



LuftBlick Report 2016001

## **ESA Ground-Based Air-Quality Spectrometer Validation Network and Uncertainties Study**

Report on Feasibility to Retrieve Trace Gases  
other than O<sub>3</sub> and NO<sub>2</sub> with Pandora

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## Document Change Record

| Issue | Date        | Section                        | Observations                                                                           |
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| 0.1   | 11 Dec 2015 | All                            | First draft version                                                                    |
| 0.2   | 28 Jan 2016 | All                            | Added final analysis results and figures                                               |
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## Acronyms and Abbreviations

|                     |                                                              |
|---------------------|--------------------------------------------------------------|
| AcL                 | Accordance level                                             |
| AMF                 | Air mass factor                                              |
| GM                  | Geometric mean                                               |
| MLE                 | Modified Langley extrapolation                               |
| NoC                 | Number of measured cycles                                    |
| Pandonia            | ESA Ground-Based Air-Quality Spectrometer Validation Network |
| RDP                 | Retrieved data product                                       |
| SNI                 | Selected network instrument                                  |
| SpecSL              | Spectral stray light                                         |
| SZA                 | Solar zenith angle                                           |
| TempNO <sub>2</sub> | Effective nitrogen dioxide temperature                       |
| TempO <sub>3</sub>  | Effective ozone temperature                                  |
| TotHCHO             | Total formaldehyde column                                    |
| TotNO <sub>2</sub>  | Total nitrogen dioxide column                                |
| TotO <sub>3</sub>   | Total ozone column                                           |
| TotSO <sub>2</sub>  | Total sulfur dioxide column                                  |
| USS                 | Unwanted spectral signal                                     |

# 1 Introduction

This report is deliverable D14 of the Pandonia project [2, 1] addressing the 'feasability' of retrieving data products from Pandora direct sun measurements other than the operational total ozone column amounts (TotO<sub>3</sub>) and total nitrogen dioxide column amounts (TotNO<sub>2</sub>).

Section 2 is an extended summary of the technique we used and the main results of this study, which are described in sections 3 and 4 with more detail.

## 1.1 Applicable Documents

- [1] Ground-Based Air-Quality Spectrometer Validation Network and Uncertainties Study [Proposal], LuftBlick Proposal 201309A, Issue 2, 2013.
- [2] ESA Ground-Based Air-Quality Spectrometer Validation Network and Uncertainties Study [Statement of Work], ENVI-SPPA-EOPG-SW-13-0003, Issue 1, Revision 3, 2013.

## 1.2 Reference Documents

- [3] A. Cede and M. Tiefengraber. Inter-calibration of ground-based spectrometers and Lidars – Minispectrometer Intercalibration and Satellite Validation, LuftBlick Report 2013002: Recommendations for Inter-Calibration of minispectrometer networks, 2013.
- [4] A. Cede, M. Tiefengraber, and A. Redondas. ESA Ground-Based Air-Quality Spectrometer Validation Network and Uncertainties Study, LuftBlick Report 2014001: Network Intercalibration Procedure, 2014.
- [5] J. Herman, A. Cede, E. Spinei, G. Mount, M. Tzortziou, and N. Abuhassan. NO<sub>2</sub> column amounts from ground-based Pandora and MFDOAS spectrometers using the direct-sun DOAS technique: Intercomparisons and application to OMI validation. *Journal of Geophysical Research (Atmospheres)*, 114:D13307, July 2009. doi: 10.1029/2009JD011848.
- [6] M. Tiefengraber and A. Cede. Inter-calibration of ground-based spectrometers and Lidars – Minispectrometer Intercalibration and Satellite Validation, LuftBlick Report 2013004: Minispectrometer Data Quality Report, 2013.
- [7] Y. Zong, S. W. Brown, B. C. Johnson, K. R. Lykke, and Y. Ohno. Simple spectral stray light correction method for array spectroradiometers. *Applied Optics*, 45(6):1111–1119, 2006.

## 2 Summary

In this study we analyze the precision of retrieved data products (RDP) from Pandora direct sun measurements in order to determine whether it is 'useful' to pursue such measurements with Pandonia. Here we define 'useful' not in the sense of how important it might be for atmospheric science to measure such atmospheric parameters, rather, whether Pandora can retrieve that parameter with sufficient precision compared to other existing remote sensing instrumentation. The RDPs we analyze are listed in Table 1.

Table 1: RDP considered in this study.

| NAME                                          | ABBREVIATION        |
|-----------------------------------------------|---------------------|
| <b>Total ozone column</b>                     | TotO <sub>3</sub>   |
| <b>Effective ozone temperature</b>            | TempO <sub>3</sub>  |
| <b>Total nitrogen dioxide column</b>          | TotNO <sub>2</sub>  |
| <b>Effective nitrogen dioxide temperature</b> | TempNO <sub>2</sub> |
| <b>Total formaldehyde column</b>              | TotHCHO             |
| <b>Total sulfur dioxide column</b>            | TotSO <sub>2</sub>  |

TotO<sub>3</sub> and TotNO<sub>2</sub> are operational data products of Pandonia included here for comparison reasons. The study is based on data from two months in autumn 2015 for two collocated instruments at Innsbruck, Pandoras 106 and 110. This period was characterized by very good weather conditions with mostly clear sky days.

We determined that the precision of an RDP using the standard Pandora spectral fitting algorithm depends mostly on 3 parameters contributing to the total uncertainty (for details see section 3.3):

- Noise: each spectra taken is affected by CCD read noise and photon noise, both purely statistical uncertainties. The Pandora measurement noise is a function of the number of cycles (NoC), i.e. the number of single spectra accumulated and averaged. A Pandora standard direct sun measurement lasts 40 s and consists of 5 to 10000 NoC depending on atmospheric conditions (time of day, cloud cover etc.). Noise values decrease approximately with the square root of NoC (more details can be found in [?], section 6.2). It is desirable to measure as many NoC's necessary that the overall precision of the RDP is not dominated by noise, i.e. 'noise limited'.
- Unwanted spectral signal (USS): is caused by interference effects in the optical system (see section 3.4), which we recently reduced significantly by applying hardware changes to the Pandora system. It is a temporary systematic effect, which 'comes and goes' at non-predictable times and can last from a few minutes to a few hours. The USS uncertainty can be reduced by averaging the data over extended time periods (e.g. one hour). Quantifying the USS uncertainty is a key part of this study.
- Spectral stray light (SpecSL): is also caused by limitations of the optical system. The effect on the RDP depends on the quality of the monochromator and on the incoming spectra. The higher the dynamic range of the spectra, the more the wavelengths with smaller signal are affected by SpecSL. Thus, the SpecSL for direct sun observations is at first order a function of the solar zenith angle (SZA) or more precisely the air mass factor (AMF). This effect could be reduced by a sophisticated spectral stray light correction method, which is not implemented for Pandora yet. Therefore, in this study SpecSL is estimated in a relative way. That is instrument 1, Pandora 106, in comparison to instrument 2, Pandora 110. The quantified values may be different for other Pandoras.

Note that for this study we have analyzed the precision rather than the accuracy of the RDPs. For the accuracy, more uncertainty sources such as the uncertainty of the algorithm or the uncertainty of the cross sections used for each absorber have to be included. We claim that a RDP from Pandora is feasible, if the precision is good enough, i.e. the difference in the measured RDP from two or more Pandoras is sufficiently small. Once the precision is good, one can try to improve the accuracy.

There are still more trace gases, which can be measured by Pandora. Some are not included in this study, as they are measured with Pandora-2S (in the visible range, e.g. water vapor), for which there is no overlapping data base with more than one unit at this time. Others, e.g. bromide oxide, are not included as they are weaker absorbers than those listed in Table 1 and we wanted to approach these first.

The results of this study are summarized in the following sub-sections and all uncertainties are given in the  $1\sigma$  level.

## 2.1 TotO<sub>3</sub> and TempO<sub>3</sub>

The final numbers of the Pandora precision for TotO<sub>3</sub>, TotO<sub>3</sub>', and TempO<sub>3</sub> are listed in Table 2. 'TotO<sub>3</sub>' stands for the retrieval of total ozone with fixed temperature values. While 'TotO<sub>3</sub>' refers to the case the effective temperature is retrieved simultaneously, which reduces the precision of the retrieved column amount. Thereby decreasing the stability of the spectral fitting algorithm, while improving accuracy. The NoC needed for the noise to have the same magnitude as the USS uncertainty for single measurements is 1988 for TotO<sub>3</sub>. This is reached with 20 ms or less exposure time. The exposure times for Pandora are below 40 ms for basically all conditions at SZA<80°, except for overcast situations, which cannot be used for direct sun measurements anyway. For 40 ms, NoC is 1000 giving a noise of about 0.7DU, in which case the ozone measurements are dominated by the noise, which suggest that we eventually should increase the total duration of the measurements. Note, that for ozone the noise does not exactly scale with the square root of NoC (see figure 8), as the ozone wavelengths are not the maximum signal in the data.

The SpecSL uncertainty drives the precision at large SZAs. Therefore, the implementation of a sophisticated SpecSL correction method, following the example of *Zong et al.* [7], is the next step to improve the precision of retrieved ozone parameters. To our knowledge, no other remote sensing instrumentation using grating technology gives TempO<sub>3</sub> as a standard product. Therefore, we consider retrieved TempO<sub>3</sub> to be a useful addition for Pandonia.

Table 2: Precision for TotO<sub>3</sub> and TempO<sub>3</sub>

| PARAMETER                                             | TotO <sub>3</sub> | TotO <sub>3</sub> ' | TempO <sub>3</sub> |
|-------------------------------------------------------|-------------------|---------------------|--------------------|
| USS uncertainty (single measurement)                  | 0.35 DU           | 0.86 DU             | 0.62 K             |
| USS uncertainty (hourly mean)                         | 0 DU              | 0.39 DU             | 0.56 K             |
| Time for USS uncertainty to be below 0.1 DU/0.5 K     | 35 min            | 2 h                 | 1 h 30 min         |
| SpecSI uncertainty for SZA<70°                        | 0.49 DU           | 1.12 DU             | 2.19 K             |
| SpecSI uncertainty at SZA=79° (AMF=5)                 | 2.21 DU           | 4.57 DU             | 4.95 K             |
| NoC needed for noise to equal USS uncertainty         | 1988              | 1284                | 478                |
| Noise at 4000 NoC                                     | 0.14 DU           | 0.22 DU             | 0.10 K             |
| Precision single measurement with NoC=4000 at SZA<70° | 0.62 DU           | 1.43 DU             | 2.27 K             |
| Precision single measurement with NoC=4000 at SZA=79° | 2.24 DU           | 4.66 DU             | 4.99 K             |
| Precision hourly mean with NoC=4000 at SZA<70°        | 0.51 DU           | 1.21 DU             | 2.26 K             |
| Precision hourly mean with NoC=4000 at SZA=79°        | 2.21 DU           | 4.59 DU             | 4.98 K             |

## 2.2 TotNO<sub>2</sub> and TempNO<sub>2</sub>

The final numbers of Pandora precision for TotNO<sub>2</sub>, TotNO<sub>2</sub>' and TempNO<sub>2</sub> are listed in Table 3. Again, 'TotNO<sub>2</sub>' stands for simultaneous temperature retrieval. USS and SpecSI have minimal effects on TotNO<sub>2</sub>. Hence, the measurements need a very large NoC in order to not be noise-limited. However, as atmospheric variation is often larger than Pandora precision NO<sub>2</sub> over short time scales (<1 min), we consider it more useful to measure the current 40 s, or less. The precision of the Pandonia TotNO<sub>2</sub> product at NoC>1000 is more than sufficient for any application (satellite validation, air quality monitoring). Currently, precision of TempNO<sub>2</sub> is not very good and at this stage we do not believe that adding TempNO<sub>2</sub> to standard Pandonia data products would be very useful.

Table 3: Precision for TotNO<sub>2</sub> and TempNO<sub>2</sub>

| PARAMETER                                             | TotNO <sub>2</sub> | TotNO <sub>2</sub> ' | TempNO <sub>2</sub> |
|-------------------------------------------------------|--------------------|----------------------|---------------------|
| USS uncertainty (single measurement)                  | 0.001 DU           | 0.009 DU             | 9.46 K              |
| USS uncertainty (hourly mean)                         | 0 DU               | 0 DU                 | 7.10 K              |
| Time for USS uncertainty to be below 0.01 DU/1 K      | -                  | -                    | 4 h                 |
| SpecSI uncertainty for SZA<79° (AMF<5)                | 0.001 DU           | 0.002 DU             | 1.44 K              |
| NoC needed for noise to equal USS uncertainty         | 3985               | 2009                 | 1533                |
| Noise at 4000 NoC                                     | 0.002 DU           | 0.005 DU             | 0.55 K              |
| Precision single measurement with NoC=4000 at SZA<79° | 0.002 DU           | 0.011 DU             | 10.13 K             |
| Precision hourly mean with NoC=4000 at SZA<79°        | 0.002 DU           | 0.005 DU             | 7.27 K              |

## 2.3 TotHCHO and TotSO<sub>2</sub>

The final numbers of the Pandora precision for TotHCHO and TotSO<sub>2</sub> are listed in Table 4.

Precision of TotHCHO is driven by USS uncertainty, meaning that there is no need to increase the currently used measurement duration of 40 s. Additional hardware changes needed to reduce USS effect are currently under consideration, however, we do not expect the reduction of USS-error by a factor of 10 as achieved by the previous hardware change.

The precision of TotSO<sub>2</sub> is driven by USS and SpecSI uncertainty. As for HCHO, it will not be easy to reduce the USS effect, but the improved stray light correction should mitigate the SpecSI effect.

The results of this study definitely suggest that adding both, TotHCHO and TotSO<sub>2</sub>, to the Pandora standard data products would be very useful considering their importance for satellite validation and air quality. Especially as there is a current lack of existing instrumentation capable of measuring these gases.

Table 4: Precision for TotHCHO and TotSO<sub>2</sub>

| PARAMETER                                             | TotHCHO    | TotSO <sub>2</sub> |
|-------------------------------------------------------|------------|--------------------|
| USS uncertainty (single measurement)                  | 0.024 DU   | 0.057 DU           |
| USS uncertainty (hourly mean)                         | 0.018 DU   | 0.044 DU           |
| Time for USS uncertainty to be below 0.01 DU          | 4 h 30 min | 5 h                |
| SpecSI uncertainty for SZA<70°                        | 0.008 DU   | 0.049 DU           |
| SpecSI uncertainty at SZA=79° (AMF=5)                 | 0.006 DU   | 0.111 DU           |
| NoC needed for noise to equal USS uncertainty         | 2026       | 3157               |
| Noise at 4000 NoC                                     | 0.016 DU   | 0.041 DU           |
| Precision single measurement with NoC=4000 at SZA<70° | 0.029 DU   | 0.086 DU           |
| Precision single measurement with NoC=4000 at SZA=79° | 0.029 DU   | 0.131 DU           |
| Precision hourly mean with NoC=4000 at SZA<70°        | 0.025 DU   | 0.078 DU           |
| Precision hourly mean with NoC=4000 at SZA=79°        | 0.025 DU   | 0.126 DU           |

## 2.4 Conclusion

Based on this study we come to the following conclusions:

- TempO<sub>3</sub>, TotHCHO, and TotSO<sub>2</sub> will be useful additions to standard Pandora data products.
- As the current precision of TempNO<sub>2</sub> is rather poor, we do not consider it a useful addition to standard Pandora data products.
- The standard measurement duration of 40 s for direct sun measurements is sufficient in avoiding noise limitation for RDP's in most situations. We do not suggest to increase it, as the natural variability of some species, e.g. NO<sub>2</sub>, is greater than current Pandora measurement precision.
- In order to improve the short UV data products TotO<sub>3</sub>, TempO<sub>3</sub>, TotSO<sub>2</sub> a better stray light correction is needed.

## 3 Materials and methods

### 3.1 Data basis

This study is based on field measurements of two collocated selected network instruments (SNIs) in Innsbruck, Austria. Throughout a period of approximately two months in autumn 2015 [solar zenith angles (SZA)  $> 61^\circ$ ], Pandora 106 (from now on SNI1) and Pandora 110 (from now on SNI2) were measuring on a direct sun schedule with a two minutes temporal resolution (alternating measurements with open hole and bandpass filter). Each measurement is set to take 40 seconds. With exposure times from 3 ms to 4 seconds, a number of 4000 measured cycles (NoC) are common under favorable atmospheric conditions. Up to now, this is the standard schedule for operational RDPs in Pandonia.

Note that all data from SNI2 used in this study are interpolated in time towards SNI1.

Figure 1: The measurement site of Innsbruck. Data from the two Pandora instruments (on the left hand side) are the basis for the feasibility study. The view is towards East, where the city center is located.



### 3.2 Retrieval technique

To retrieve the RDPs listed in table 1, the spectral fitting algorithm explained in detail in [?], is applied. The reference spectra used by the spectral fitting algorithm are calculated for each SNI as the mean value of approximately 50 measurements recorded around noon on one excellent clear sky day (for both SNIs the same day and period is chosen).

The evaluation of all RDPs except of TempGAS could in principle be done using relative values. However, since TempGAS non-linearly depends on GAS slant column and its TempGAS included in the reference, a comparison can only be carried out using reference spectra which are free of absorption for GAS<sup>1</sup> (we denote this as synthetic reference spectrum). For each GAS, one SNI is declared to be the reference instrument where to other SNI is calibrated against (more details follow in the respective paragraphs in section 4). The first two weeks of the evaluation period, which are characterized by predominately clear sky conditions, are used in this field calibration.

<sup>1</sup>This is also the reason why the reference spectrum is composed of only a relatively small number of single spectra of one day over a short period. Over a short period the effective GAS temperature is not expected to change a lot.

### 3.3 Parameters affecting the precision

Referring to *Cede and Tiefengraber* [3] there are a number of parameters which embrace data precision in terms of a spectrometer network. Quickly summarized they are

- **Instrumental noise:** purely statistical measurement-to-measurement variation.
- **Temporary systematic effects:** systematic effects, which are not always present, i.e. they 'come and go'. They are often triggered by external events and are very hard to characterize.
- **Permanent systematic effects:** systematic effects, which are always present during certain conditions, e.g. at high SZA.
- **Calibration transfer:** depending on the atmospheric conditions, transferring the calibration from one instrument to another increases the calibration uncertainty.
- **Transport:** deviations introduced by installation and removal of the SNI, as well as due to transportation.
- **Drift:** deviations by e.g. optical filter degradation and changes in the spectral response of the SNI.

For the overall precision of a network, all parameters given in the list should be considered. However, for this study we can neglect several of the uncertainty parameters:

- ad **Drift:** the evaluation period of two months is way to short be be affected by drift (see also *Cede and Tiefengraber* [3], section 2.3).  
⇒ Parameter is negligible.
- ad **Transport:** the SNIs are stationary.  
⇒ Parameter is negligible.
- ad **Calibration transfer:** the field calibration period is based on roughly two weeks of clear sky days.  
⇒ Parameter is negligible.
- ad **Permanent systematic effects:** SNI data correction is based on profound, standardized laboratory calibration and analysis (see *Cede et al.* [4]). Not characterized are spectral stray light (SpecSL) and absolute radiometric response. The latter is assumed to be stable throughout the evaluation period and hence captured by using the synthetic reference spectrum. The first is a function of SZA and mitigated by restricting the evaluation period to  $SZA < 80^\circ$ .  
⇒ SpecSL to be considered.
- ad **Temporary systematic effects:** SNIs are affected by a so-called "unwanted spectral signal" (USS), a spectral feature stemming from interference effects initiated by the entrance window with quasi parallel beams (see section 3.4.2).  
⇒ USS to be considered.
- ad **Instrumental noise:** inherent in each measurement. The characterization of it is often affected by atmospheric noise.  
⇒ Parameter to be considered.

The feasibility evaluation of RDPs is finally based on the data precision parameters *noise* uncertainty, *USS* uncertainty and *SpecSL* uncertainty. We define a RDP to be feasible, if these precision parameters are reasonable.

### 3.4 How we address the data precision parameters

To be able to distinguish between (instrumental) noise, USS and SpecSL, we claim that each uncertainty parameter shows independent functional dependencies. Furthermore we state that each SNI is prone to USS and SpecSL differently. On the other hand, due to there identical construction and standardized calibration, noise is assumed to be comparable for each SNI.

Noise, defined as the variation from measurement to measurement, is solely dependent on the NoC used for each data point. Noise is a matter of a few minutes and can be eliminated by sufficient averaging. We estimate noise using one SNI only.

USS is caused by interference of the direct beam in the optical system (see figure 2). For the RDP it is seen in the data as a smooth variation with time scales of several hours. Before the latest hardware changes, the USS decreased the precision of TotO<sub>3</sub> and TotNO<sub>2</sub> by 5 DU and 0.07 DU respectively [3]. Since USS is assumed to be evenly distributed over the day, there is no SZA (air mass factor, AMF) dependency and hence only a temporal dependency left. Data averaging over a couple of hours reduces the USS uncertainty. To estimate USS uncertainty we need two SNIs.

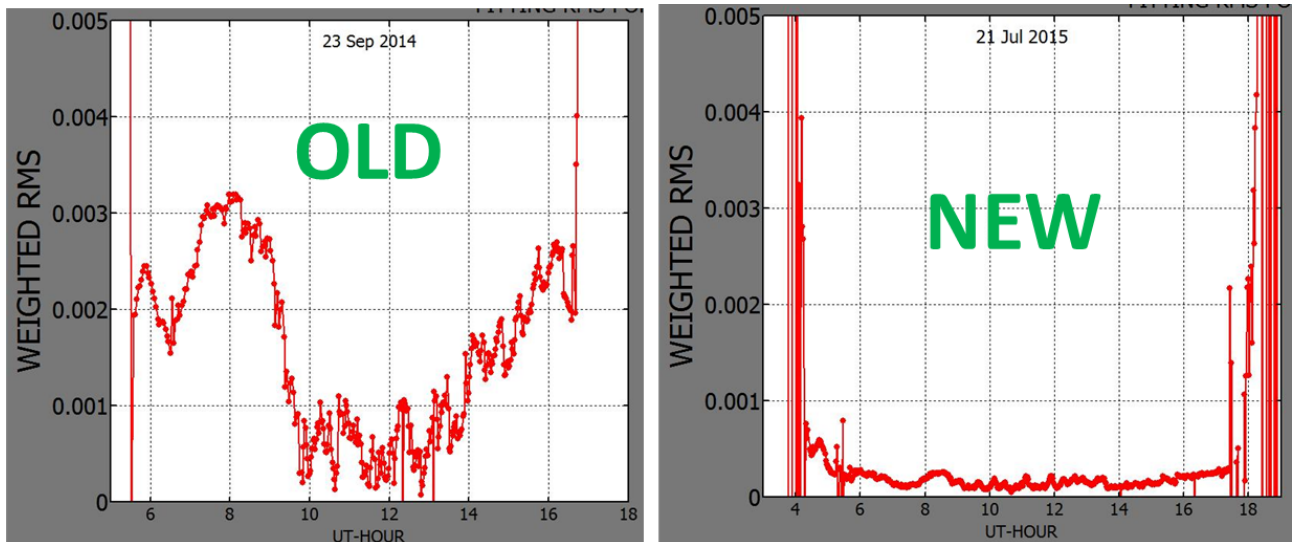


Figure 2: RMS of spectral fitting for TotNO<sub>2</sub> for SNI1 before the hardware change (left) and after the hardware change (right).

SpecSL is at first order a function of SZA (AMF). Unfortunately we do not yet have a sophisticated spectral stray light correction method available for reasons outlined in *Tiefengraber and Cede* [6]. Therefore we can only estimate SpecSL in a relative way by comparing SNI1 and SNI2.

### 3.4.1 SpecSL

The SNI data processing software applies a simple SpecSL correction by subtracting the mean irradiance below 290 nm. Hence, the far field SpecSL (a change of the baseline) is corrected, the near field SpecSL (having a similar effect as a broadened slit function) not. Since we do not have a SpecSL free measurement for comparison, we can just make a relative statement about SpecSL uncertainty. Provided both SNIs are differently prone to SpecSL, comparing  $\Delta\text{RDP}(\text{AMF})$  as a function of AMF reveals whether a RDP is sensitive to SpecSL affected SNIs.

As an estimate of the SpecSL uncertainty (at least for this study), we simply apply a linear fit to  $\Delta\text{RDP}(\text{AMF})$  as a function of AMF. The  $\Delta\text{RDP}$  at the most frequent AMF (in this study found to be 3.3) is then assumed to be tantamount to the SpecSL uncertainty.

Note that this approach attributes all deviations in  $\Delta\text{RDP}(\text{AMF})$  to SpecSL, since we claim that SpecSL is by far the most dominant SZA (AMF) dependent error source. Further note that effects which are also a function of SZA (AMF) but equal for both SNIs are considered to be an accuracy rather than precision issue (e.g. algorithm deficiencies which affect all SNIs the same way). Therefore it is possible that the true effect of SpecSL is still somewhat larger than what this relative analysis shows, but we will not know until we can compare to a system that is not affected by SpecSL.

### 3.4.2 USS

In order to distinguish if a point-to-point variation for a RDP is connected to atmospheric changes rather than instrumental features, we check if the gradient in time for both SNIs (DD) agree in direction (DD+), or not (DD-). If not, the corresponding data point is assumed to be affected by USS.

The data set which is used to address USS is cleared for SpecSL as explained in the previous section. This is necessary to avoid interpreting large scale discordance in the data as USS.

To be able to quantify USS uncertainty, RDP for both SNIs, recognized to be of category DD-, are two times averaged in time: the first averaging time,  $t_N$ , is selected to ensure the RDP to be clearly out of noise (this is usually about averaging 1 to 3 measurements for e.g. NO<sub>2</sub> or 5 to 10 averages for e.g. HCHO). The second averaging time,  $t_U$ , claims to be “out of” USS already. The USS uncertainty is then simply the standard deviation of  $RDP_{t_N} - RDP_{t_U}$  of all recognized category DD- values.

For this, data for both SNIs are merged for calculating the standard deviation. This is meaningful, since if DD- is recognized, either SNI1 or SNI2 could be the reason for the discordance. By considering both SNIs together this effect should be compensated to a good extent.

This second averaging time  $t_U$  allows to be more or less stringent by the consideration what is still accounted to USS. This is why we want to introduce what we call an *accordance level* (AcL). AcL is simply the relative frequency of DD+ categories (relative to the number of data points in total). Let's assume an AcL at 80 % (AcL<sub>80</sub> %). AcL is calculated for a number of averaging times. Those averaging time which delivers AcL = 80 % is said to be  $t_U$  (simply speaking, at  $t_U$  are 80 % of the data points of SNI1 and SNI2 in accordance with respect to their gradients). The USS<sub>80%</sub> uncertainty then equals to  $\text{std}(RDP_{t_N} - RDP_{t_U})$ . This also means, if  $t_N$  is chosen to be equal to  $t_N$ , we are “out of” USS at AcL<sub>80</sub> %.

For this study we always show a range of AcLs for comparability. Figure 3 shows several AcLs as a function of the number binned measurements for a certain averaging time. Since the number of measurement bins and averaging time is interchangeable, Figure 4 shows their relationship.

Figure 3: AcLs for all RDP as a function of measurement bins. Shown are AcL at 75, 97, 82, 85, 89 %.

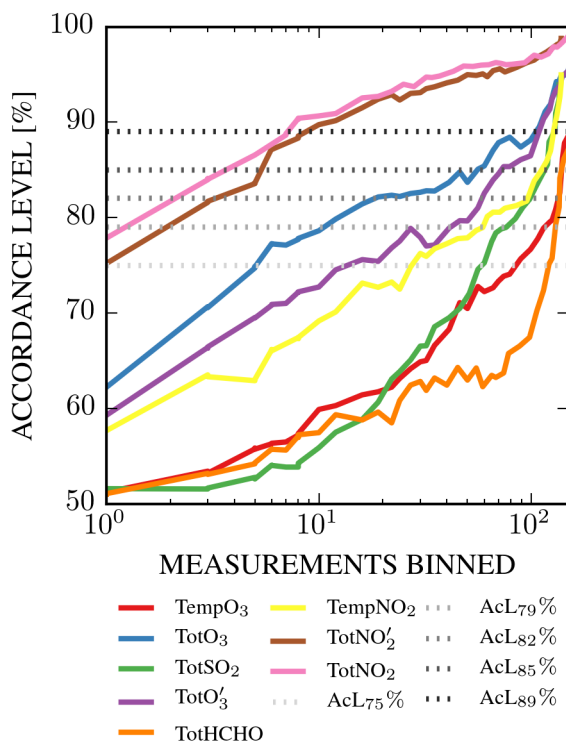
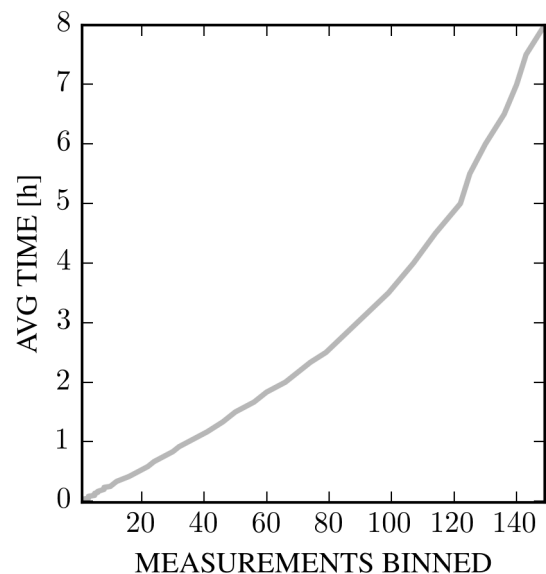


Figure 4: Relationship between averaging time and the number of binned measurements. Each measurement is set to take 40 seconds.



### 3.4.3 Noise

The SNI processing software delivers an uncertainty value which includes the uncertainties added by the algorithms (e.g. data correction, spectral fitting) and the standard error of the mean of the data point. This kind of combined uncertainty also includes atmospheric noise. To be able to extract what we defined to be instrumental noise, we need to exclude data affected by atmospheric noise. We assume that a sufficiently long data set contains subsets which are free of atmospheric noise.

For this purpose we translate the combined uncertainty to slant columns<sup>2</sup> and subdivide the data in groups

<sup>2</sup>Uncertainties as vertical columns would give lower actual values at higher SZA, since the slant column value is divided by the

of NoC. For each NoC group the most frequent uncertainty value is regarded to be tantamount to the noise for that NoC range. We can do this, since the evaluation period was dominated by clear sky conditions.

The noise value at the group containing the highest NoC values is further regarded as the minimum noise.

### 3.4.4 Precision

The combination of SpecSL, USS and noise ( $\sqrt{\text{SpecSL}^2 + \text{USS}^2 + \text{noise}^2}$ ) is finally our quantification of the precision of a RDP. However, each method used to estimate a precision parameter comes with a certain amount of error. E.g. to estimate SpecSL with a linear fit is a strong approximation and might be not representative for e.g. TotO<sub>3</sub>. Also, USS uncertainty might be underrated in cases where SNI1 and SNI2 are affected equally by chance. Furthermore, since SNI2 is interpolated in time to SNI1, errors may be introduced for e.g. TotNO<sub>2</sub> due to its strong temporal variability. All this could be condensed to *residual* uncertainty.

In order to have an estimation about this residual uncertainty we compare the quantified precision to a generic uncertainty estimate based on the direct comparison of the data of SNI1 and SNI2. This generic uncertainty is calculated applying a log normal [ $\mathcal{LN}(\mu, \sigma^2)$ ] fit to the distribution of the absolute difference of the 1 $\sigma$  RDP value retrieved from SNI1 and SNI2. The geometric mean (GM) of this fit is said to be equivalent to the generic uncertainty ( $\text{GM}[X]$ ,  $X := |\text{RDP}_{1\sigma, \text{SNI1}} - \text{RDP}_{1\sigma, \text{SNI2}}|$ , whereas  $X$  is  $\mathcal{LN}(\mu, \sigma^2)$  distributed.)

## 4 Results

This section shows the results for all RDPs mentioned in Table 1. The structure is the same for each RDP and is as follows: First the data filtering criteria and the parameters for the spectral fitting are shown. The following paragraph visualizes the three data precision parameters SpecSL, USS and noise. In addition a scatter plot of SNI1 vs. SNI2 is shown with basic statistical information. The final paragraph lists all feasibility criteria and also depicts example diurnal variations of the RDP from SNI1 and SNI2.

TotO<sub>3</sub> and TotNO<sub>2</sub> are further compared to the case when TempO<sub>3</sub> and TempNO<sub>2</sub>, respectively, are fitted in addition to the column amounts.

### 4.1 Total ozone: TotO<sub>3</sub>

#### Retrieval parameters

Table 5: Data filtering for TotO<sub>3</sub> retrievals.

| <b>FILTER CRITERIA</b> | <b>SNI1[%], SNI2[%]</b> |
|------------------------|-------------------------|
| <b>AMF</b> < 5.0       | 76.2, 73.7              |
| <b>UNC</b> < 1.00 DU   | 60.4, 51.8              |
| <b>RMS</b> < 0.01      | 58.9, 53.3              |
| <b>ΔWVL</b> < 0.01 nm  | 75.2, 67.3              |
|                        | Σ54.6, Σ35.7*           |

\* also filtered for pointing inaccuracies

Table 6: Spectral fitting setup used for TotO<sub>3</sub>.

| <b>FITTING CRITERIA</b>                | <b>VALUE</b>                                                |
|----------------------------------------|-------------------------------------------------------------|
| <b>Reference spectrum</b>              | synthetic                                                   |
| <b>Start WVL [nm]</b>                  | 310.0                                                       |
| <b>End WVL [nm]</b>                    | 330.0                                                       |
| <b>Background polynomial order</b>     | 1                                                           |
| <b>Offset polynomial order</b>         | 0                                                           |
| <b>WVL adjustment polynomial order</b> | 1                                                           |
| <b>Fitted parameters</b>               | HCHO, NO <sub>2</sub> ,<br>O <sub>3</sub> , SO <sub>2</sub> |

Table 5 shows the filter criteria applied to the data and Table 6 lists the spectral fitting setup.

The TotO<sub>3</sub> retrievals are based on a synthetic reference spectrum (for brief explanation see section 3.2). As absolute reference, the TotO<sub>3</sub> retrievals (based on a theoretical=extraterrestrial reference spectrum) from SNI2 are applied. . TotO<sub>3</sub> of SNI1 is than calibrated against TotO<sub>3</sub> of SNI2. To base the TotO<sub>3</sub> retrieval on a (absolute) synthetic reference is mandatory for fitting also TempO<sub>3</sub> (as mentioned in section 3.2).

## Uncertainty parameters

Figure 5

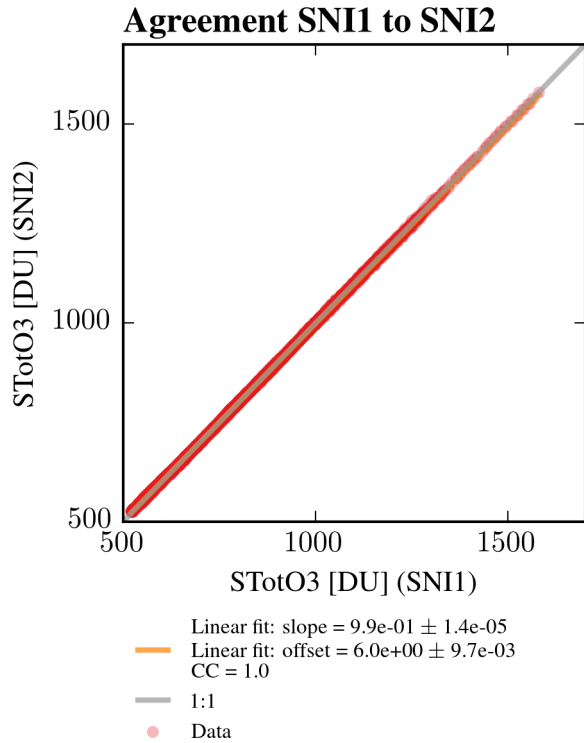


Figure 6

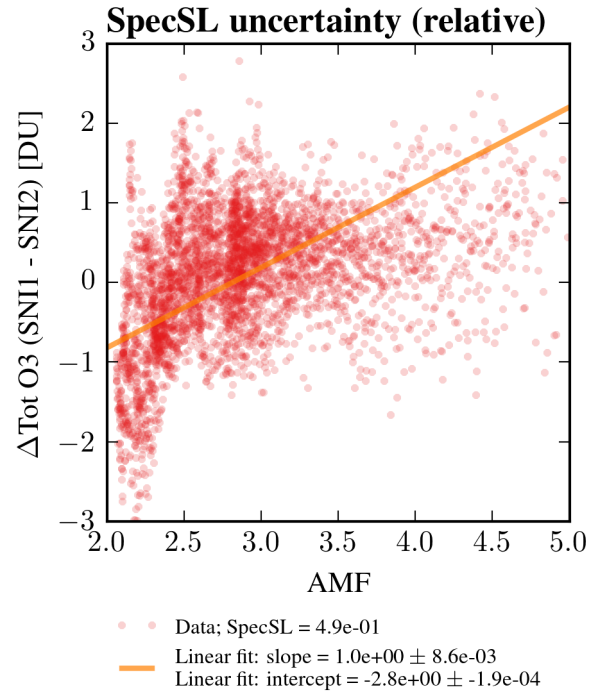


Figure 7

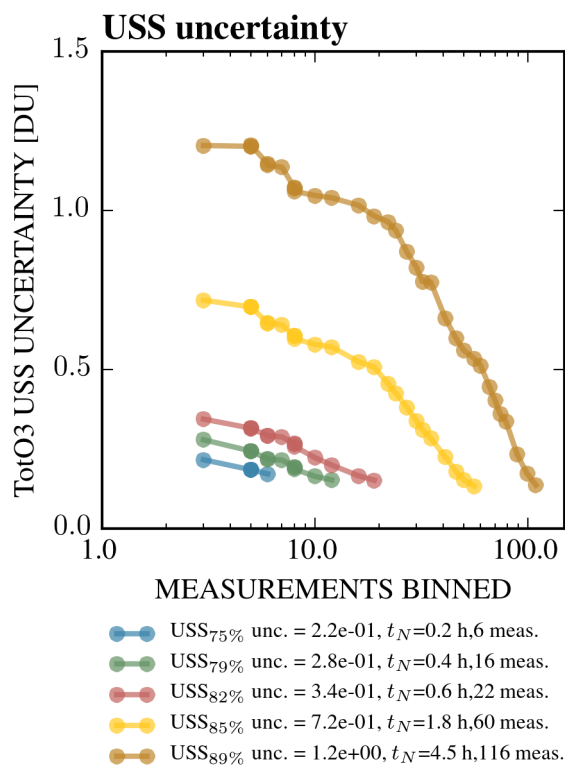
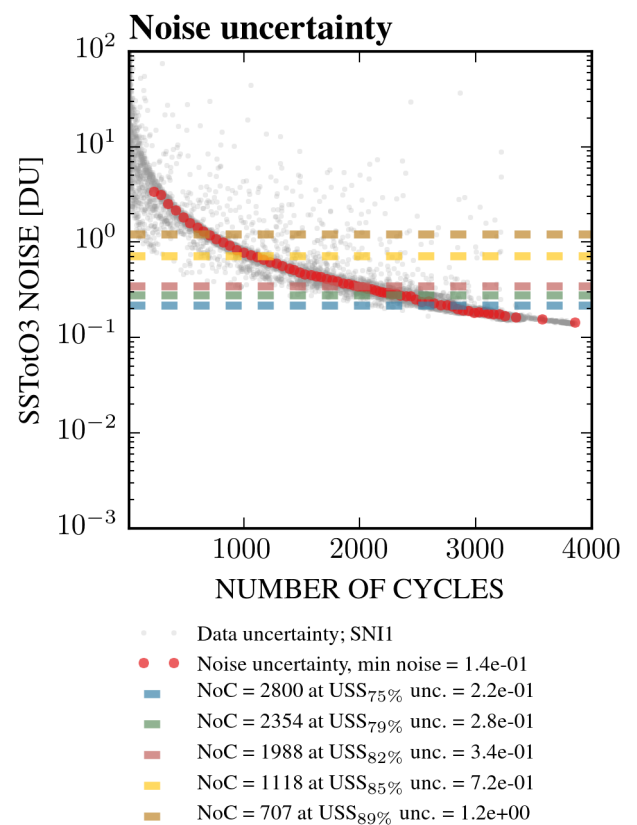
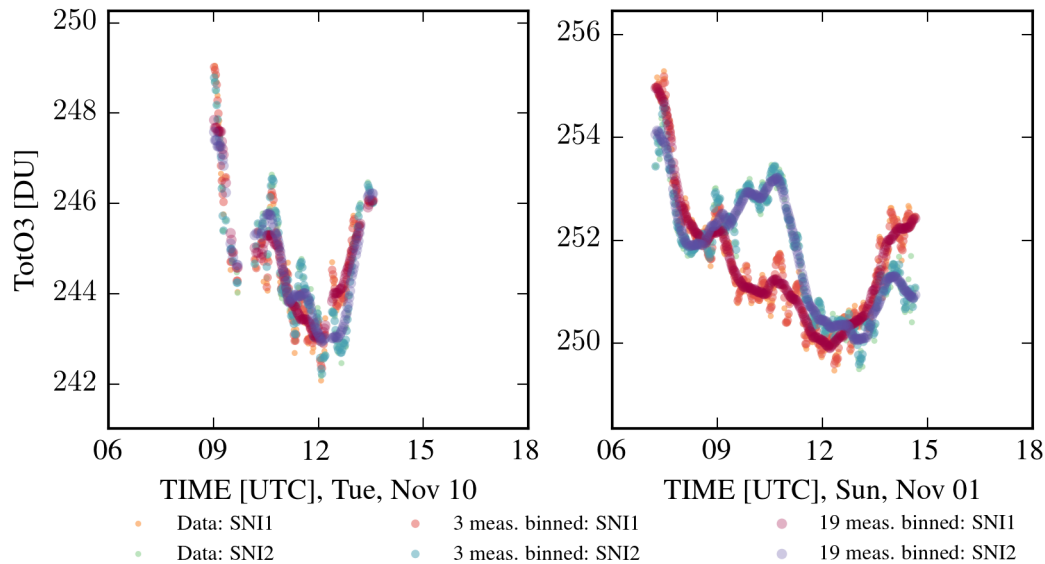


Figure 8



## Feasibility of TotO<sub>3</sub>

Figure 9: Example diurnal variation of TotO<sub>3</sub> for a positive (left panel) and a negative (right panel) case. The positive (negative) example is a representative day where the data agreement for both SNIs is high (low) for all averaging cases. Both y-axis limits are deliberately different since we want to emphasize the difference in small scale features for both SNIs.



Example diurnal variations for TotO<sub>3</sub> for SNI2 (bluish colors) and SNI1 (reddish colors) are given in Figure 9. The left (right) panel of Figure 9 shows a positive (negative) example of the agreement between SNI1 and SNI2. Whereas the smallest circles indicate un-averaged data, the small circles indicate  $t_N$  averaged data (clearly out of noise) and the larger circles depict  $t_U$  averaged data (out of USS). The small scale variations agree well in both cases. In the negative example, a clear difference in magnitude of SNI1 to SNI2, as a function of SZA is obvious.

Table 7: Feasibility criteria considered for TotO<sub>3</sub>

| PARAMETER                                                        | VALUE    |
|------------------------------------------------------------------|----------|
| <b>CC</b>                                                        | 1.00     |
| <b>Slope</b>                                                     | 0.99     |
| <b>Offset [DU]</b>                                               | 6.03     |
| <b>SpecSl uncertainty [DU]</b>                                   | 0.493    |
| <b>USS<sub>82%</sub> uncertainty [DU]</b>                        | 0.345    |
| <b>NoC at USS<sub>82%</sub></b>                                  | 1988     |
| <b><math>t_N</math> to be out of USS<sub>82%</sub> [bins(h)]</b> | 22 (0.6) |
| <b>Noise (minimum) [DU]</b>                                      | 0.143    |
| <b>Precision [DU]</b>                                            | 0.618    |
| <b>Generic uncertainty [DU]</b>                                  | 0.920    |
| <b>Unexplained uncertainty [DU]</b>                              | 0.302    |

TotO<sub>3</sub> measured by SNI1 and SNI2 is, as expected, in very high agreement with a correlation coefficient and slope (from a linear fit) of 1 (see Figure 5). The offset of approximately 6 DU (driven by low AMFs) is probably a consequence of the SpecSL, which is significantly different for both SNIs (see Figure 6). The limiting uncertainty parameter is SpecSL. Neglecting SpecSL and assuming AcL<sub>82%</sub>, a restriction of NoC to about 2000 (or almost halve the actual measurement assuming 10 ms exposure time) is valid to be not limited by noise (see Figure 8). In this case, to average 22 measurements (or half an hour) is sufficient to suppress USS.

## TotO<sub>3</sub> vs. TotO<sub>3</sub>' (with temperature fit)

Figure 10

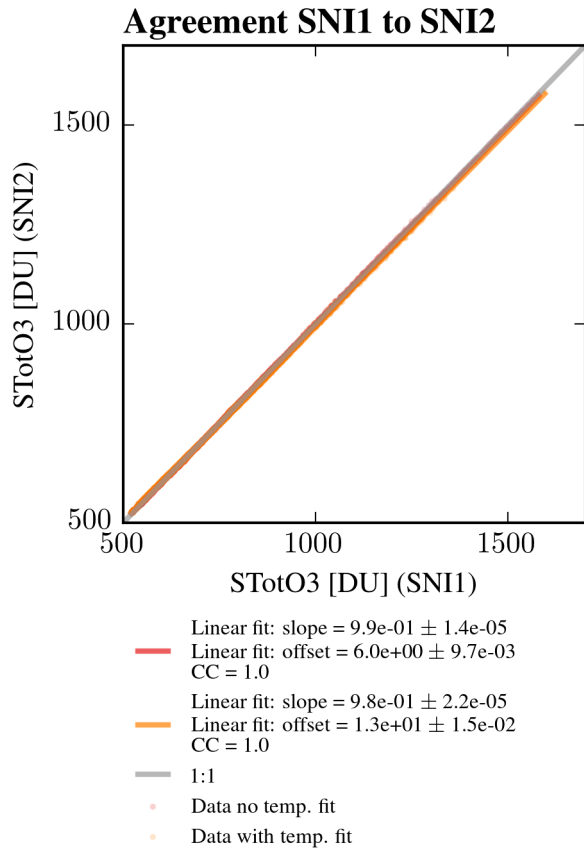


Figure 11

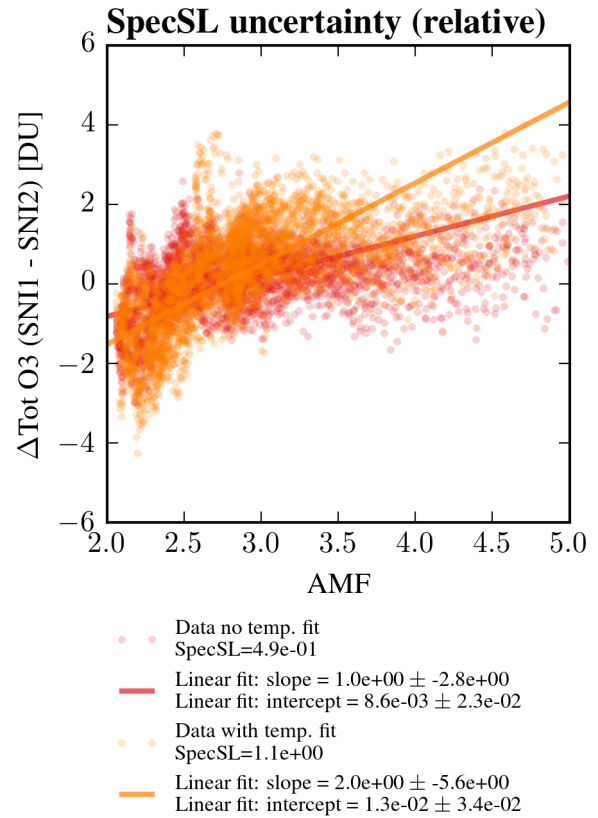


Figure 12

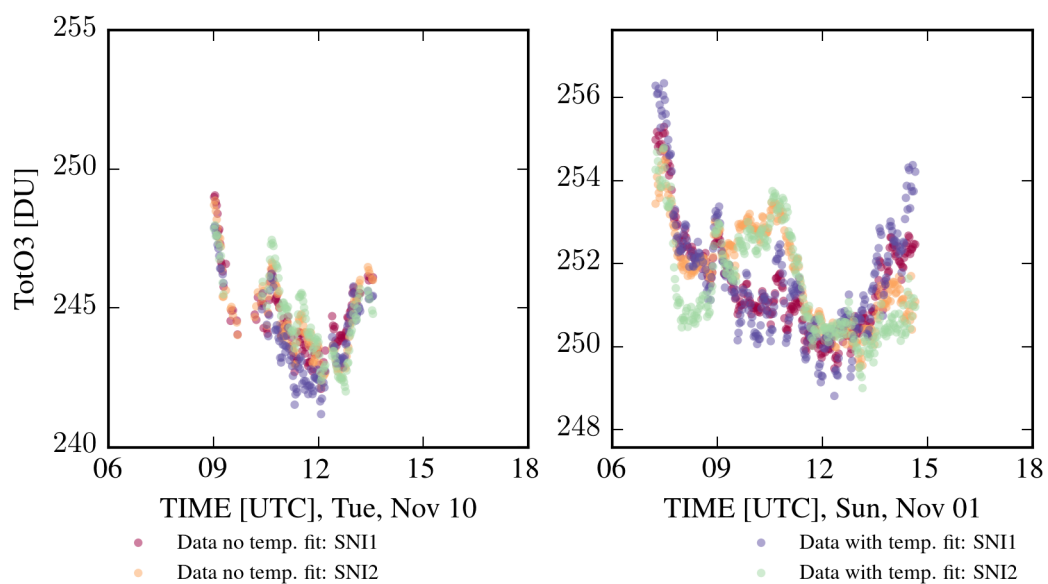


Table 8

| PARAMETER                                  | TotO <sub>3</sub> | TotO <sub>3</sub> ' |
|--------------------------------------------|-------------------|---------------------|
| CC                                         | 1.00              | 1.00                |
| Slope                                      | 0.99              | 0.98                |
| Offset [DU]                                | 6.03              | 13.47               |
| SpecSl uncertainty [DU]                    | 0.49              | 1.12                |
| USS <sub>82%</sub> uncertainty [DU]        | 0.345             | 0.864               |
| NoC at USS <sub>82%</sub>                  | 1988              | 1284                |
| t <sub>N</sub> to be out of USS [bins (h)] | 22 (0.6)          | 66 (2.0)            |
| Noise (minimum) [DU]                       | 0.143             | 0.216               |
| Precision [DU]                             | 0.618             | 1.429               |
| Generic uncertainty [DU]                   | 0.920             | 1.465               |
| Unexplained uncertainty [DU]               | 0.302             | 0.035               |

TotO<sub>3</sub>' is comparable to TotO<sub>3</sub> in terms of correlation coefficient and slope (from linear fit). TotO<sub>3</sub>' suffers, however, even more from SpecSL (see Figure 11), which further lifts the offset (see Figure 10). This can be clearly seen in the example diurnal variation on the right panel of Figure 12. USS<sub>82%</sub> uncertainty is more than double for TotO<sub>3</sub>' which would need to enhance the binning of data points from 19 to 60 to be out of USS influence.

## 4.2 Effective ozone temperature: TempO<sub>3</sub>

### Retrieval parameters

Table 9: Data filtering for TempO<sub>3</sub> retrievals.

| FILTER CRITERIA | SNI1[%], SNI2[%] |
|-----------------|------------------|
| AMF < 5.0       | 76.2, 73.7       |
| UNC < 3.00 K    | 63.1, 57.3       |
| RMS < 0.01      | 59.1, 53.3       |
| ΔWVL < 0.01 nm  | 75.2, 67.3       |

Σ53.4, Σ34.0

Table 10: Spectral fitting setup used for TempO<sub>3</sub>.

|                                 |                                                                               |
|---------------------------------|-------------------------------------------------------------------------------|
| Start WVL [nm]                  | 310.0                                                                         |
| End WVL [nm]                    | 330.0                                                                         |
| Background polynomial order     | 2                                                                             |
| Offset polynomial order         | 1                                                                             |
| WVL adjustment polynomial order | 1                                                                             |
| Fitted parameters               | HCHO, NO <sub>2</sub> ,<br>O <sub>3</sub> , SO <sub>2</sub> , TO <sub>3</sub> |

Table 9 shows the filter criteria applied to the data and table 10 lists the spectral fitting setup. Note that this fitting setup is the same as it is used for retrieving TotO<sub>3</sub>' and TotSO<sub>2</sub> 0.

The TempO<sub>3</sub> retrievals are based on a the same synthetic reference spectrum as explained in section 4.1. At this stage synthetic reference spectra are generated by correcting for O<sub>3</sub> absorption at 225 K. The magnitude of TempO<sub>3</sub> and the diurnal variation are however strongly dependent on whether this 225 K have actually been present or not. Since we chose the same data period for both SNIs to build the synthetic reference spectrum, this bias should be the same for both SNIs (except for cross-correlation features).

## Uncertainty parameters

Figure 13

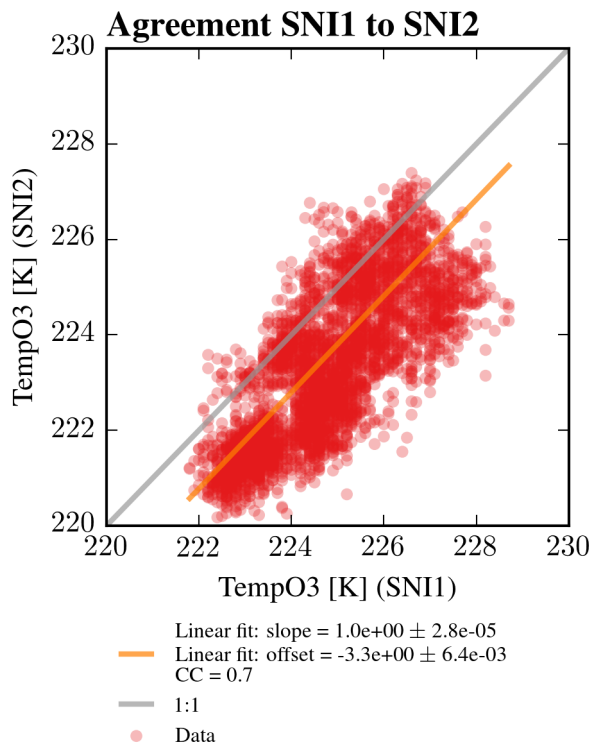


Figure 14

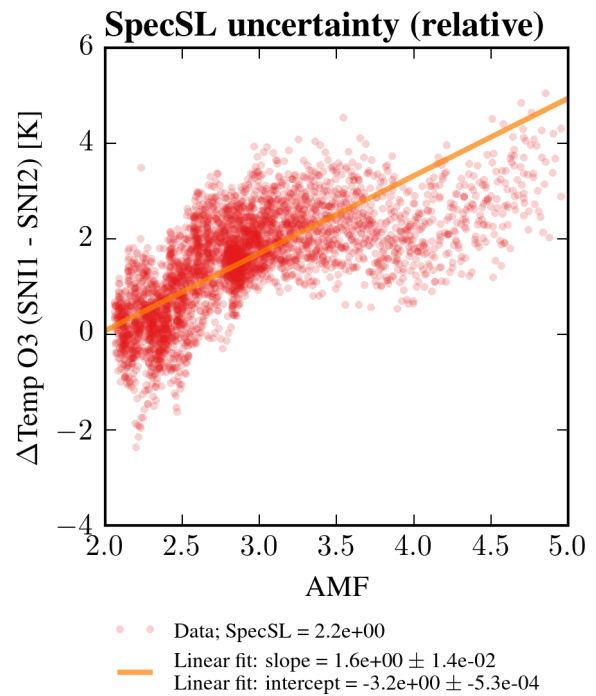


Figure 15

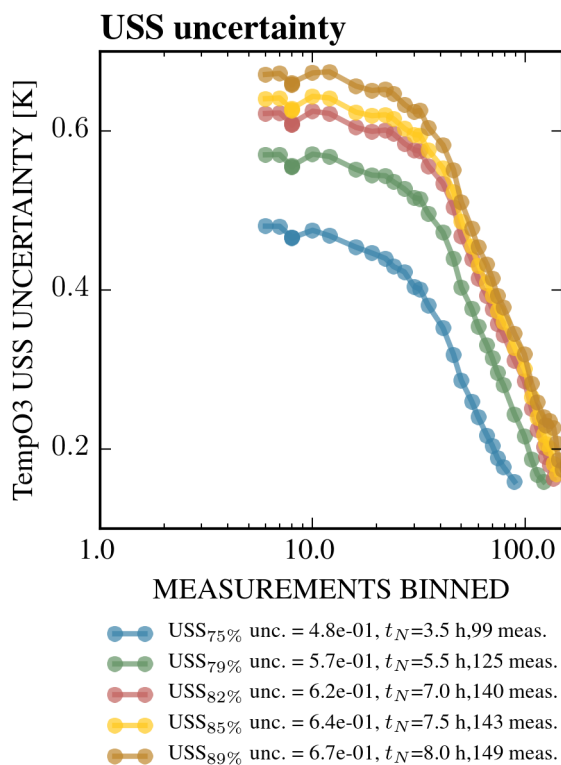
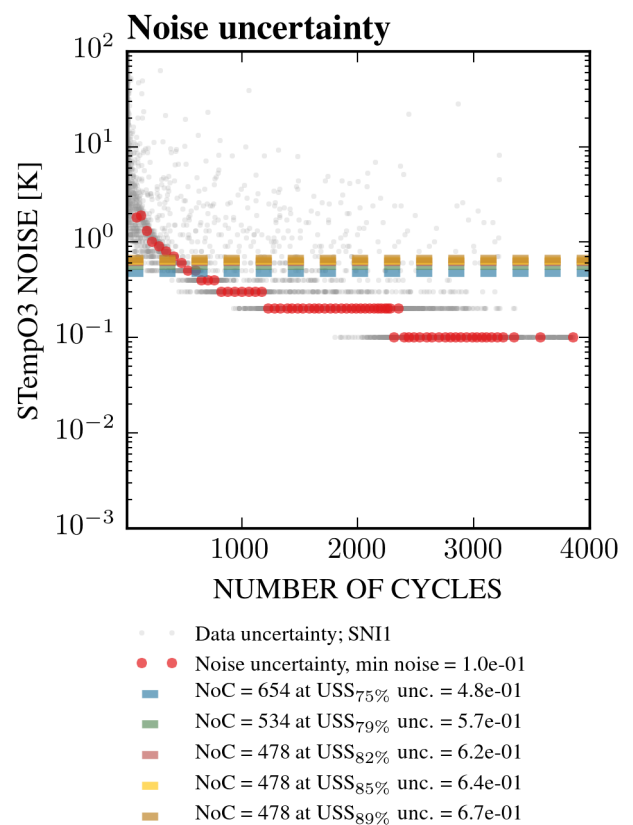
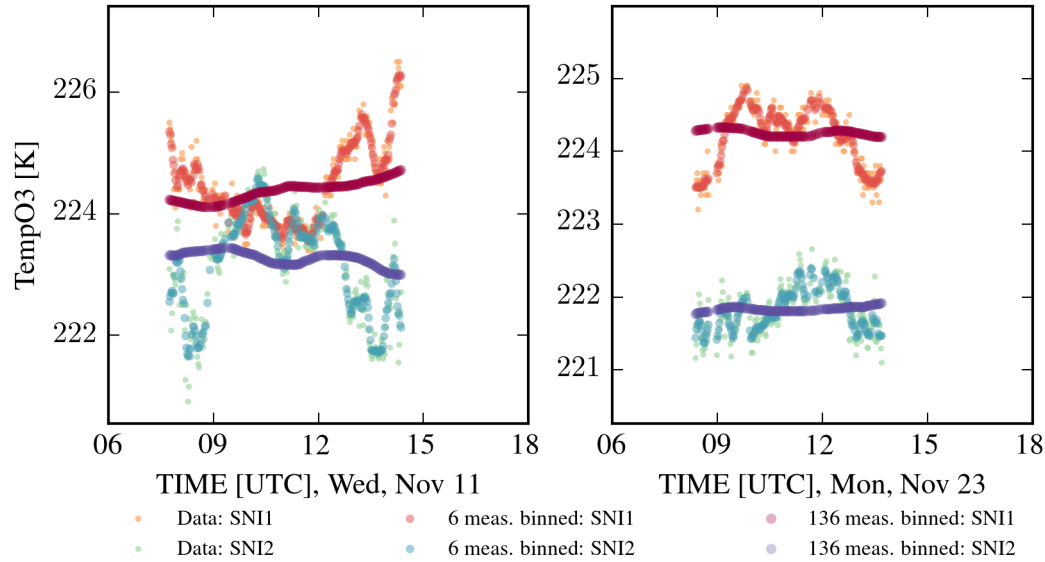


Figure 16



## Feasibility of TempO<sub>3</sub>

Figure 17: Example diurnal variation of TempO<sub>3</sub> for a positive (left panel) and a negative (right panel) case. Further explanations like in Figure 9.



Example diurnal variations for TempO<sub>3</sub> for SNI2 (bluish colors) and SNI1 (reddish colors) are given in Figure 17. The left (right) panel of Figure 17 shows a positive (negative) example of the agreement between SNI1 and SNI2. Whereas the smallest circles indicate un-averaged data, the small circles indicate  $t_N$  averaged data (clearly out of noise) and the larger circles depict  $t_U$  averaged data (out of USS). In the positive example, the magnitude and small scale variations agree quite well for low AMFs. The SpecSL influence is quite dominant for higher AMFs. The negative example also shows a pronounced offset in magnitude over the entire day.

Table 11: Feasibility criteria considered for TempO<sub>3</sub>

| PARAMETER                                                        | VALUE     |
|------------------------------------------------------------------|-----------|
| <b>CC</b>                                                        | 0.75      |
| <b>Slope</b>                                                     | 1.01      |
| <b>Offset [K]</b>                                                | -3.33     |
| <b>SpecSI uncertainty [K]</b>                                    | 2.185     |
| <b>USS<sub>82%</sub> uncertainty [K]</b>                         | 0.622     |
| <b>NoC at USS<sub>82%</sub></b>                                  | 478       |
| <b><math>t_N</math> to be out of USS<sub>82%</sub> [bins(h)]</b> | 140 (7.0) |
| <b>Noise (minimum) [K]</b>                                       | 0.100     |
| <b>Precision [K]</b>                                             | 2.274     |
| <b>Generic uncertainty [K]</b>                                   | 1.847     |
| <b>Unexplained uncertainty [K]</b>                               | -0.427    |

TempO<sub>3</sub> agree for SNI1 and SNI2 with a correlation coefficient of 0.75. The slope (from a linear fit) to be almost 1 (see Figure 13) seems to be a numerical coincidence, since, looking at Figure 17, one would suggest something different. The roughly -3 K offset is forced by high SZAs and presumably a consequence of the enhanced SpecSL (see Figure 14). SpecSL probably is slightly overestimated (the fit is forced by low AMFs), which leads to negative unexplained uncertainty. USS does not really change a lot when extending the averaging time, but is still significantly larger than a possible minimum noise and also lower than SpecSL uncertainty. SpecSL is again the limiting uncertainty parameter. Considering AcL<sub>82%</sub> about 480 NoC for each measurement (or only about 5 seconds measurement time at 10 ms exposure time) would be sufficient to be not limited by noise (see Figure 16). In this case, binning 140 individual measurements would help to get out of

the USS.

## 4.3 Total nitrogen dioxide: TotNO<sub>2</sub>

### Retrieval parameters

Table 12: Data filtering for TotNO<sub>2</sub> retrievals.

| FILTER CRITERIA | SNI1[%], SNI2[%] |
|-----------------|------------------|
| AMF < 5.0       | 74.3, 71.8       |
| UNC < 0.01 DU   | 70.2, 62.8       |
| RMS < 0.01      | 87.5, 80.8       |
| ΔWVL < 0.01 nm  | 95.9, 81.7       |
|                 | Σ56.3, Σ41.0     |

Table 13: Spectral fitting setup used for TotNO<sub>2</sub>.

|                                 |                                  |
|---------------------------------|----------------------------------|
| Start WVL [nm]                  | 400.0                            |
| End WVL [nm]                    | 440.0                            |
| Background polynomial order     | 1                                |
| Offset polynomial order         | 0                                |
| WVL adjustment polynomial order | 1                                |
| Fitted parameters               | NO <sub>2</sub> , O <sub>3</sub> |

Table 12 shows the filter criteria applied to the data and table 13 lists the spectral fitting setup.

The TotNO<sub>2</sub> retrievals are based on a synthetic reference spectrum (for brief explanation see section 3.2). As absolute reference served TotNO<sub>2</sub> amounts from SNI1 corrected by a modified Langley extrapolation technique (MLE) *Herman et al.* [e.g. 5]. As SNI1 has a longer time series in Innbruck and the MLE gets more robust for longer data sets, SNI1 was chosen to be the reference. TotNO<sub>2</sub> from SNI2 are calibrated against the corrected TotNO<sub>2</sub> from SNI1. As for TotO<sub>3</sub> it is mandatory to base the TotNO<sub>2</sub> retrieval on an (absolute) synthetic reference to be also able to retrieve TempNO<sub>2</sub>.

### Uncertainty parameters

Figure 18

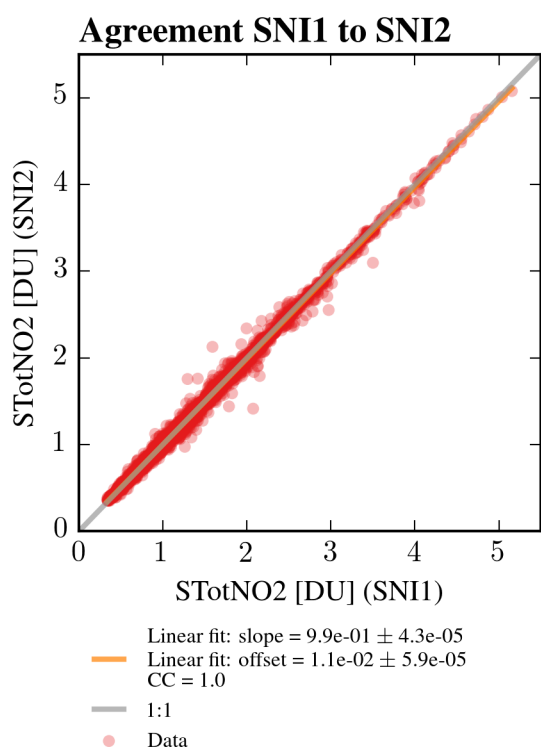


Figure 19

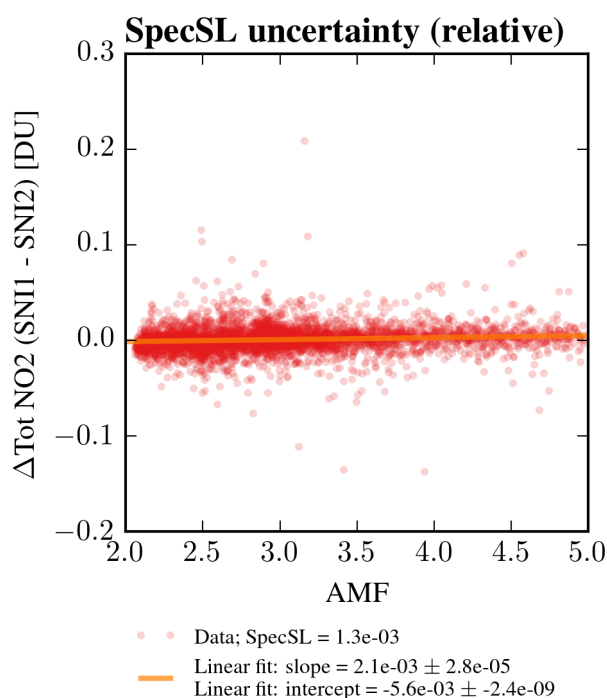


Figure 20

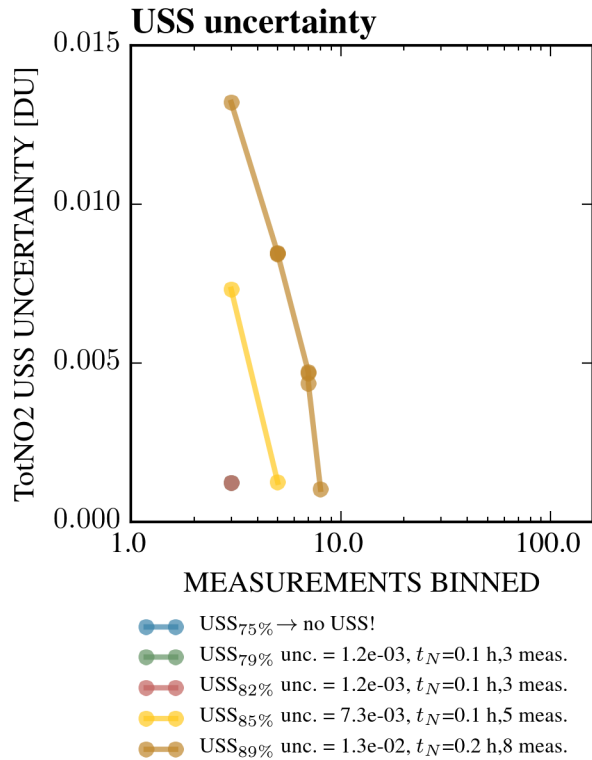
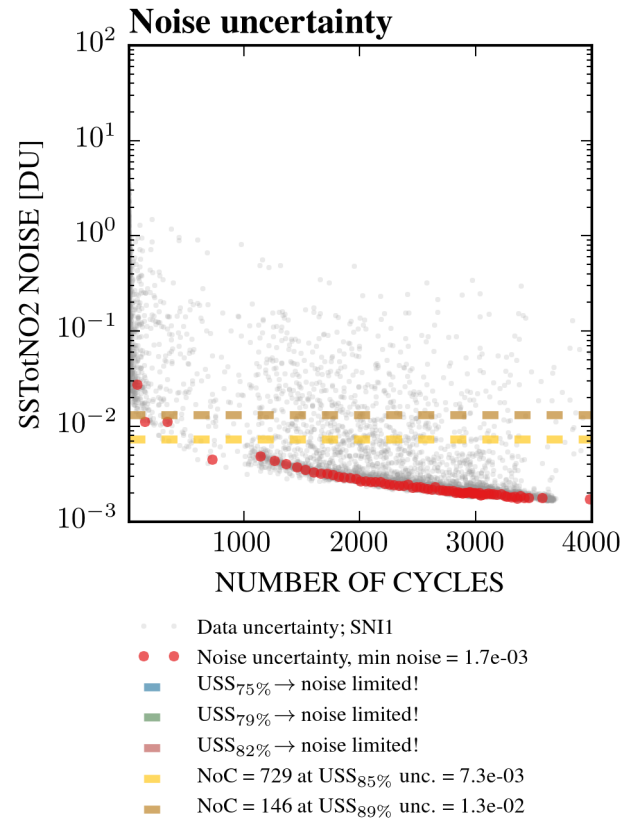
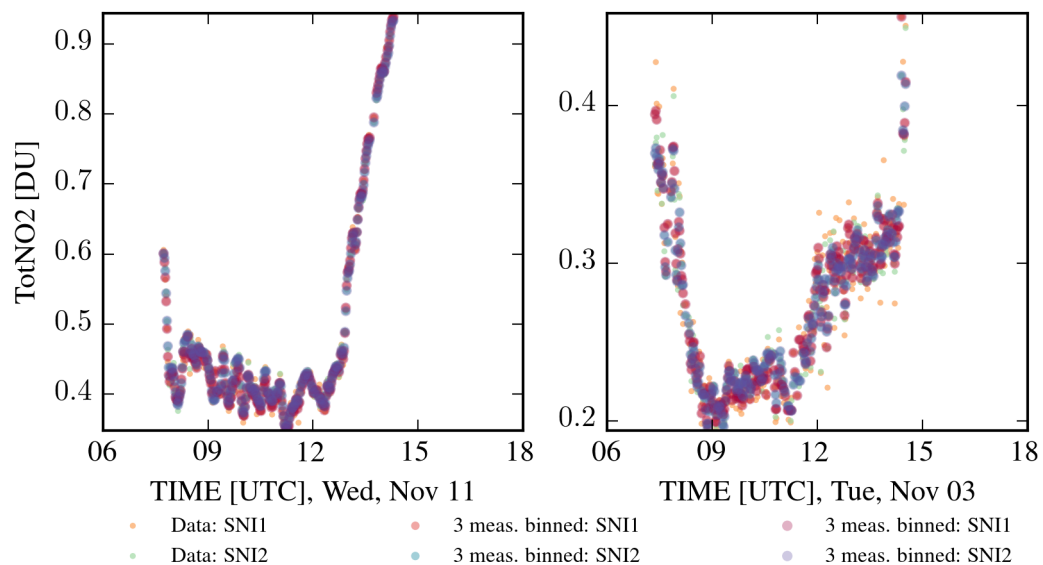


Figure 21



## Feasibility of TotNO<sub>2</sub>

Figure 22: Example diurnal variation of TotNO<sub>2</sub> for a positive (left panel) and a negative (right panel) case. Further explanations like in Figure 9.



Example diurnal variations for TotNO<sub>2</sub> for SNI2 (bluish colors) and SNI1 (reddish colors) are given in Figure 22. The left (right) panel of Figure 22 shows a positive (negative) example of the agreement between SNI1 and SNI2. Whereas the smallest circles indicate un-averaged data, the small circles indicate  $t_N$  averaged data.

data (clearly out of noise) and the larger circles depict  $t_U$  averaged data (out of USS). SNI1 and SNI2 agree extraordinarily good both in small scale variation and magnitude.

Table 14: Feasibility criteria considered for TotNO<sub>2</sub>

| PARAMETER                                                        | VALUE   |
|------------------------------------------------------------------|---------|
| <b>CC</b>                                                        | 1.00    |
| <b>Slope</b>                                                     | 0.99    |
| <b>Offset [DU]</b>                                               | 0.01    |
| <b>SpecSl uncertainty [DU]</b>                                   | 0.001   |
| <b>USS<sub>82%</sub> uncertainty [DU]</b>                        | 0.001   |
| <b>NoC at USS<sub>82%</sub></b>                                  | 3985    |
| <b><math>t_N</math> to be out of USS<sub>82%</sub> [bins(h)]</b> | 3 (0.1) |
| <b>Noise (minimum) [DU]</b>                                      | 0.002   |
| <b>Precision [DU]</b>                                            | 0.002   |
| <b>Generic uncertainty [DU]</b>                                  | 0.009   |
| <b>Unexplained uncertainty [DU]</b>                              | 0.006   |

It was to expect that TotNO<sub>2</sub> retrieved from SNI1 and SNI2 agree remarkably good. A correlation coefficient and slope (from linear fit) are virtually 1, with a very small offset of 0.01 DU (see Figure 18). Also SpecSL is not an issue (see Figure 19). At AcL<sub>82%</sub> and below, TotNO<sub>2</sub> is practically free of USS (see Figure 20). For this case the limiting uncertainty parameter is indeed noise, even for approximately 4000 NoC (see Figure 21).

## TotNO<sub>2</sub> vs. TotNO<sub>2</sub>' (with temperature fit)

Figure 23

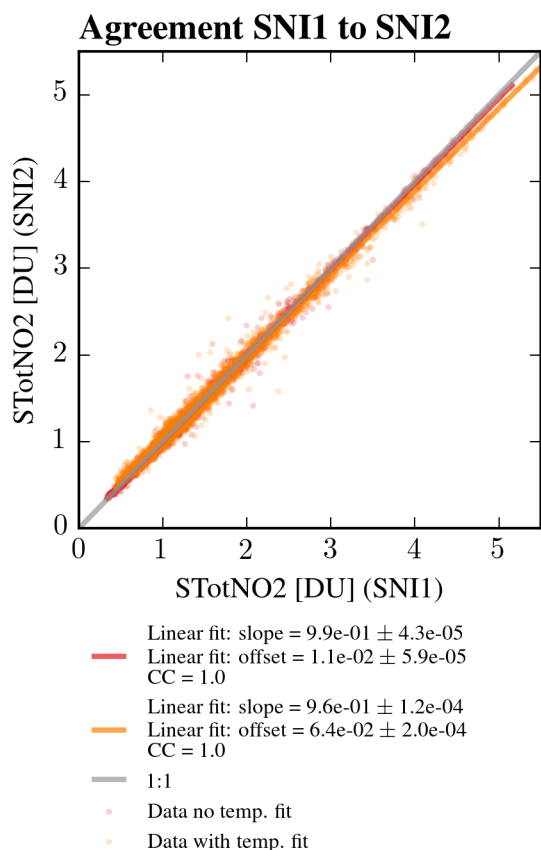


Figure 24

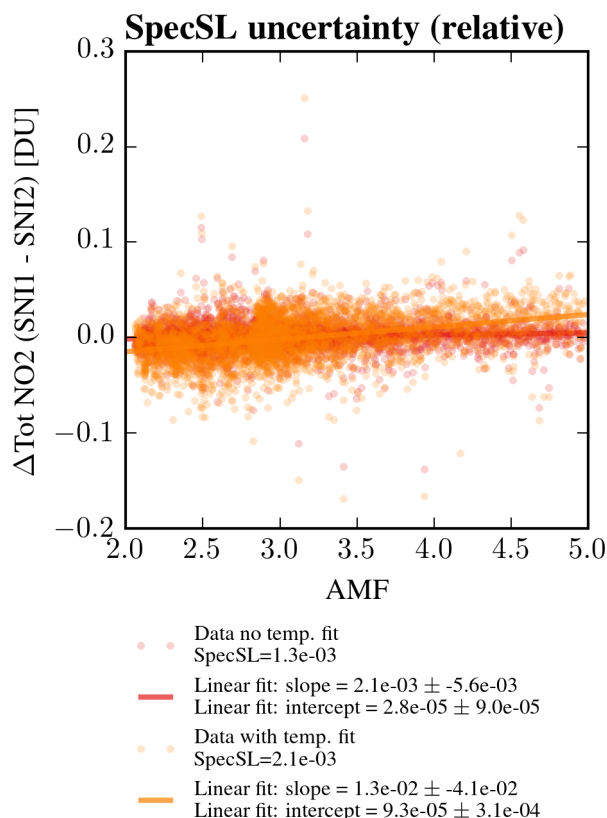


Figure 25

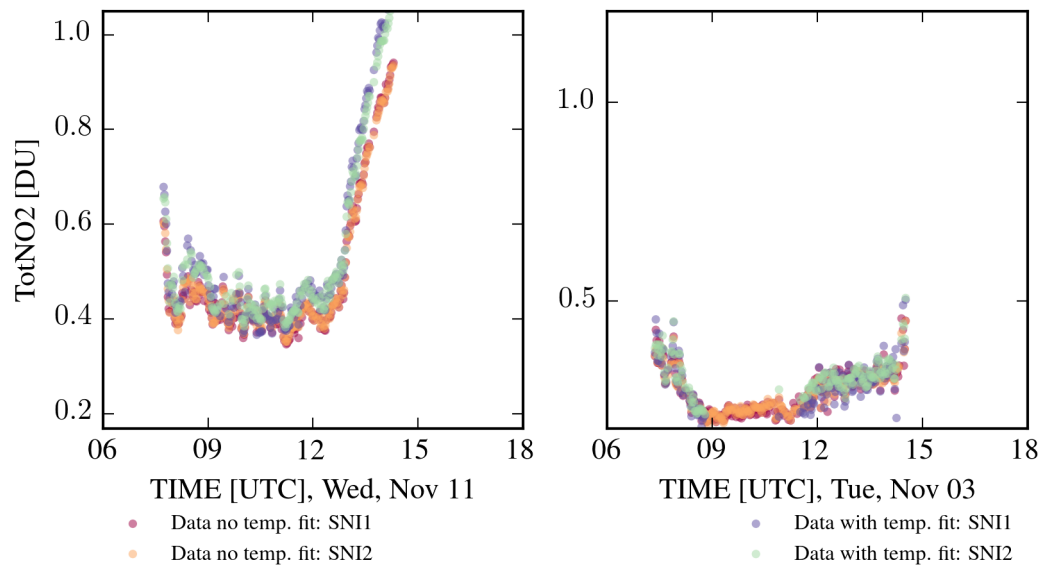


Table 15

| PARAMETER                                       | TotNO <sub>2</sub> | TotNO <sub>2</sub> ' |
|-------------------------------------------------|--------------------|----------------------|
| CC                                              | 1.00               | 0.99                 |
| Slope                                           | 0.99               | 0.96                 |
| Offset [DU]                                     | 0.01               | 0.06                 |
| SpecSI uncertainty [DU]                         | 0.001              | 0.002                |
| USS <sub>82%</sub> uncertainty [DU]             | 0.001              | 0.009                |
| NoC at USS <sub>82%</sub>                       | 3985               | 2009                 |
| $t_N$ to be out of USS <sub>82%</sub> [bins(h)] | 3 (0.1) h          | 5 (0.1)              |
| Noise (minimum) [DU]                            | 0.002              | 0.005                |
| Precision [DU]                                  | 0.002              | 0.011                |
| Generic uncertainty [DU]                        | 0.009              | 0.020                |
| Unexplained uncertainty [DU]                    | 0.006              | 0.010                |

TotNO<sub>2</sub>' is very similar to TotNO<sub>2</sub> with only marginally worse agreement between both SNIs (see Figure 23). TotNO<sub>2</sub>' in contrast to TotNO<sub>2</sub> suffers more from USS. SpecSL is only slightly enhanced for TotNO<sub>2</sub>' (see Figure 24), which is mirrored by a higher offset value.

## 4.4 Effective nitrogen dioxide temperature: TempNO<sub>2</sub>

### Retrieval parameters

Table 16: Data filtering for TempNO<sub>2</sub> retrievals.

| FILTER CRITERIA        | SNI1[%], SNI2[%]             |
|------------------------|------------------------------|
| AMF < 5.0              | 74.3, 71.8                   |
| UNC < 5.00 K           | 55.8, 49.7                   |
| RMS < 0.01             | 92.2, 85.5                   |
| $\Delta$ WVL < 0.01 nm | 95.9, 81.7                   |
|                        | $\Sigma$ 47.8, $\Sigma$ 34.0 |

Table 17: Spectral fitting setup used for TotNO<sub>2</sub>.

|                                 |                                                     |
|---------------------------------|-----------------------------------------------------|
| Start WVL [nm]                  | 400.0                                               |
| End WVL [nm]                    | 440.0                                               |
| Background polynomial order     | 2                                                   |
| Offset polynomial order         | 1                                                   |
| WVL adjustment polynomial order | 1                                                   |
| Fitted parameters               | NO <sub>2</sub> , O <sub>3</sub> , TNO <sub>2</sub> |

Table 16 shows the filter criteria applied to the data and table 17 lists the spectral fitting setup.

The TempNO<sub>2</sub> retrievals are based on a the same synthetic reference spectrum as explained in section 4.3. Regarding TempNO<sub>2</sub>, the same comments apply as mentioned in section 4.2.

## Uncertainty parameters

Figure 26

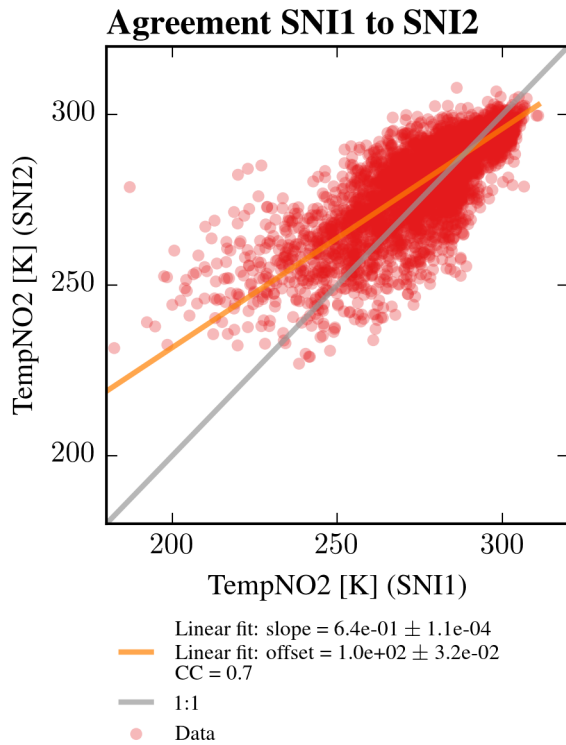


Figure 27

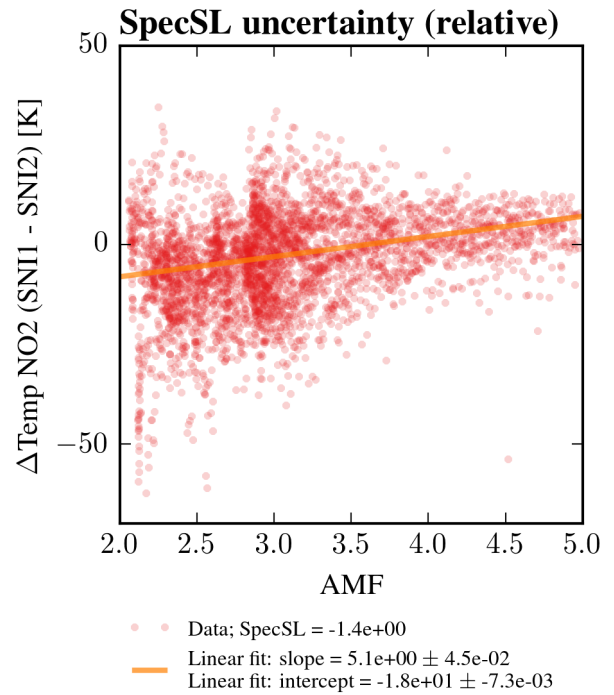


Figure 28

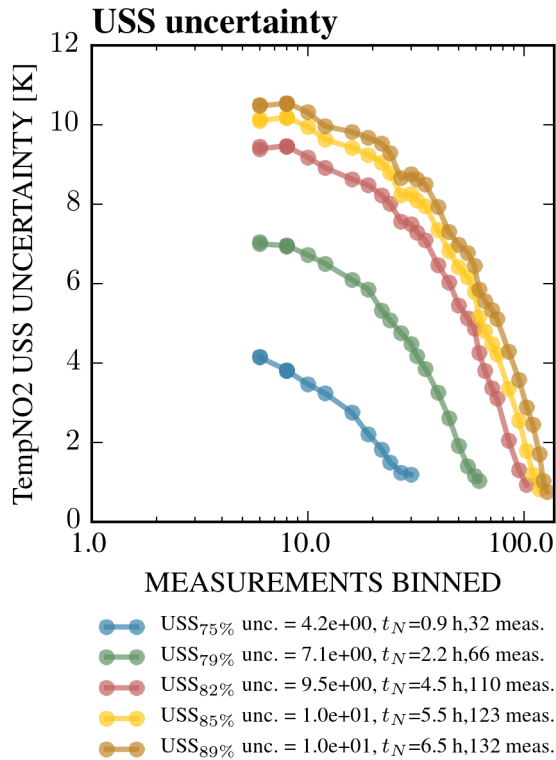
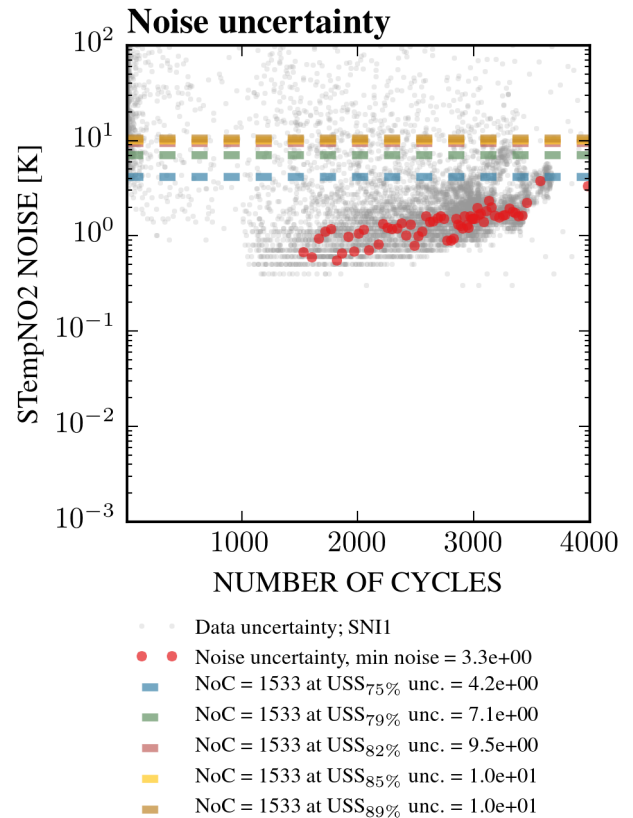
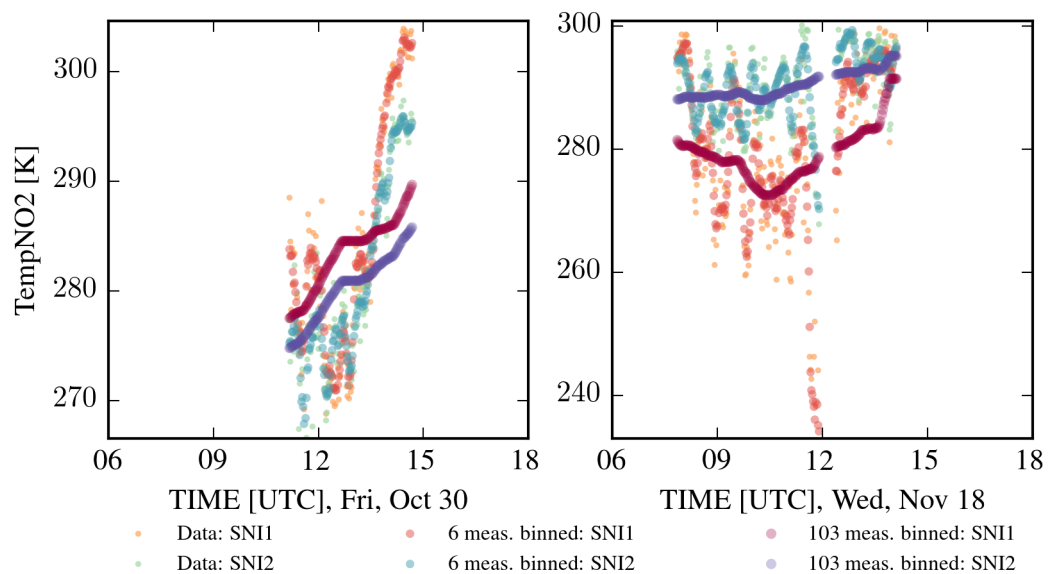


Figure 29



## Feasibility of TempNO<sub>2</sub>

Figure 30: Example diurnal variation of TempNO<sub>2</sub> for a positive (left panel) and a negative (right panel) case. Further explanations like in Figure 9.



Example diurnal variations for TempNO<sub>2</sub> for SNI2 (bluish colors) and SNI1 (reddish colors) are given in Figure 30. The left (right) panel of Figure 30 shows a positive (negative) example of the agreement between SNI1 and SNI2. Whereas the smallest circles indicate un-averaged data, the small circles indicate  $t_N$  averaged data

(clearly out of noise) and the larger circles depict  $t_U$  averaged data (out of USS). The small scale agreement is reasonable. The impact of USS is obvious in the negative example.

Table 18: Feasibility criteria considered for TempNO<sub>2</sub>

| PARAMETER                                       | VALUE     |
|-------------------------------------------------|-----------|
| CC                                              | 0.75      |
| Slope                                           | 0.64      |
| Offset [K]                                      | 103.34    |
| SpecSI uncertainty [K]                          | 1.444     |
| USS <sub>82%</sub> uncertainty [K]              | 9.460     |
| NoC at USS <sub>82%</sub>                       | 1533      |
| $t_N$ to be out of USS <sub>82%</sub> [bins(h)] | 110 (4.5) |
| Noise (minimum) [K]                             | 0.552     |
| Precision [K]                                   | 10.127    |
| Generic uncertainty [K]                         | 11.038    |
| Unexplained uncertainty [K]                     | 0.911     |

TempNO<sub>2</sub> retrieved from SNI1 and SNI2 agree reasonably good. A correlation coefficient of about 0.8 is sufficient. Concurrently, SNI1 tends to underestimate TempNO<sub>2</sub> with respect to SNI2 expressed in a slope of about 0.6 (from a linear fit) (see Figure 26). SpecSL significantly affects both SNIs differently (see Figure 27). The USS uncertainty is comparably high, which would allow to restrict NoC to about 1500 (roughly 15 seconds measurement time at 10 ms exposure time). USS is clearly the limiting uncertainty parameters. Considering AcL<sub>82%</sub>, to bin 110 individual measurements would mitigate USS adequately (see Figure 28). The expected relationship for noise to NoC (which usually decreases  $\propto \text{NoC}^{-0.5}$ ) is not given. At this stage we do not have an explanation for this behavior.

## 4.5 Total formaldehyde: TotHCHO

### Retrieval parameters

Table 19: Data filtering for TotHCHO retrievals.

| FILTER CRITERIA              | SNI1[%], SNI2[%]       |
|------------------------------|------------------------|
| AMF < 5.0                    | 74.0, 71.7             |
| UNC < 0.05 DU                | 57.9, 50.7             |
| RMS < 0.01                   | 76.7, 64.1             |
| $\Delta\text{WVL}$ < 0.01 nm | 75.2, 67.3             |
|                              | $\sum 51.0, \sum 32.7$ |

Table 20: Spectral fitting setup used for TotNO<sub>2</sub>.

|                                 |                                                                           |
|---------------------------------|---------------------------------------------------------------------------|
| Start WVL [nm]                  | 332.0                                                                     |
| End WVL [nm]                    | 359.0                                                                     |
| Background polynomial order     | 4                                                                         |
| Offset polynomial order         | 1                                                                         |
| WVL adjustment polynomial order | 1                                                                         |
| Fitted parameters               | HCHO, NO <sub>2</sub> ,<br>O <sub>2</sub> O <sub>2</sub> , O <sub>3</sub> |

Table 19 shows the filter criteria applied to the data and table 20 lists the spectral fitting setup.

The TotHCHO retrievals are also based on a synthetic reference spectrum (for brief explanation see section 3.2). As absolute reference served MLE corrected TotHCHO amounts from SNI2. As mentioned in section 4.1, SNI2 TotO<sub>3</sub> data showed better agreement to OMI. Presumably, SNI2 is less prone to SpecSL as SNI1. This is why SNI2 is chosen to be the reference, where SNI1 TotHCHO is calibrated to.

Technically, applying MLE for absolute calibration would assume to have a quasi constant, significant stratospheric background concentration. This assumption maybe does not hold true. However this would introduce just the same bias in both instruments which does not matter for this study.

## Uncertainty parameters

Figure 31

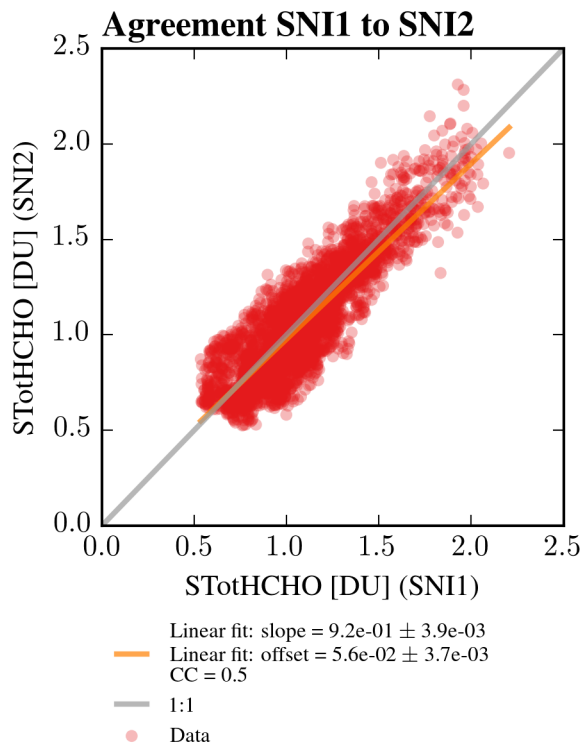


Figure 32

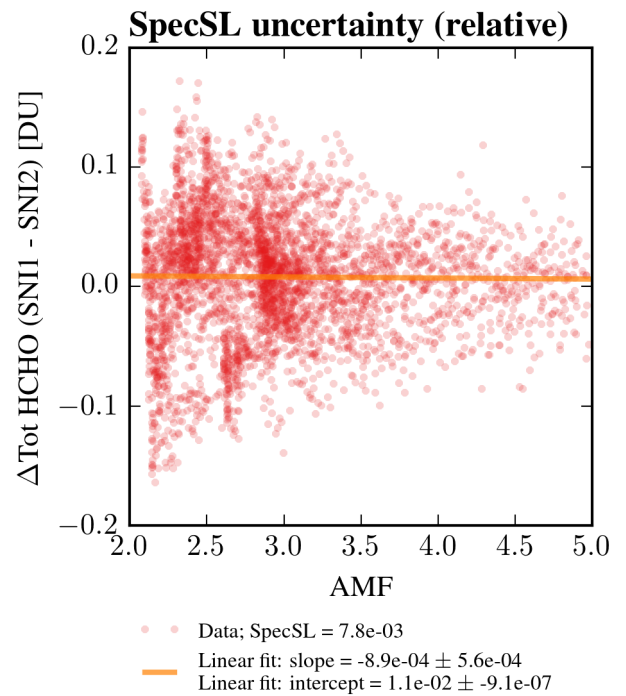


Figure 33

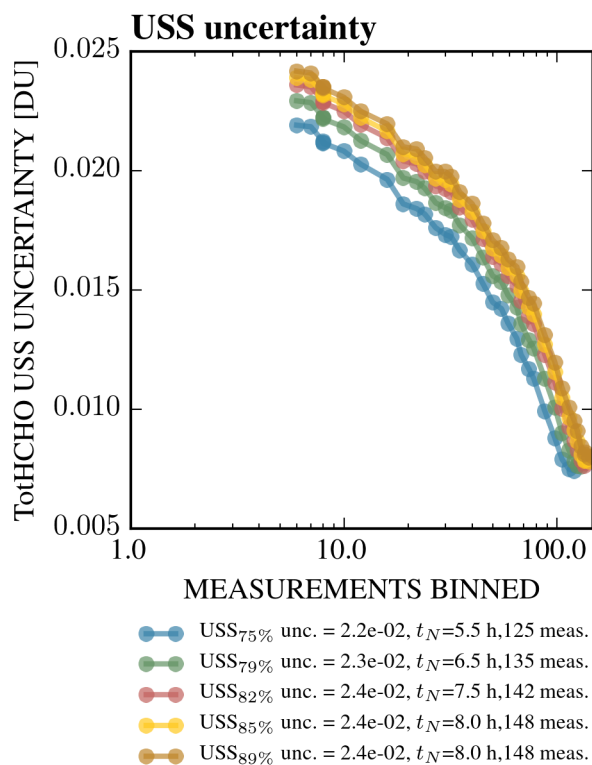
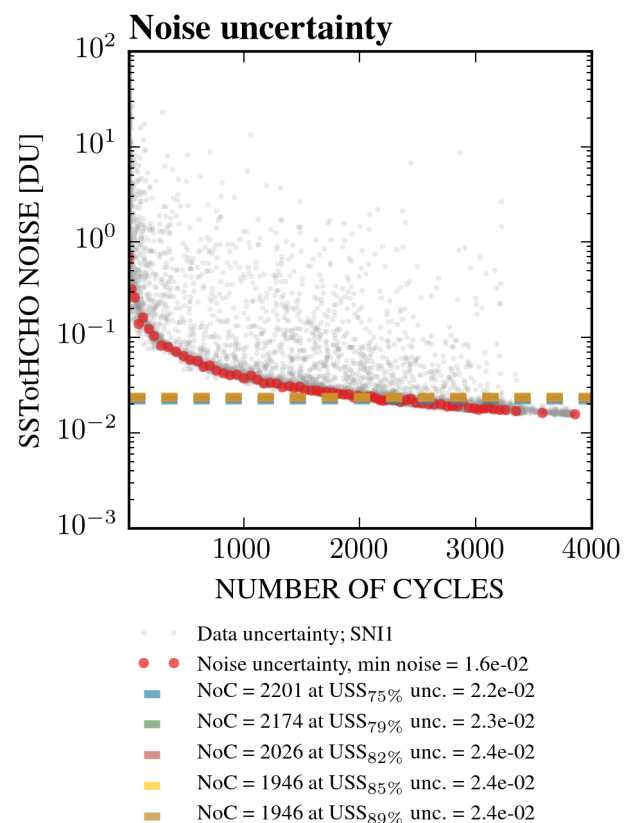
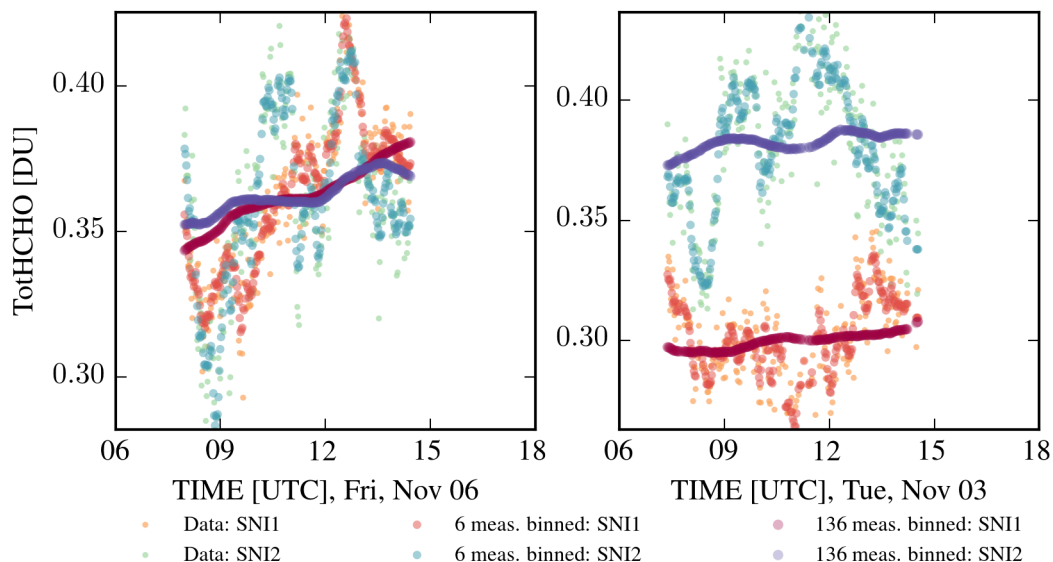


Figure 34



## Feasibility of TotHCHO

Figure 35: Example diurnal variation of TotHCHO for a positive (left panel) and a negative (right panel) case. Further explanations like in Figure 9.



Example diurnal variations for TotHCHO for SNI2 (bluish colors) and SNI1 (reddish colors) are given in Figure 35. The left (right) panel of Figure 35 shows a positive (negative) example of the agreement between SNI1 and SNI2. Whereas the smallest circles indicate un-averaged data, the small circles indicate  $t_N$  averaged data (clearly out of noise) and the larger circles depict  $t_U$  averaged data (out of USS). The impact of USS is particularly obvious in the negative example.

Table 21: Feasibility criteria considered for TotHCHO

| PARAMETER                                                        | VALUE     |
|------------------------------------------------------------------|-----------|
| <b>CC</b>                                                        | 0.52      |
| <b>Slope</b>                                                     | 0.92      |
| <b>Offset [DU]</b>                                               | 0.06      |
| <b>SpecSl uncertainty [DU]</b>                                   | 0.008     |
| <b>USS<sub>82%</sub> uncertainty [DU]</b>                        | 0.024     |
| <b>NoC at USS<sub>82%</sub></b>                                  | 2026      |
| <b><math>t_N</math> to be out of USS<sub>82%</sub> [bins(h)]</b> | 142 (7.5) |
| <b>Noise (minimum) [DU]</b>                                      | 0.016     |
| <b>Precision [DU]</b>                                            | 0.029     |
| <b>Generic uncertainty [DU]</b>                                  | 0.064     |
| <b>Unexplained uncertainty [DU]</b>                              | 0.034     |

The agreement of TotHCHO for SNI1 and SNI2 is reasonably good, evincing a correlation coefficient of about 0.5 and a quite good slope (from a linear fit) of about 0.9 (see Figure 31). This time the offset of about 0.06 DU can not be explained directly by SpecSL, which tends to act for both SNI in the same direction (see Figure 32). The USS is virtually not dependent on the choice of AcL (see Figure 33), but always needs to have a considerably long averaging time to be flattened out. At AcL<sub>82%</sub>, 142 measurements would have to be binned (67 h average). In this case about 2000 NoC (about halve of the current measurement time at 10 ms exposure time) would be sufficient to be still out of the noise limit (see Figure 34). Overall, also USS is the limiting uncertainty parameter.

## 4.6 Total sulfur dioxide: TotSO<sub>2</sub>

### Retrieval parameters

Table 22: Data filtering for TotSO<sub>2</sub> retrievals.

| FILTER CRITERIA | SNI1[%], SNI2[%] |
|-----------------|------------------|
| AMF < 5.0       | 74.0, 71.7       |
| UNC < 0.10 DU   | 49.0, 36.3       |
| RMS < 0.01      | 59.1, 53.3       |
| ΔWVL < 0.01 nm  | 75.2, 67.3       |
|                 | Σ48.2, Σ26.1     |

Table 23: Spectral fitting setup used for TotNO<sub>2</sub>.

|                                 |                                                                               |
|---------------------------------|-------------------------------------------------------------------------------|
| Start WVL [nm]                  | 310.0                                                                         |
| End WVL [nm]                    | 330.0                                                                         |
| Background polynomial order     | 2                                                                             |
| Offset polynomial order         | 1                                                                             |
| WVL adjustment polynomial order | 1                                                                             |
| Fitted parameters               | HCHO, NO <sub>2</sub> ,<br>O <sub>3</sub> , SO <sub>2</sub> , TO <sub>3</sub> |

Table 22 shows the filter criteria applied to the data and table 23 lists the spectral fitting setup. Note that this fitting setup is the same as it is used for retrieving TempO<sub>3</sub> and TotO<sub>3</sub>'.

TotSO<sub>2</sub> retrievals suffer from algorithm deficiencies which lead to negatively biased data in environments with hardly any SO<sub>2</sub>. We are still working on this topic. For this study, where the absolute value is not further investigated, the calibration is carried out in a way to make the diurnal variations “reasonable”. By this we accept negative values. The TotSO<sub>2</sub> retrievals are carried out the same way with the same limitations as explained in section 4.5. SNI2 is again the reference instrument.

### Uncertainty parameters

Figure 36

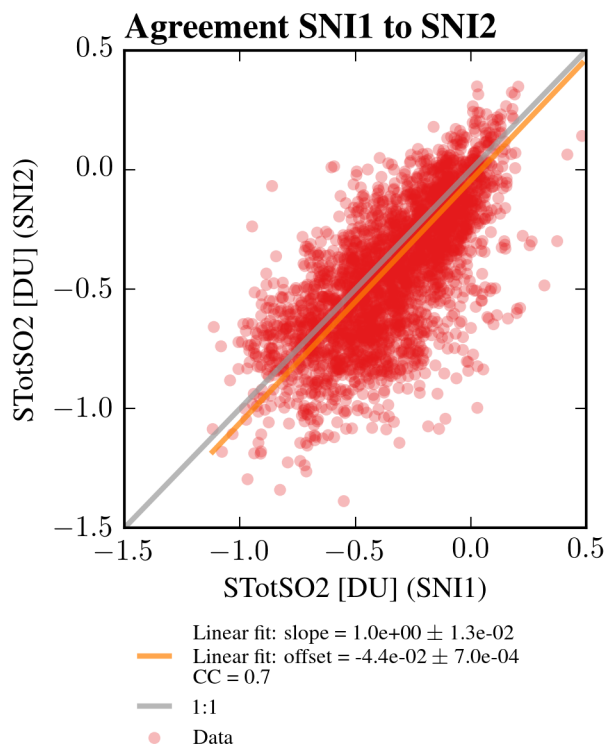


Figure 37

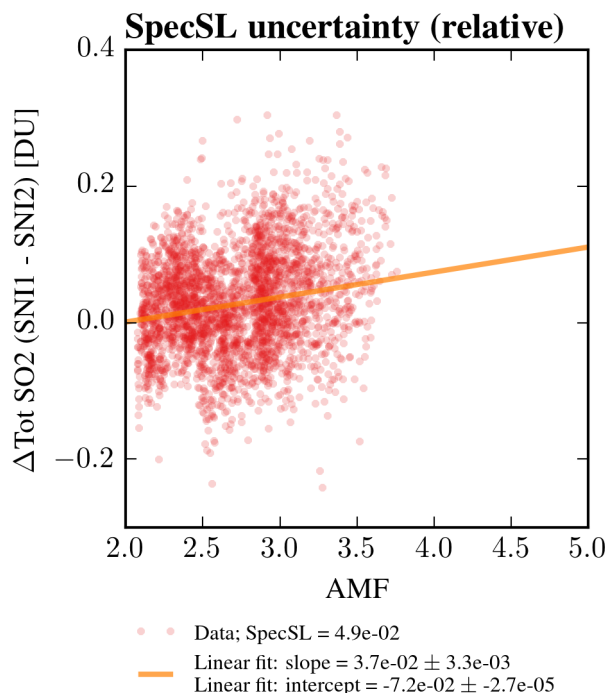


Figure 38

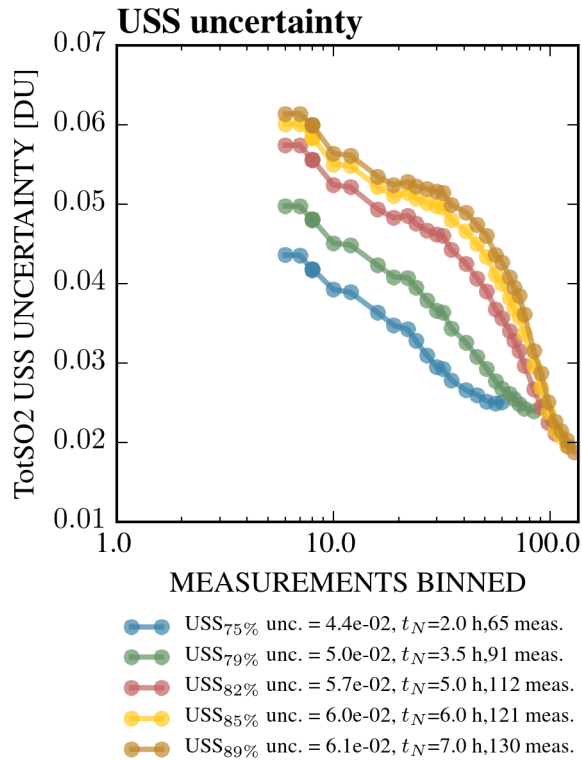
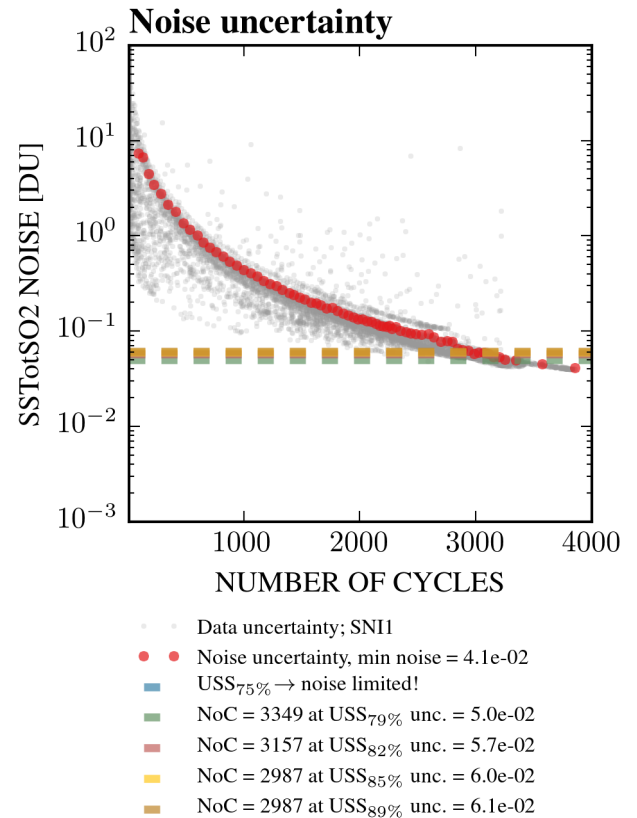
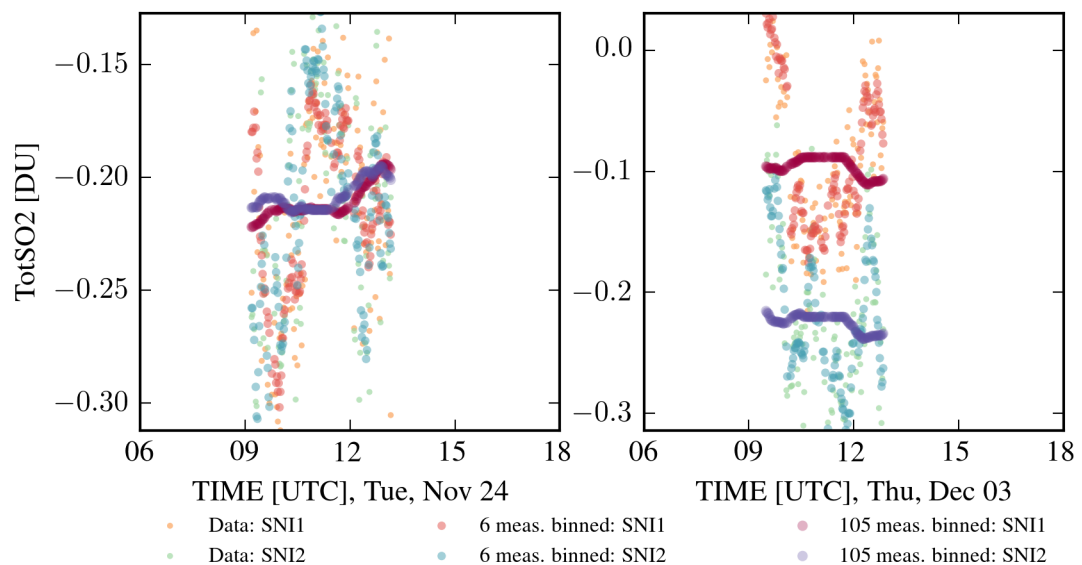


Figure 39



## Feasibility of TotSO<sub>2</sub>

Figure 40: Example diurnal variation of TotSO<sub>2</sub> for a positive (left panel) and a negative (right panel) case. Further explanations like in Figure 9.



Example diurnal variations for TotSO<sub>2</sub> for SNI2 (bluish colors) and SNI1 (reddish colors) are given in Figure 40. The left (right) panel of Figure 40 shows a positive (negative) example of the agreement between SNI1 and SNI2. Whereas the smallest circles indicate un-averaged data, the small circles indicate  $t_N$  averaged data

(clearly out of noise) and the larger circles depict  $t_U$  averaged data (out of USS). Differences in the magnitude in the negative example, are driven by a combination of USS and SpecSL.

Table 24: Feasibility criteria considered for TotSO<sub>2</sub>

| PARAMETER                                                        | VALUE     |
|------------------------------------------------------------------|-----------|
| <b>CC</b>                                                        | 0.67      |
| <b>Slope</b>                                                     | 1.02      |
| <b>Offset [DU]</b>                                               | -0.04     |
| <b>SpecSI uncertainty [DU]</b>                                   | 0.049     |
| <b>USS<sub>82%</sub> uncertainty [DU]</b>                        | 0.057     |
| <b>NoC at USS<sub>82%</sub></b>                                  | 3157      |
| <b><math>t_N</math> to be out of USS<sub>82%</sub> [bins(h)]</b> | 112 (5.0) |
| <b>Noise (minimum) [DU]</b>                                      | 0.041     |
| <b>Precision [DU]</b>                                            | 0.086     |
| <b>Generic uncertainty [DU]</b>                                  | 0.144     |
| <b>Unexplained uncertainty [DU]</b>                              | 0.059     |

The TotSO<sub>2</sub> agreement between SNI1 and SNI2 is reasonably good with a correlation coefficient of roughly 0.7 and excellent slope (from a linear fit) of almost 1. The slight offset between both SNIs may also be connected to SpecSL (see Figure 37). The USS at AcL<sub>82%</sub> is just slightly above the minimum noise, which makes measuring with more than 3150 NoC necessary (see Figure 39). Choosing a lower AcL would mean to be limited by noise. In this scenario averaging over 112 measurements (this would correspond 4.5 h) would flatten out the USS uncertainty (see Figure 38). Still, USS is the limiting uncertainty parameter.

## 4.7 Overview table for retrieval products

Table 25: Uncertainty parameters obtained for each RDP. The last row gives a hierarchical order of the limiting uncertainty parameters.

| PARAMETER                                                  | TotO <sub>3</sub>                       | TotO <sub>3</sub> '                     | TempO <sub>3</sub>                | TotNO <sub>2</sub>                      | TotNO <sub>2</sub> '                    | TempNO <sub>2</sub>                       | TotHCHO                                   | TotSO <sub>2</sub>                        |
|------------------------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------|-----------------------------------------|-----------------------------------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|
| <b>CC</b>                                                  | 1.00                                    | 1.00                                    | 0.75                              | 1.00                                    | 0.99                                    | 0.75                                      | 0.52                                      | 0.67                                      |
| <b>Slope</b>                                               | 0.99                                    | 0.98                                    | 1.01                              | 0.99                                    | 0.96                                    | 0.64                                      | 0.92                                      | 1.02                                      |
| <b>Offset [DU, K]</b>                                      | 6.03                                    | 13.47                                   | -3.33                             | 0.01                                    | 0.06                                    | 103.34                                    | 0.06                                      | -0.04                                     |
| <b>SpecSl uncertainty [DU, K]</b>                          | 0.493                                   | 1.117                                   | 2.185                             | 0.001                                   | 0.002                                   | 1.444                                     | 0.008                                     | 0.049                                     |
| <b>USS<sub>82%</sub> uncertainty [DU, K]</b>               | 0.345                                   | 0.864                                   | 0.622                             | 0.001                                   | 0.009                                   | 9.460                                     | 0.024                                     | 0.057                                     |
| <b>NoC at USS<sub>82%</sub></b>                            | 1988                                    | 1284                                    | 478                               | 3985                                    | 2009                                    | 1533                                      | 2026                                      | 3157                                      |
| <b>t<sub>U</sub> to be out of USS<sub>82%</sub> [bins]</b> | 22                                      | 66                                      | 140                               | 3                                       | 5                                       | 110                                       | 142                                       | 112                                       |
| <b>Noise (minimum) [DU, K]</b>                             | 0.143                                   | 0.216                                   | 0.100                             | 0.002                                   | 0.005                                   | 0.552                                     | 0.016                                     | 0.041                                     |
| <b>Precision [DU, K]</b>                                   | 0.618                                   | 1.429                                   | 2.274                             | 0.002                                   | 0.011                                   | 10.127                                    | 0.029                                     | 0.086                                     |
| <b>Generic uncertainty [DU, K]</b>                         | 0.920                                   | 1.465                                   | 1.847                             | 0.009                                   | 0.020                                   | 11.038                                    | 0.064                                     | 0.144                                     |
| <b>Unexplained uncertainty [DU, K]</b>                     | 0.302                                   | 0.035                                   | -0.427                            | 0.006                                   | 0.010                                   | 0.911                                     | 0.034                                     | 0.059                                     |
| <b>Uncertainty limitation hierarchy</b>                    | SpecSL ><br>USS ><br>unexpl. ><br>noise | SpecSL ><br>USS ><br>noise ><br>unexpl. | SpecSL ><br>USS ><br>noise ><br>- | unexpl. ><br>noise ><br>USS ≈<br>SpecSL | unexpl. ><br>USS ><br>noise ><br>SpecSL | USS ><br>SpecSL ><br>unexpl. ><br>noise > | unexpl. ><br>USS ><br>noise ><br>SpecSL > | unexpl. ><br>USS ><br>SpecSL ><br>noise > |

