WP4-NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides
Deliverable D4.12: Link between surface and column information of NO₂

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2 Intention of this document

The aim of this report is to investigate the link between ground-based in-situ NO₂ surface concentration observations and vertical profiles and columns densities measured by the MAX-DOAS (Multi-AXis Differential Optical Absorption Spectroscopy) remote sensing technique. This study was focused on two stations where in-situ and MAX-DOAS observations of NO₂ are performed in parallel: the International Scientific Station of the Jungfraujoch (ISSJ) in the Swiss Alps (3580m asl) and the Meteorological Observatory Hohenpeissenberg (MOHp) in the South of Germany (980m asl).

3 MAX-DOAS NO₂ observations

3.1 ISSJ

MAX-DOAS is a passive DOAS technique consisting of measuring scattered sunlight radiance spectra at zenith and at different elevation angles towards the horizon (the so-called off-axis geometry), increasing therefore the sensitivity to absorbers present close to the ground such as NO₂. A dual-channel (UV + visible) MAX-DOAS instrument has been operating by BIRA-IASB at the ISSJ since July 2010 in the framework of NDACC (Network for the Detection of Atmospheric Composition Change). As illustrated in Figure 1, the pointing direction is North West towards the city of Berne and the pre-Alpine terrain. A full MAX-DOAS scan consists of 16 elevation angles (-10°, -8°, -6°, -4°, -2°, 0° (horizon), 1°, 3°, 4°, 5°, 8°, 10°, 12°, 15°, 30°, and 90° (zenith)) and lasts about 20 minutes. The negative elevation angles correspond to measurements for which the instrument is pointing downwards, in the direction of the valley. It should be noted that these latter observations have not been exploited here.

For each MAX-DOAS scan, NO₂ and O₄ slant column densities (SCDs) are retrieved by applying the DOAS method to measured radiance spectra in the visible region (425-490 nm). NO₂ vertical profiles for 13 layers between 3.6 and 8 km altitude are then obtained by using the bePRO profiling tool (Clémer at al., 2010; Hendrick et al., 2014; Wang et al., 2014). In brief, the bePRO algorithm is based on the Optimal Estimation Method (OEM; Rodgers, 2000) and uses a two-step approach. First, the aerosol extinction vertical profiles are retrieved at 477 nm for each MAX-DOAS scan from the corresponding measured O₄...
SCDs. This first step is required since the light path length through the atmosphere (and thus the measured NO$_2$ SCDs) strongly depends on the aerosols and therefore a good estimate of the vertical distribution of the aerosols is needed to perform accurate NO$_2$ profile retrievals. In the second step, OEM is applied to measured NO$_2$ SCDs using the retrieved aerosol extinction vertical profiles as input for the forward modelling. An example of NO$_2$ profile retrieval is presented in Figure 2. The examination of the averaging kernels combined to a mean DOFS (degrees of freedom for signal) of about 1.5-2 shows that the MAX-DOAS technique is essentially sensitive to the near-surface concentration (200m layer above the station) and to the overhead column.

![Figure 2: Example of MAX-DOAS NO$_2$ profile retrieval at ISSJ.](image)

Because it is based on a remote sensing technique, MAX-DOAS measurements show a maximum of sensitivity over a distance of up to several dozen of kilometers from the instrument and not at the location of the instrument itself. This distance depends on the sky conditions and this is illustrated in Figure 3 where the horizontal distance representative of the MAX-DOAS measurements at ISSJ is plotted for the July 2010-December 2012 period. We see that when a cloud filter is applied in order to select mostly clear-sky conditions, the effective distance reaches 40-65 km from the station, i.e. above the region between Thounes and Berne (see Figure 1).

![Figure 3: Horizontal distance representative of the MAX-DOAS measurements at ISS estimated by applying the modified geometric approach developed by Gomez et al. (2014) to O$_3$ SCDs measured at 477nm and 0° elevation. 'No CF' is for 'no cloud filtering' and 'CF' for 'cloud filtering' meaning that only mostly clear-sky scans are selected.](image)

### 3.2 MOHp

The MAX-DOAS instrument operated by DWD at MOHp is similar to the one at ISSJ, i.e. an optical head collecting the scattered light at various elevation angles and connected through optical fibres to
thermally-stabilized UV and visible spectrometers. As illustrated in Figure 4, the instrument is pointing towards the North-West direction and also allows for downwards and upwards elevation angles.

![Figure 4: Pointing direction of the MAX-DOAS instrument at MOHp.](image)

As for ISSJ, the aerosol extinction and NO₂ vertical profiles are retrieved by applying an OEM-based profiling algorithm (the HEIPRO code; see Friess et al., 2006 and 2011) to measured O₃ and NO₂ SCDs. In contrast to ISSJ, measurements corresponding to negative viewing angles have been included in the profile inversion. The retrieval altitude range is 0.75-4.75km asl with 0.1km thick atmospheric layers. The time period investigated here is July – December 2012.

4 In-situ NO₂ measurements

The in-situ NO₂ measurements at ISSJ are performed within the framework of the WMO Global Atmospheric Watch (GAW) programme and NABEL, the National Air Pollution Network in Switzerland (Pandey Deolal et al., 2012). The site mainly resides in the free troposphere in the autumn and winter season, while in late spring and summer it is often influenced by the planetary boundary layer (PBL). The in-situ data involved in the present study have been provided by EMPA and correspond to consolidated hourly means (outliers due to local pollution by snowmobiles, helicopters, work at the station are filtered out). At MOHp, in-situ NO₂ observations are also performed within the framework of WMO/GAW. Generally, the site is affected by relatively clean air masses (yearly average of NOₓ is below 3.5 ppb), however, maximum values can sometimes reach 12–14 ppb, particularly during stagnant inversion conditions in winter when the site is within the boundary layer (Mannschreck et al., 2004).

5 Link between in-situ and MAX-DOAS NO₂ measurements

5.1 In-situ versus MAX-DOAS direct comparisons

In a first step, in-situ data have been directly compared to coincident MAX-DOAS near-surface concentrations at both stations. Figure 5 shows the time-series of timely coincident in-situ and MAX-DOAS NO₂ near-surface concentration for the July 2010-December 2012 period at ISSJ. The corresponding scatterplot is shown in Figure 6. Although the scatter of the data is important, a reasonably good correlation is found (R~0.7) with a slope of 1.14 indicating that MAX-DOAS concentrations are larger than in-situ.
Figure 5: Time-series of timely coincident in-situ and MAX-DOAS NO$_2$ near-surface concentration at ISSJ. MAX-DOAS data correspond to the NO$_2$ volume mixing ratio retrieved in the 3.6-3.8km altitude range (200m thick layer above the station).

Figure 6: Scatterplot of in-situ against MAX-DOAS NO$_2$ surface concentration. The number of comparison pairs is 1815.

Figure 7 shows the comparison between in-situ and MAX-DOAS NO$_2$ surface concentrations at MOHp for a selection of days in September 2012. The observation geometry is further illustrated in Figure 8.

A good consistency is found between both techniques in reproducing the diurnal variations of the NO$_2$ surface concentrations, including the short-term changes. This is further supported by the good correlation found between both data sets over the July-December 2012 period (R is equal to 0.67 on average for both clear-sky and cloudy conditions (1827 comparison pairs); R is significantly lower (0.13) in the presence of fog). It should be noted that 0.67 is similar to the R value derived at ISSJ.
These results show that a reasonably good agreement can be reached between both techniques, even if the spatial representativeness of the MAX-DOAS observations is not taken into account. This is probably related to the mostly remote character of the sites considered here. In the future, the consistency between MAX-DOAS observations at MOHp and in-situ measurements performed at the bottom of the hill will be also investigated. This could provide additional information on the relationship between surface measurements and the vertical distribution of NO$_2$.

### 5.2 Link between in-situ NO$_2$ surface concentrations and MAX-DOAS profiles

In a second comparison exercise performed by EMPA and using the ISSJ data only, the difference in spatial representativeness between both techniques is taken into account using the Lagrangian Particle Dispersion Model (LPDM) FLEXPART initialized with MACC re-analysis atmospheric composition fields (Inness et al., 2013). Back-trajectory simulations from FLEXPART are used to characterize the air mass history of both MAX-DOAS and in-situ sampling volumes and, in fine, to select comparison pairs having a similar air mass history. In the case of MAX-DOAS, a first approximation of the sampling volume is estimated from (1) the horizontal viewing distance derived by the modified geometrical approach (see Figure 3), (2) the pointing direction of the instrument (see Figure 1), and (3) the altitude boundaries defined by the profiling algorithm (see Section 3.1). These simulations also generate high-resolution vertical profiles which, when adjusted to match the surface in-situ observations, provide a set of reference tropospheric profiles to be compared to MAX-DOAS vertical profiles and corresponding columns. It should be noted that due to its short lifetime and its close link with NO, NO$_2$ is not transported separately in the model but in the form of NO$_x$ (sum of NO$_2$ and NO). The NO$_x$ loss is parameterised as a first order process with a seasonally-dependent lifetime from 5 hours in summer to 22 hours in winter (Schaub et al., 2007). The NO$_2$ concentration at the sampling volume is then derived by converting the NO$_x$ mole fraction to NO$_2$ assuming a photostationary equilibrium between O$_3$, NO, and NO$_2$ (during daytime, NO$_2$ is rapidly photolysed to form NO but also rapidly reformed by the reaction between NO and O$_3$).

Figure 9 shows comparison results for lower tropospheric columns (up to 4.1 km asl). For the July 2010 – December 2012 period, a total of 915 hourly MAX-DOAS/in-situ pairs remain after additional filtering of (1) the cases where the model adjustment by in-situ observations produced unrealistic corrections, and (2) remaining outliers due to local activities around the site. A moderate correlation ($R=0.59$) is found when comparing directly the MAX-DOAS lower tropospheric columns to the surface in-situ observations. The estimated bias of $-30 \pm 90$ ppt is in the range of the detection limit of the in-situ analyser. The adjustment of the FLEXPART model profiles with the in-situ measurements significantly increases the level of agreement between MAX-DOAS and in-situ ($R=0.7$ and mean bias $=-4 \pm 62$ ppt). The scatter of the data points is also largely reduced. These features indicate that the inclusion of both the horizontal representativeness of the MAX-DOAS observations and the transport history of the probed air masses
leads to a significant improvement of the comparability of both data sets. Regarding the regression slope, it increases from 0.8 to 1.2, which suggests that MAX-DOAS slightly over-estimates the lower tropospheric mole fractions. It should be also noted that applying the MAX-DOAS averaging kernels (AVKS) to the reference model profiles does not lead to significant changes in the comparison results due to the fact that AVKs are mainly focused in the first altitude layers close to the ground.

Figure 9: Linear regression analysis of mean free tropospheric (FT) NO\textsubscript{2} mole fractions as obtained from MAX-DOAS and in-situ observations at ISSJ. MAX-DOAS sub-columns up to 4.1 km asl were averaged (pressure weighted mean). Left plot corresponds to in-situ observations while right plot is for the reference model profiles adjusted to in-situ observations and smoothed by the MAX-DOAS averaging kernels. ‘Y-X’ is the mean bias and ‘BRMS’ is the standard deviation of the difference between MAX-DOAS and in-situ/reference observations.

6 Conclusions

The consistency between MAX-DOAS and in-situ NO\textsubscript{2} observations made in parallel at the two mostly remote sites of Jungfraujoch and Hohenpeissenberg has been investigated. In a first step, the NO\textsubscript{2} surface concentrations measured by both techniques have been directly compared. A reasonably good agreement is found between both data sets at both stations, with a correlation coefficient around 0.7. In a second comparison exercise involving the ISSJ data only, a more sophisticated approach has been developed. It consists of taking into account the history of the air volumes sampled by both instruments using back-trajectory simulations from the FLEXPART dispersion model initialized with atmospheric composition fields from the last MACC re-analysis. FLEXPART has been also utilized to generate reference model profiles adjusted or not by the in-situ observations. Considering the low NO\textsubscript{2} levels at ISSJ, a good overall agreement is obtained between MAX-DOAS lower tropospheric columns (3.6 - 4.1 km asl) and those derived from the in-situ-adjusted model profiles (correlation coefficient around 0.7; slope around 1.2). One of the most relevant features is that the adjustment of the model profiles with surface in-situ concentrations significantly improves the comparability of both data sets, with a correlation coefficient increasing from 0.59 to 0.71. This pilot study appeals for a further extension of the number of sites where MAX-DOAS and in-situ instruments are measuring in parallel tropospheric NO\textsubscript{2}. The complementarity of both techniques combined to back-trajectory model simulations could be used in the future to establish the link between in-situ networks and satellite nadir data.

7 References


