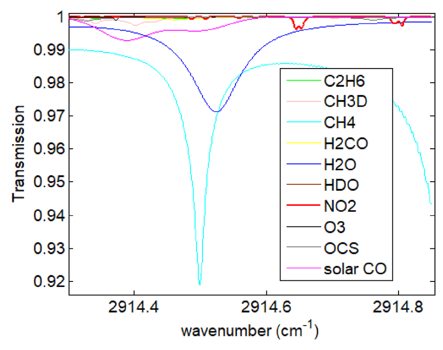
Abstract

- Fourier Transform Infrared (**FTIR**) instruments have the capability to measure NO_2, with a **sensitivity** mainly located **in the stratosphere** However, only a **few** FTIR sites exploited this until now, using **different retrieval settings**.
- We have **optimized the NO_2 retrieval settings and applied them consistently to the whole FTIR network** (mostly from NDACC, Network for the Detection of Atmospheric Composition Change, but also including additional NDACC candidate sites and TCCON sites operated in NDACC mode). We have obtained a **unique harmonized NO_2 data set covering 24 sites**, ensuring consistency of the results if used as reference data for validation.
- This **FTIR stratospheric** NO_2 data set can **complement the zenith-sky DOAS data that have been previously used for TROPOMI validation (Verhoelst et al., 2021)**. Indeed, the zenith-sky DOAS observations are made during sunset and sunrise which imposes the use of a photochemical box model to adjust the observations to the time of the TROPOMI overpasses, **while the FTIR measurements are made during the whole day, allowing direct comparison between measurements that are collocated in time**.
- We will show validation results of more than three years of **S5P stratospheric NO_2 data**, allowing robust statistics on the comparisons. Conclusions about the accuracy and the precision of the S5P stratospheric NO_2 products will be drawn and compared to the ones obtained using zenith-sky DOAS data (Verhoelst et al., 2021).

FTIR harmonized NO_2 data set

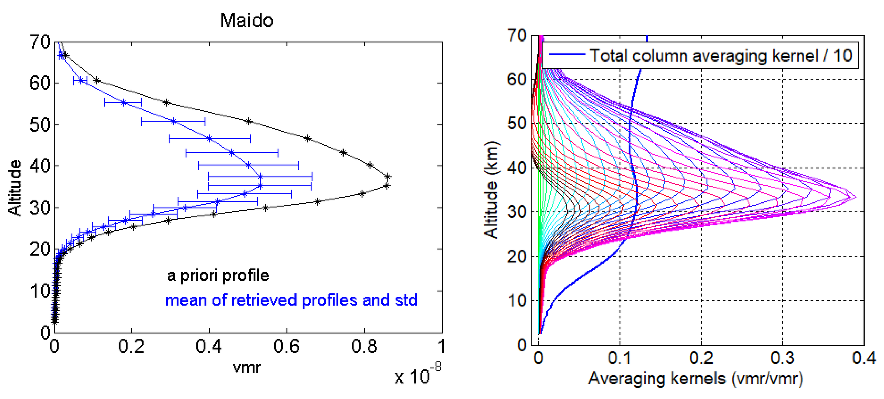
- **Harmonized retrieval settings**:
  - Same **spectral window**:
  - Same regularization: Tikhonov L1.



  - Same **spectroscopic parameters** for NO_2 and interfering gases: atm20 from G. Toon (https://mark4sun.jpl.nasa.gov/toon/linelist/linelist.html). For NO_2, it corresponds to HITRAN 2008.
  - Pressure-temperature profiles from NCEP.
  - A priori profiles are from WACCM climatology.

- **Harmonized instruments**: FTIR **high-resolution solar absorption** measurements (along the line of sight instrument-sun) are performed under **clear-sky** conditions, using primarily the **Bruker 120/5M or Bruker 120/5HR.**
- **Harmonized retrieval codes**: only 2 different codes: SFIT4 (Pougatchev et al., 1995) and PROFITT (Hase, 2000); both based on **Optimal Estimation** (**Rodgers, 2000**):

$$x_{retrieved} = x_{apriori} + A\,[x_{true} - x_{apriori}] + \varepsilon$$

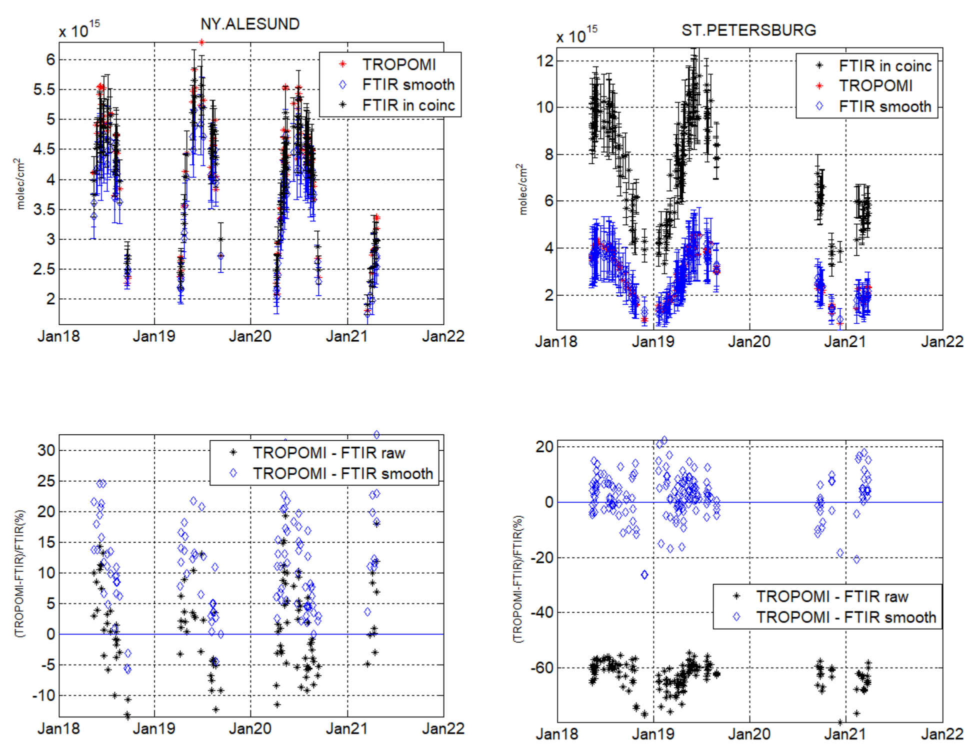


The Degrees of Freedom for Signal (DOFS)= Trace(A) are 1.0-1.4 for the total column; and 1.0-1.3 for the 12-100km column.

- The **sensitivity** is given by the averaging kernel matrix A: **mainly in the stratosphere.** The retrieved total column are sensitive to the stratospheric variability. In the troposphere: mainly the a priori profile is reflected.
- **Harmonized uncertainty budget**: also based on Rodgers (2000):
  - **Random**: median of **3.3E14 molec/cm²** (from 1.3 to 7.7E14 depending mostly on clean vs polluted sites)
  - **Systematic:** median of **10.2%.**

Validation Methodology

- **Collocation:** The collocation is **not** above the FTIR site, we calculate the **position along the line-of-sight** corresponding to the altitude where the NO_2 FTIR averaging kernels shows the maximum of sensitivity (**~30-35km**).
  - Then, **S5P pixels are selected within 50 km of this position (about 150-200 pixels).** Only pixels with a qa_value > 0.5 are used.
  - The time coincidence criterion is set **to ±1 hour of the satellite overpass time.**
- **Compared pairs:** same comparison methodology as for HCHO validation using FTIR data (see Vigouroux et al., 2020 for details):
  - The FTIR a priori profile is substituted with the TROPOMI L2_NO2 one to **take into account the different TROPOMI and FTIR a priori profiles** (Rodgers and Connor, 2003).
  - The corrected profile is **smoothed with the TROPOMI averaging kernel** (Rodgers and Connor, 2003). In this process, since the TROPOMI averaging kernels are zero below the tropopause for the stratospheric NO_2, the tropospheric part of the FTIR profile is removed, and only stratospheric columns from both products are indeed compared.
  - Both individual manipulated FTIR columns and individual S5P manipulated pixel columns are then **averaged**.

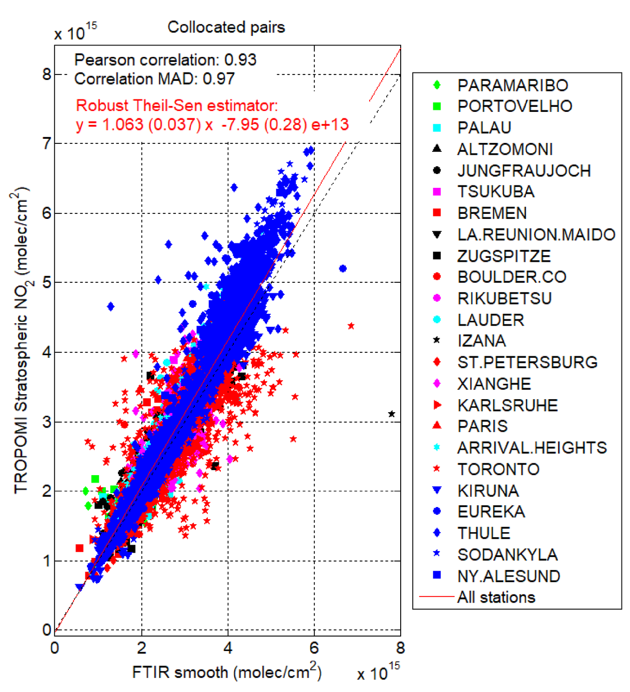


Effect of removing the tropospheric part by the use of TROPOMI stratospheric AK: about 10% at clean site (Ny-Alesund); much larger for polluted sites (e.g. St Petersburg).

- **Metrics for validation :**
  - The **bias** at a single station is estimated by the median relative difference:
    BIAS=Median[(TROPOMI-FTIR)/FTIR].
    To be compared to systematic error budget / S5P requirements.
  - The **dispersion** at a single station is estimated by the scaled median absolute deviation of the differences TROPOMI-FTIR:
    MAD=1.4826*Median[ABS(DIFF-Median(DIFF))].
    The scaling factor of 1.4826 ensures that for a normal distribution, the MAD = 1sigma standard deviation.
    To be compared to random error budget / S5P requirements.

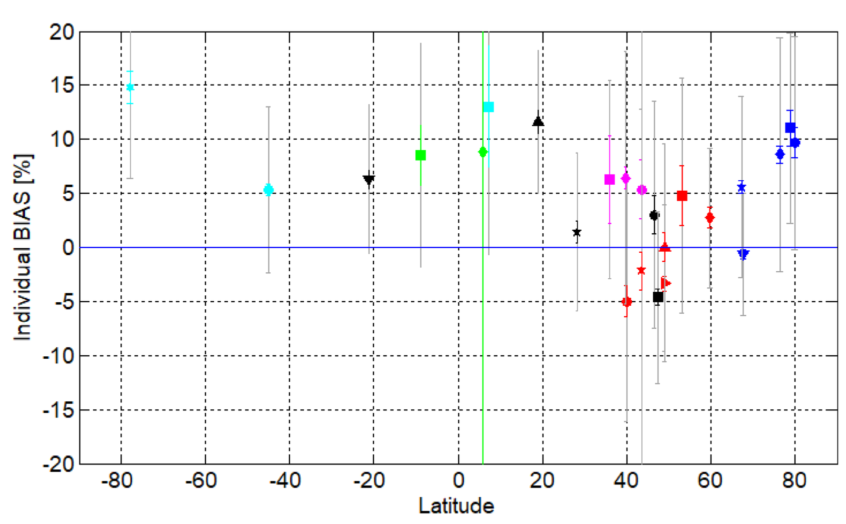
Validation results

I) Statistics for all sites together



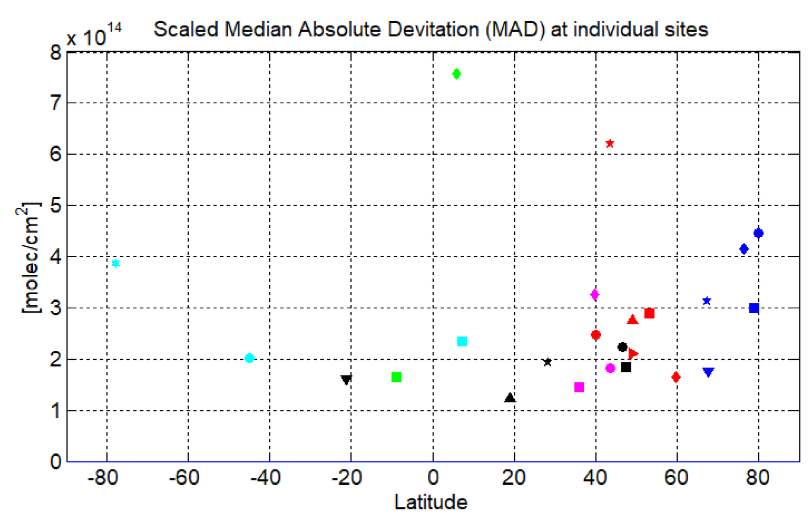
- **BIAS= +3.4% for all collocated pairs together** (7430 coincidences). This is within the **S5P mission requirements of 10% maximum bias**. However this is not always true for individual sites.
- **Correlation is very good= 0.97.**
- **~ zero offset= -0.8x10^{14} molec/cm² (~1%)**
- **MAD=2.9 x10^{14} molec/cm² . This is within the S5P requirements of 5.0 x10^{14} molec/cm²**. And similar to S5P comparison with zenith-sky (Verhoelst et al., 2021)

II) BIAS at individual sites



- The **individual BIAS are within 7%** (so < **S5P mission requirements of 10%) except for high latitude and tropical sites, where they are +8-14%.**
- Median of the individual bias: +5.5%
- **TROPOMI validation with zenith-sky DOAS data gives a negative bias (-6%)**, approx. −2 % in summer to −15 % in winter (Verhoelst et al., 2021).
- A possible reason for the different obtained biases (DOAS higher by about 10%) is that Verhoelst et al. (2021) use **DOAS total columns**, assuming a negligible impact of the tropospheric NO_2.
- **Station-to-station dispersion=5.5%**, very similar to DOAS network dispersion.

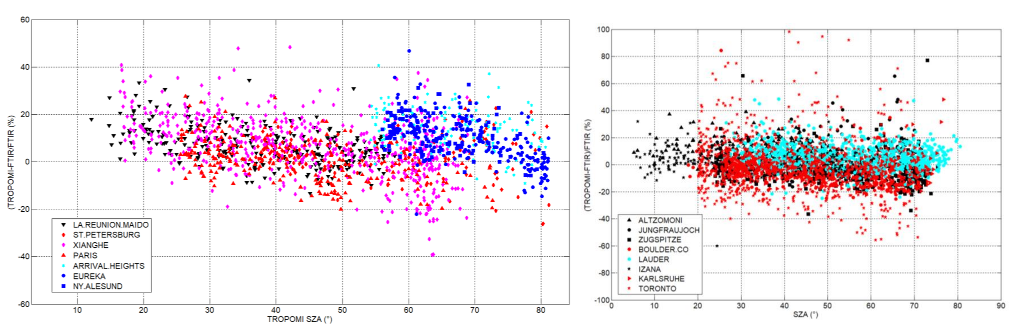
III) MAD at individual sites



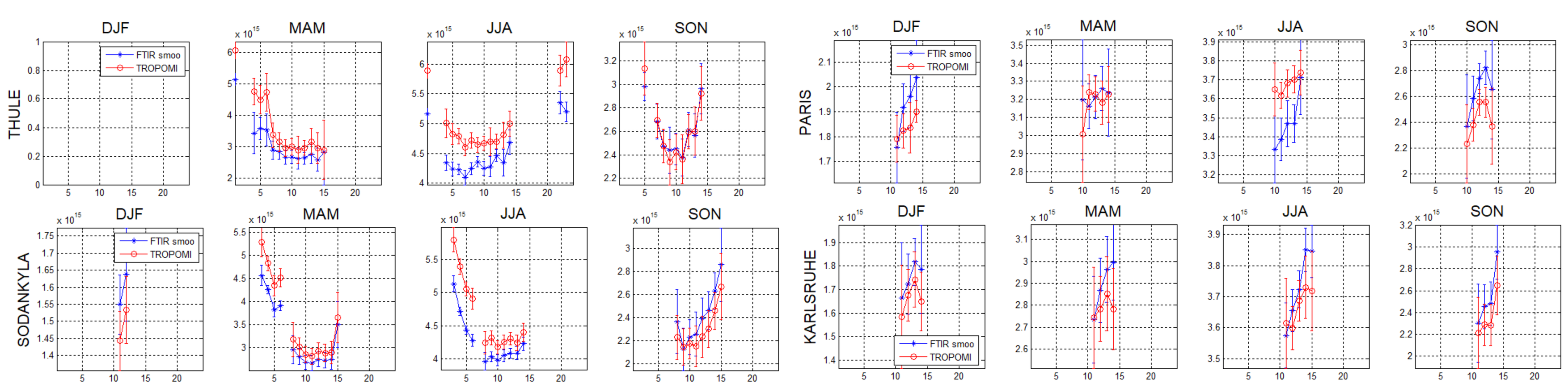
- The **individual MAD are within 3x10^{14} molec/cm²** except for highest latitude sites (=4x10^{14} still < S5P requirements of 5x10^{14} molec/cm²) and for 2 "worse" sites: Toronto (the only site using a different spectrometer Bomem giving larger random FTIR uncertainty 7.5x10^{14}), and Paramaribo (a site with only 7 coincidences).

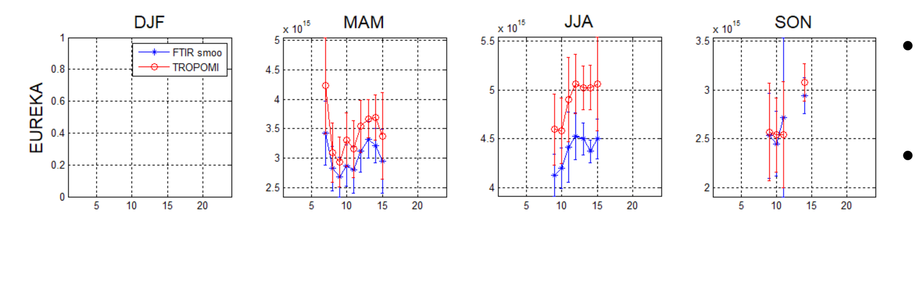
IV) Seasonal cycle in the bias ? SZA dependence ?

- At some sites, the differences do show a seasonal cycle, also seen if we plot the differences versus the S5P solar zenith angle (SZA). Some sites does not show this – or as strong - behavior.
- The reason for this still need to be investigated.



V) Diurnal cycles





- The TROPOMI and FTIR diurnal cycles look in good agreement at all sites.
- They can differ from one site to another similar one (e.g. Thule vs Eureka; Paris vs Karlsruhe): to explore when more years of data will be available.

Summary and outlook

- We showed that **TROPOMI stratospheric NO_2 reaches the requirements of maximum 10% bias** (except at 2 high latitude and 2 tropical sites), and of **5.0 x10^{14} molec/cm² precision** (MAD usually < 3x10^{14} molec/cm²).
- All metrics using FTIR are **as good as when using zenith-sky DOAS network** (Verhoelst et al., 2021), with the additional advantage to provide comparisons of the diurnal cycle.
- While the individual BIAS and MAD show an **overall good network consistency** and the station–to-station dispersion is similar to the zenith-sky network (5.5%), we would like to **understand/improve the extreme values: inherent to TROPOMI or to FTIR ? Same question for the observed SZA dependence.**
- We want to confirm the reason for different bias when using FTIR vs DOAS: **we will perform the same methodology on zenith-sky data.**