

Solar spectrophotometry for the retrieval of nitrogen dioxide (NO₂)

A comparison between Brewer and Pandora spectrophotometers in the frame of the BAQUNIN project



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NO₂ in the atmosphere

Nitrogen dioxide (NO₂) is a key component of the Earth's atmosphere,

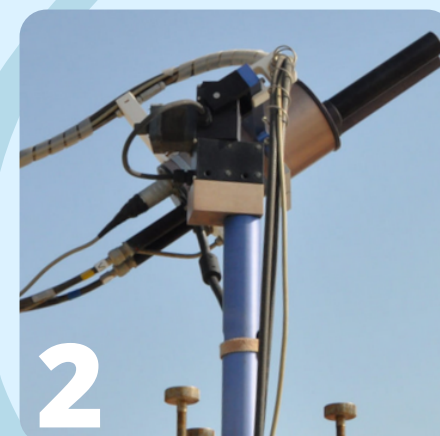
- driving several chemical reactions both in the stratosphere (production/destruction of ozone) and in the troposphere (photochemical smog);
- absorbing solar radiation, thus altering the radiative balance of the planet and interfering with other photometric measurements.

Brewer spectrophotometers

Brewer spectrophotometers have been deployed worldwide since the 1980's to retrieve the columnar content of ozone. Some of them (MkIV models) are capable of measuring visible solar radiation and retrieve the total column of NO₂. In Italy, only two MkIV Brewers are in operation, one at Sapienza – University of Rome (#067, Fig. 1) and one at the atmospheric observatory of ARPA Valle d'Aosta (#066).



Aim of the study



In the framework of the Boundary layer Air Quality Using Network of INstruments (BAQUNIN) project, launched in 2018, various instruments dedicated to monitoring (both along the atmospheric column and at the surface) of the main trace gases and aerosols are operated for purely scientific purposes or in the context of calibration and validation (Cal/Val) of satellite products.

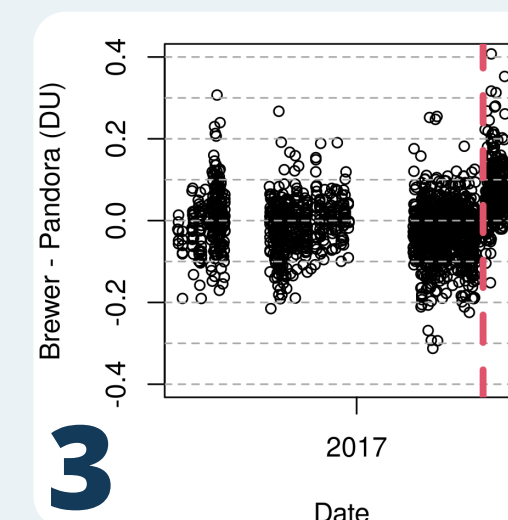
Aim of this study is the independent comparison of NO₂ retrievals between the Brewer spectrophotometer #067 and a co-located new-generation spectrophotometer, Pandora #117 (Fig. 2), this latter providing a complete dataset for the same site starting from 2016 (L2 data taken from <http://data.pandonia-global-network.org>, file version rnvslp1-7, processor v1.7.28). This will reinforce the reliability of NO₂ retrievals from Brewer #067, which date back to the early 90's. To our knowledge, this is the first NO₂ inter-comparison ever conducted between MkIV Brewer and Pandora instruments.

Results and conclusions

The results of the inter-comparison at the BAQUNIN supersite look promising (Fig. 4, Fig. 5). The metrics of the comparison (Pearson's correlation index: 0.97, slope 1.08, offset 0.04 DU, RMSD 0.06 DU, 90% of points within Pandora's confidence limits, no airmass dependence) are very satisfactory considering that the two instruments belong to very different technological generations. The advances beyond the current state of retrievals from Brewer #067, operating at Sapienza since the 1990's, will allow us to reprocess the whole NO₂ dataset for long-term trend studies.

Brewer algorithm details

- Brewer #067 was accurately characterised and calibrated with bootstrap methods (Herman et al, 2009). The algorithm developed by Diémoz et al. (2014), further adapted to the same spectroscopic dataset used by Pandora, was tested on the Brewer. The replacement of a neutral density filter in July 2017 introduced a problematic dependence with temperature, which limits the comparison to up to that date;



- As visible from Fig. 3, the retrieval is very sensitive to slight instrumental changes in the Brewer wavelength scale (e.g., jump in June 2017 due to replacement of the mercury lamp). The algorithm was updated and made less sensitive by introducing the derivative of the solar spectrum with respect to wavelength in the calculation;

- The resulting dataset was found to be slightly sensitive to the Brewer internal temperature. A correction similar to the one applied on ozone measurement is sufficient to further improve the results (Fig. 4).

References

- Herman et al., NO₂ column amounts from ground-based Pandora and MFDOAS spectrometers using the direct-sun DOAS technique: Intercomparisons and application to OMI validation, J. Geophys. Res., 2009
- Diémoz et al., Improved retrieval of nitrogen dioxide (NO₂) column densities by means of MKIV Brewer spectrophotometers, Atmos. Meas. Tech., 2014

