Long-term observations of halogen oxides in the Arctic: project overview and first results

EGU General Assembly 2024
EGU24-3149

Bianca Lauster[1,2], Sebastian Donner[1], Udo Frieß[2], Ulrich Platt[1,2], Lucas Reischmann[1], William Simpson[3], Steffen Ziegler[1], and Thomas Wagner[1,2]

1 Satellite Remote Sensing Group, Max Planck Institute for Chemistry, Mainz, Germany
2 Institute of Environmental Physics, Heidelberg University, Heidelberg, Germany
3 Department of Chemistry and Biochemistry & Geophysical Institute, University of Alaska Fairbanks, Fairbanks, AK, USA

Correspondance:
b.lauster@mpic.de

Link to Abstract

MAX PLANCK INSTITUTE FOR CHEMISTRY

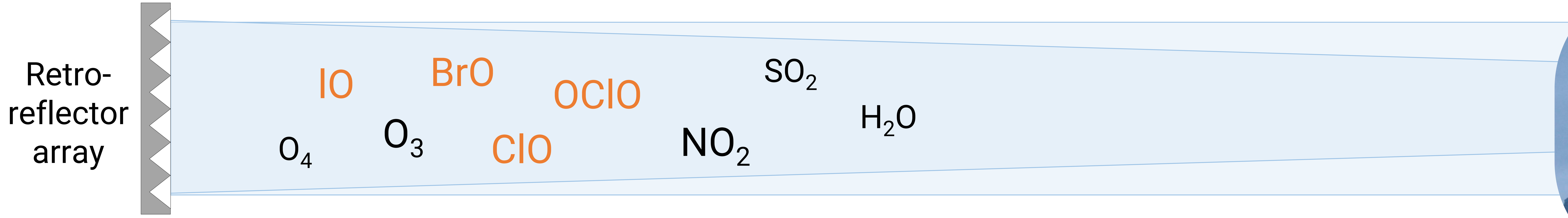
INSTITUTE OF ENVIRONMENTAL PHYSICS

UNIVERSITÄT HEIDELBERG ZUKUNFT SEIT 1386

UNIVERSITY OF ALASKA FAIRBANKS

Previous study by Nasse (2019):
High ClO abundances (> 100 ppt) in Antarctica

Atmospheric light path: 2 × 1.6 km = 3.2 km



Long-path DOAS

- Deployed in Utqiaġvik (Barrow), Alaska
- Year-round measurements

Influence by anthropogenic pollution

Sea ice / snow interaction

Implications on polar ozone chemistry and further processes

PICO SPOT 5.1

Long-term observations of halogen oxides in the Arctic: project overview and first results

Bianca Lauster[1,2], Sebastian Donner[1], Udo Frieß[2], Ulrich Platt[1,2], Lucas Reischmann[1], William Simpson[3], Steffen Ziegler[1], and Thomas Wagner[1,2]

1 Satellite Remote Sensing Group, Max Planck Institute for Chemistry, Mainz, Germany
2 Institute of Environmental Physics, Heidelberg University, Heidelberg, Germany
3 Department of Chemistry and Biochemistry & Geophysical Institute, University of Alaska Fairbanks, Fairbanks, AK, USA

EGU General Assembly 2024

EGU24-3149

Correspondance: b.lauster@mpic.de

Link to Abstract

MAX PLANCK INSTITUTE FOR CHEMISTRY

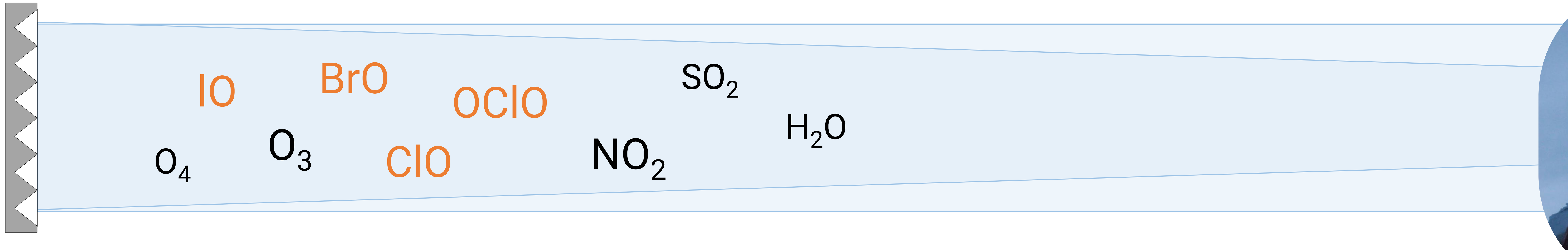
INSTITUTE OF ENVIRONMENTAL PHYSICS

UNIVERSITÄT HEIDELBERG ZUKUNFT SEIT 1386

UNIVERSITY OF ALASKA FAIRBANKS

Previous study by Nasse (2019):
High ClO abundances (> 100 ppt) in Antarctica

Atmospheric light path: 2 × 1.6 km = 3.2 km



Long-path DOAS

- Deployed in Utqiaġvik (Barrow), Alaska
- Year-round measurements

Influence by anthropogenic pollution

Sea ice / snow interaction

Implications on polar ozone chemistry and further processes

Introduction

Long-path DOAS

Setup in Utqiaġvik (Barrow), Alaska

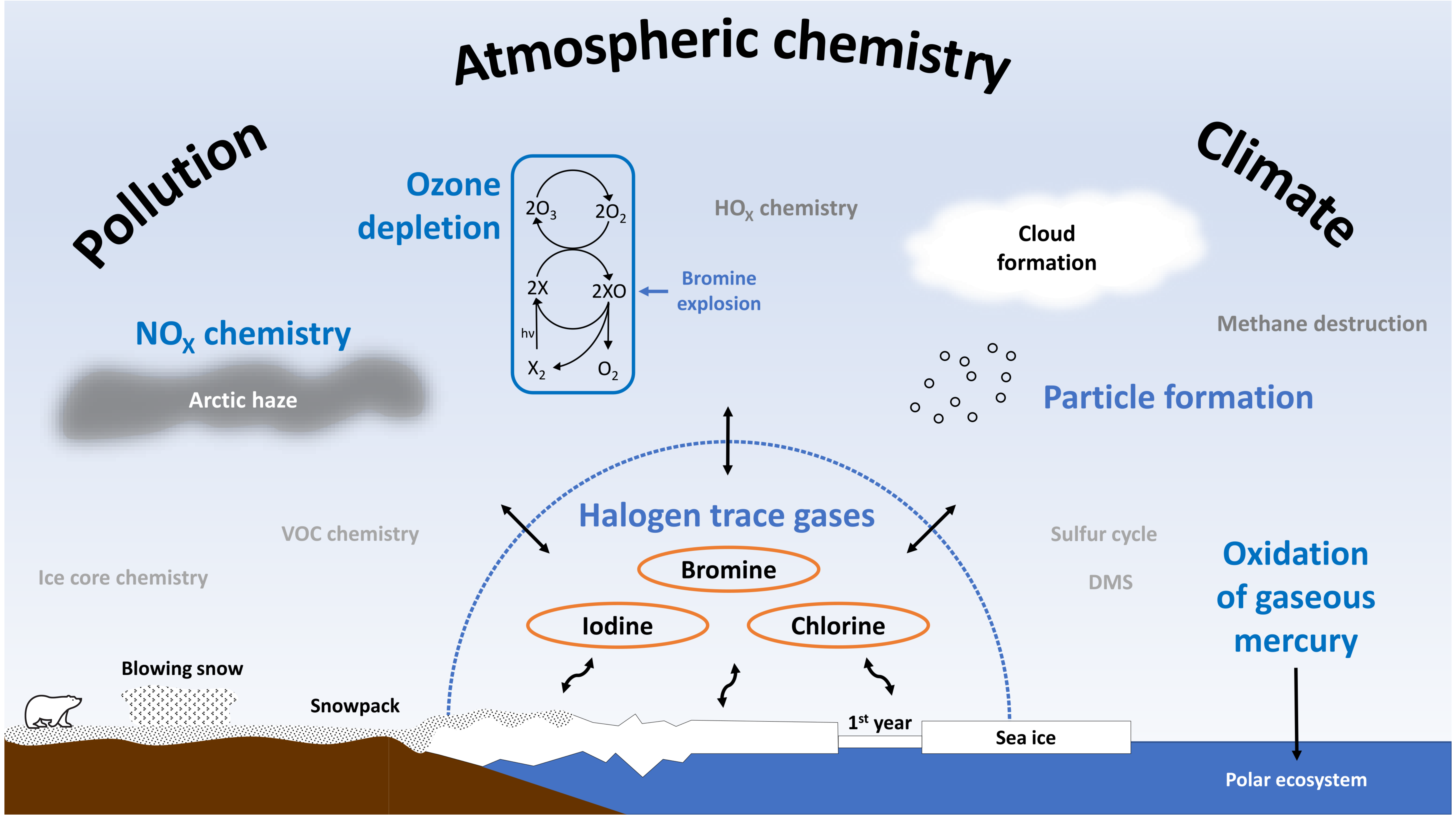
Measurement routine

Example analysis

First results & Outlook

References & Acknowledgements

Correspondance:
b.lauster@mpic.de
Link to Abstract



Simplified scheme on the impact of halogen chemistry in polar regions (Simpson et al., 2007, 2015; Saiz-Lopez and von Glasow, 2012).

- Polar regions are unique:
  - dominated by cold temperatures
  - stable stratification of the atmospheric boundary layer
  - heterogeneous chemistry at the interface to ice/snow surfaces
- Contrary to the pristine Antarctic atmosphere, the Arctic is affected by pollution due to atmospheric transport from lower latitudes
- Halogen chemistry is a central element of tropospheric ozone depletion events (ODEs) in polar spring
- Halogen (instead of ozone)-dominated oxidation alters lifetimes of species, e.g. mercury, in the environment
- Many other chemical reaction cycles are influenced by reactive halogen species
- Key processes such as source mechanisms of reactive halogen species, their transport and inter-halogen interactions are still not fully understood

⇨ We set up an instrument at Utqiaġvik (Barrow), Alaska to further enhance our understanding of halogen activation chemistry.

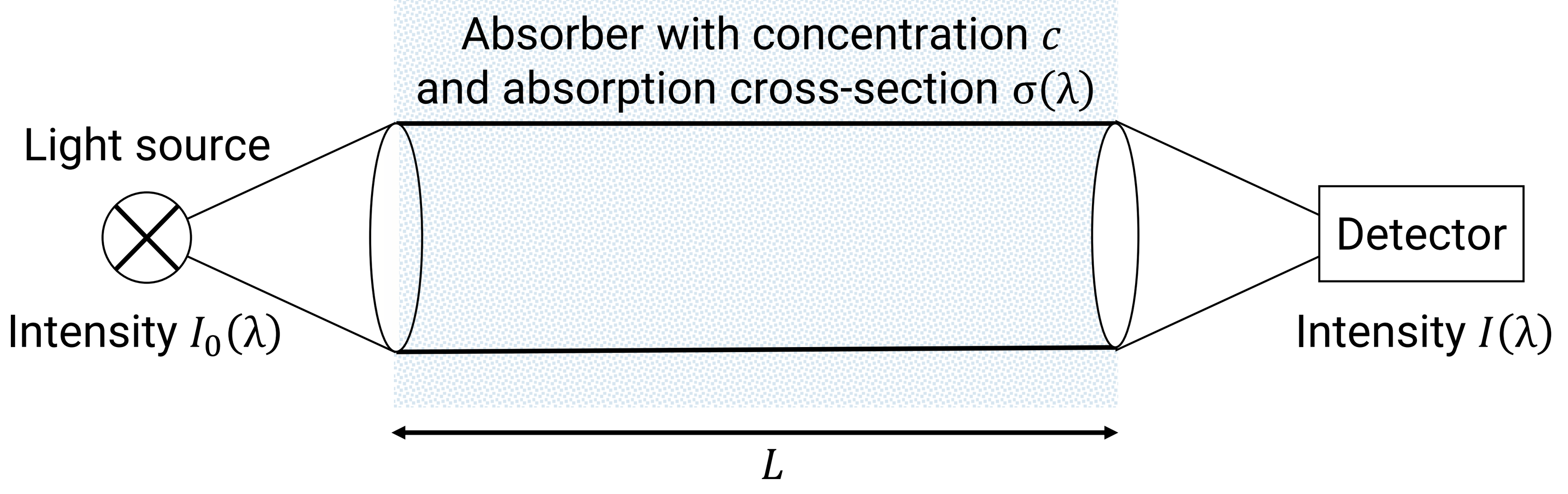
EGU General Assembly 2024
EGU24-3149

Correspondance: b.lauster@mpic.de

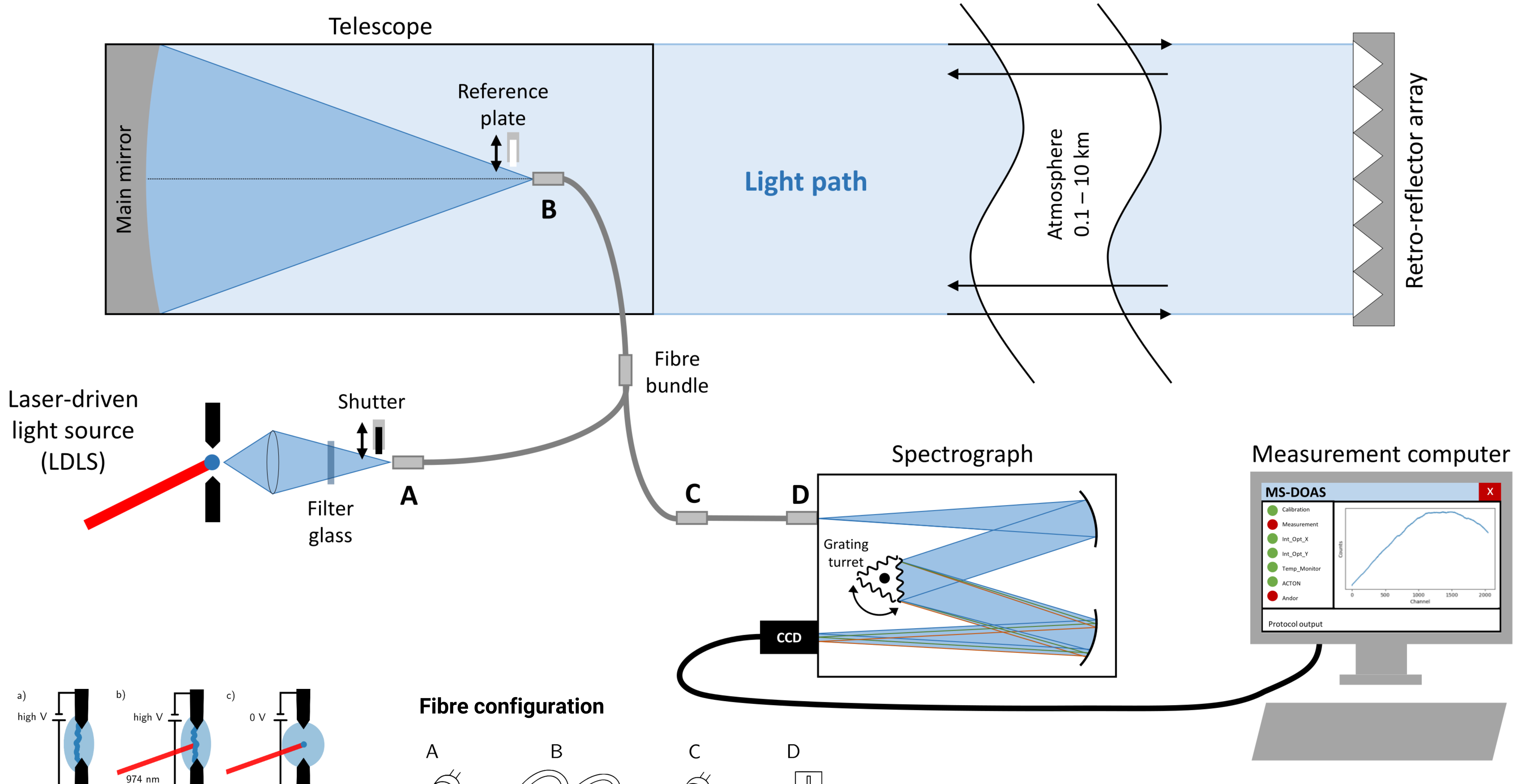
Link to Abstract

Lambert-Beer's law:

$$I(\lambda) = I_0(\lambda) \times \exp(-\sigma(\lambda)\, c\, L)$$



Adapted from Platt and Stutz, 2008.



Schematic depiction of the LP-DOAS setup. Adapted from Nasse, 2019.

Based on the DOAS (Differential Optical Absorption Spectroscopy) principle, the abundances c of various atmospheric trace gases with absorption cross-sections $\sigma(\lambda)$ along the light path L can be retrieved by applying Lambert-Beer's law.

Long-path DOAS (LP-DOAS) is an active DOAS application, i.e. an artificial light source is used.
⇨ Independent from sun light (esp. imporant during polar night)
⇨ Measurements in the short UV (below 300 nm) possible
⇨ Well-defined light path L (no radiative transfer calculations needed)
⇨ Highly sensitive to various halogen oxides and other trace gases
The instrument was purpose-built for its previous deployment in Antarctica (Nasse, 2019).

Technical details

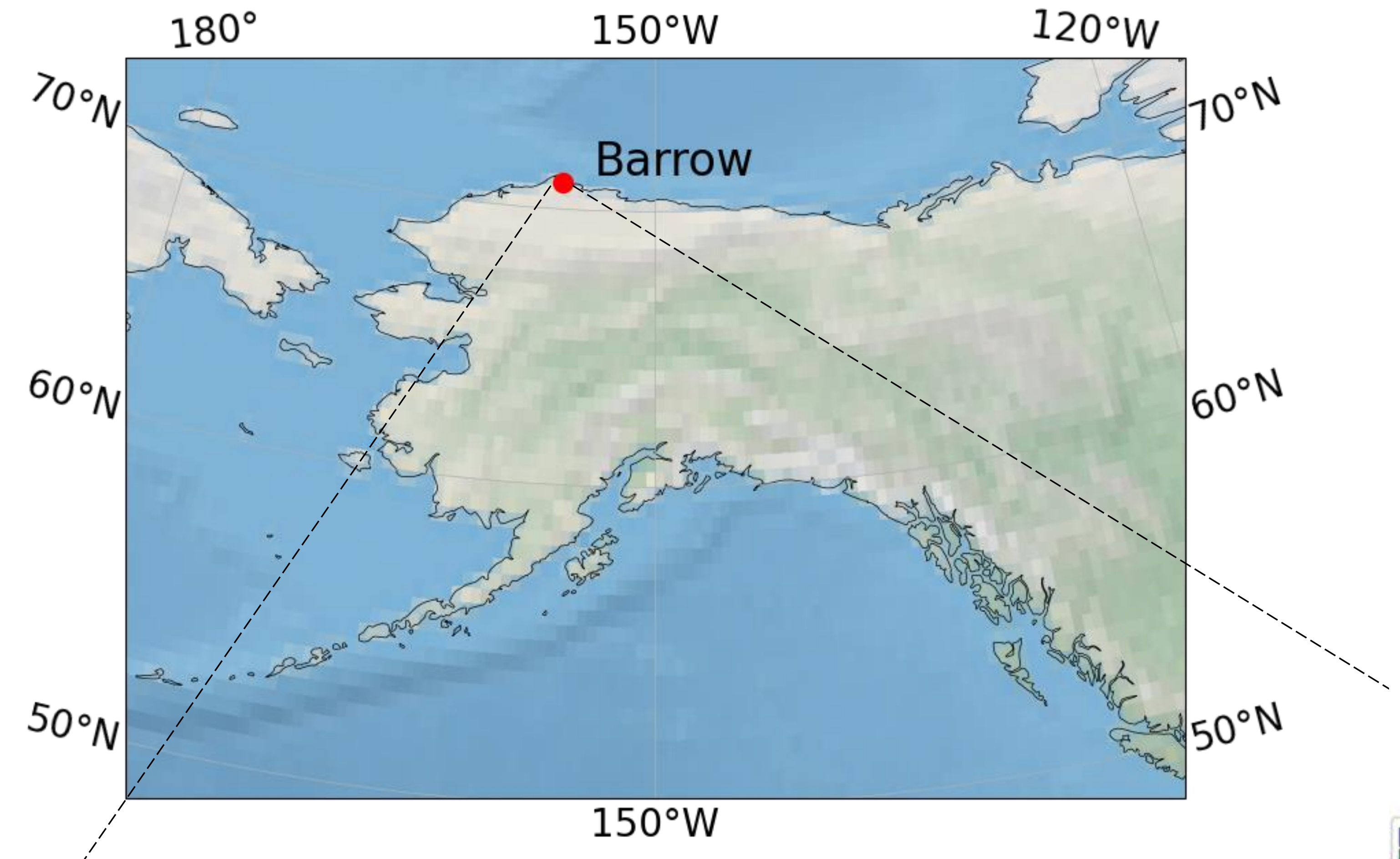
- Laser-driven light source (LDLS) emits at high intensity from 180 to 800 nm
- Stepper motors for pointing/focusing the beam (at A + B in the scheme)
- Temperature stabilised spectrometer box
- Spectrograph hosts two gratings (mostly 1200 gr/mm covering ca. 68 nm, coarser 600 gr/mm for specific purposes)
- Spectral resolution: ca. 0.6 nm

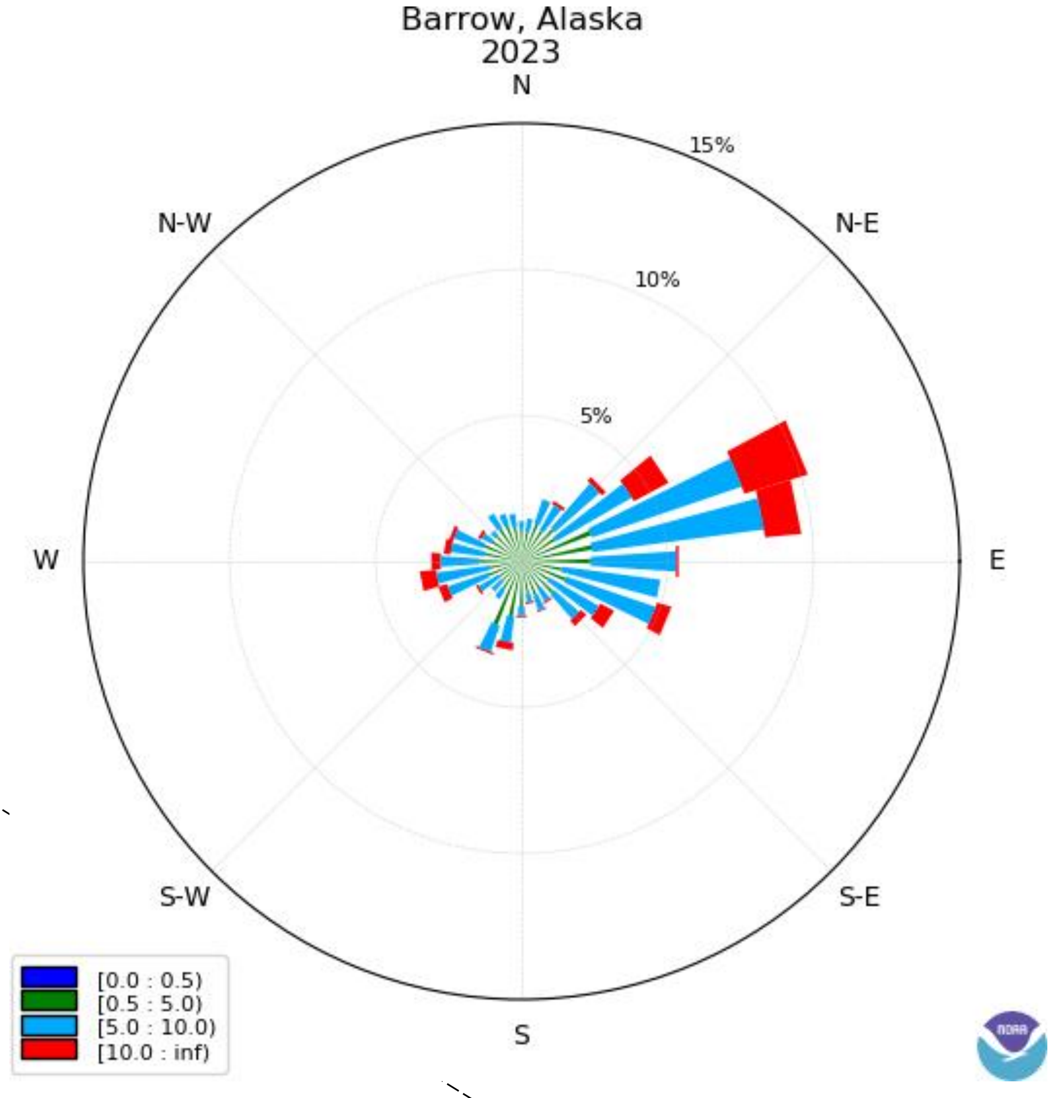
EGU General Assembly 2024

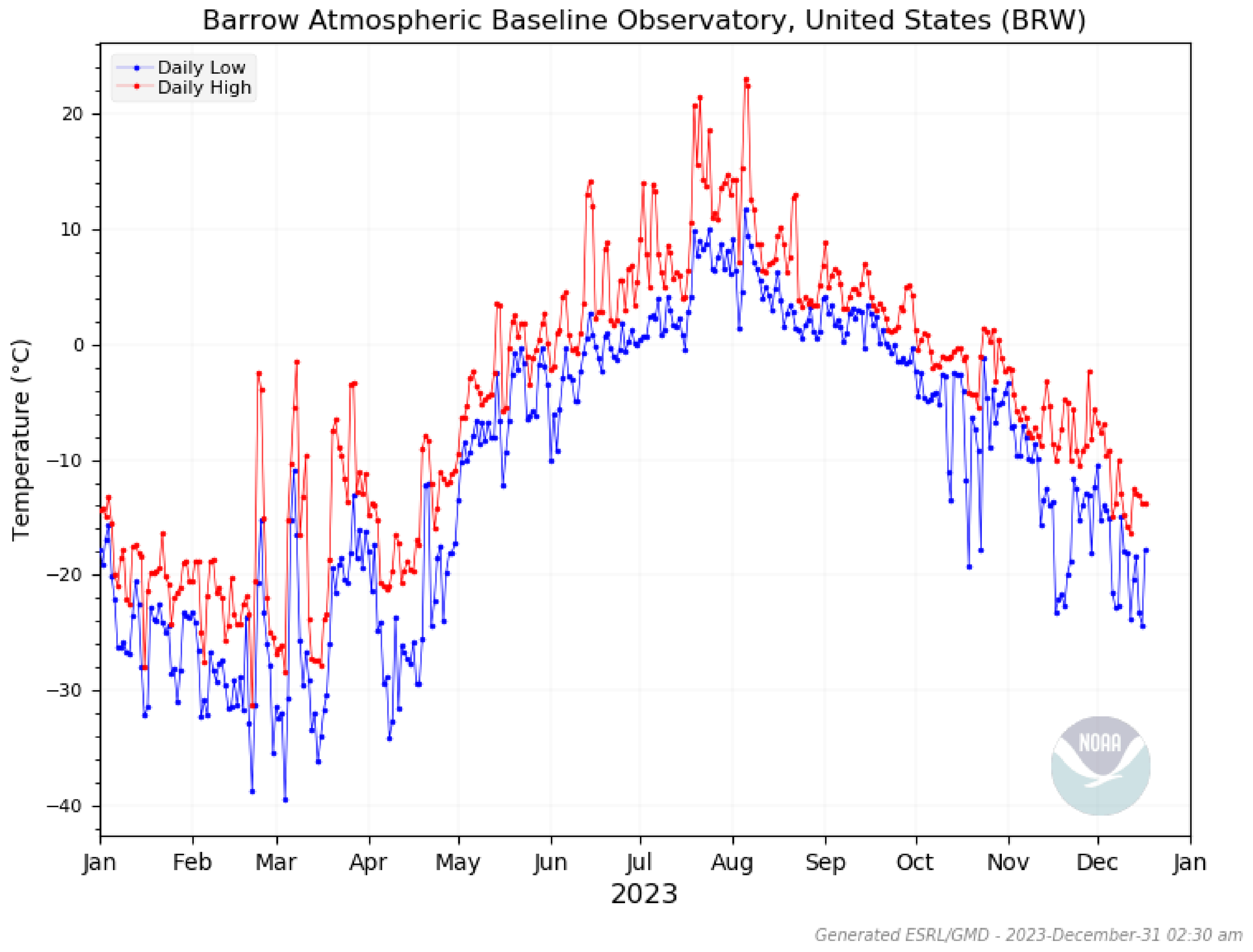
EGU24-3149

Correspondance:
b.lauster@mpic.de

Link to Abstract







Measurement site

- About 5 km south-east of Utqiaġvik (Barrow)
- Approx. 6 km south of the Chukchi Sea and ca. 15 km south-west of the Beaufort Sea
- Prevailing wind direction from the north-east, i.e. from the Arctic Ocean
- Prudhoe Bay and the North Slope of Alaska oil fields are located roughly 320 km to the east

LP-DOAS instrument

- Installed at two huts in the BEO (Barrow Environmental Observatory) area
- Runs mainly autonomously (only regular calibration + maintenance needed on-site)

↖
Minimum and maximum air temperatures (left) as well as wind speed and direction (right) for the year 2023 (taken from *https://gml.noaa.gov*).

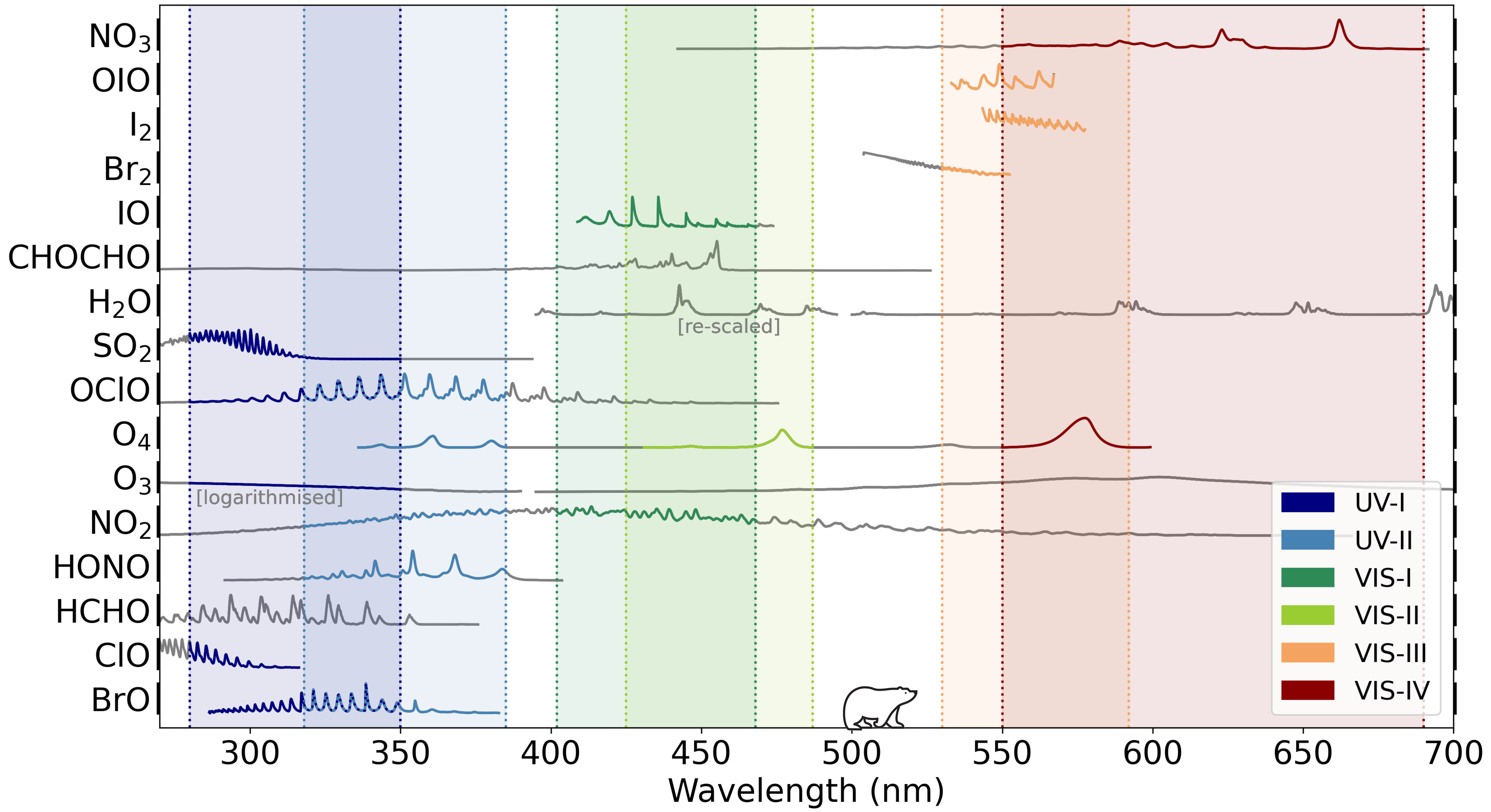
← Telescope mounted on the hut (top) in Barrow, Alaska, and its open side view (bottom).

EGU General Assembly 2024

EGU24-3149

Link to Abstract

Correspondance:
b.lauster@mpic.de



- Six different spectral windows cover wavelengths from nearly 280 to 690 nm (see Fig.)
- Alternating acquisition of atmospheric and reference spectra within each spectral window
  ⇨ Lower RMS compared to *classical* approach
- Correction of atmospheric background and instrumental effects by background measurements (i.e. with closed shutter)
- Temporal resolution of about 2 min between spectra within and approx. 30 min between the spectral windows for optimal conditions
- Lamp emission line spectra are measured manually to conduct wavelength calibration

← Normalised absorption cross-sections of fitted species in the six measured spectral windows (UV-I to VIS-IV). Coloured cross-sections are of particular interest.

Initialisation

Load configuration settings

Initialise variables

→

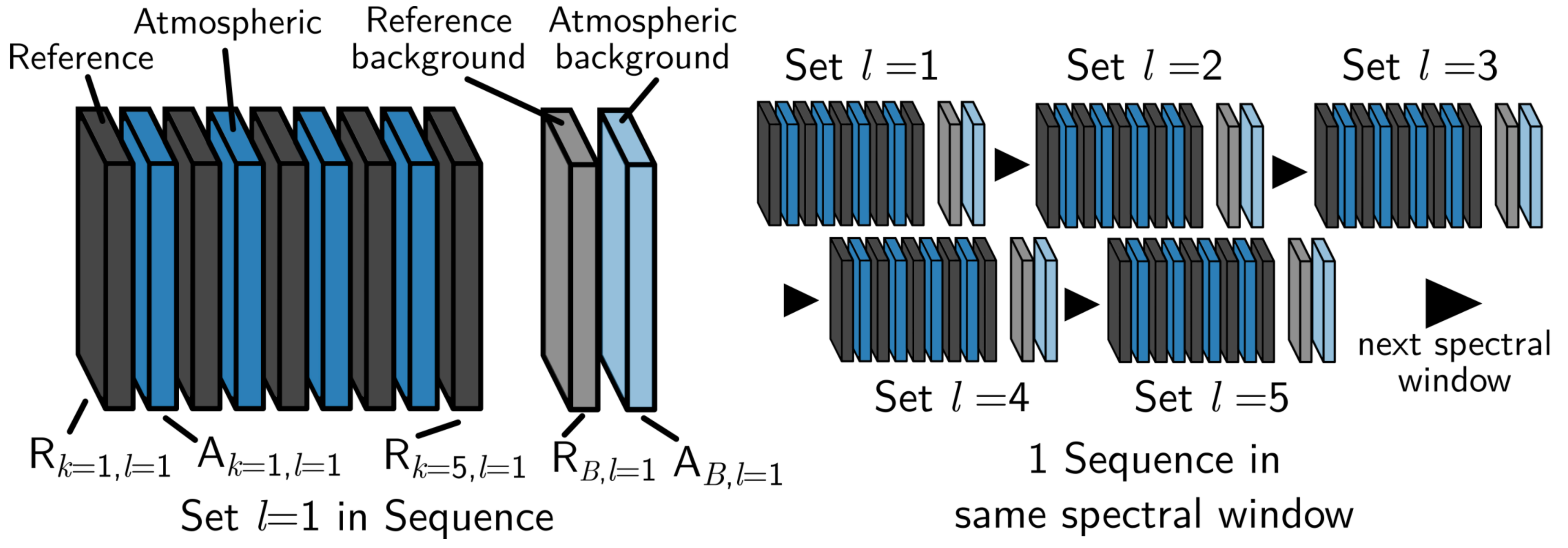
Measurement preparation

Check, if spectral window should be measured, and set motor positions and acquisition settings

→

Spectra acquisition

Iterate over spectrum pairs as illustrated (taken from Nasse, 2019)



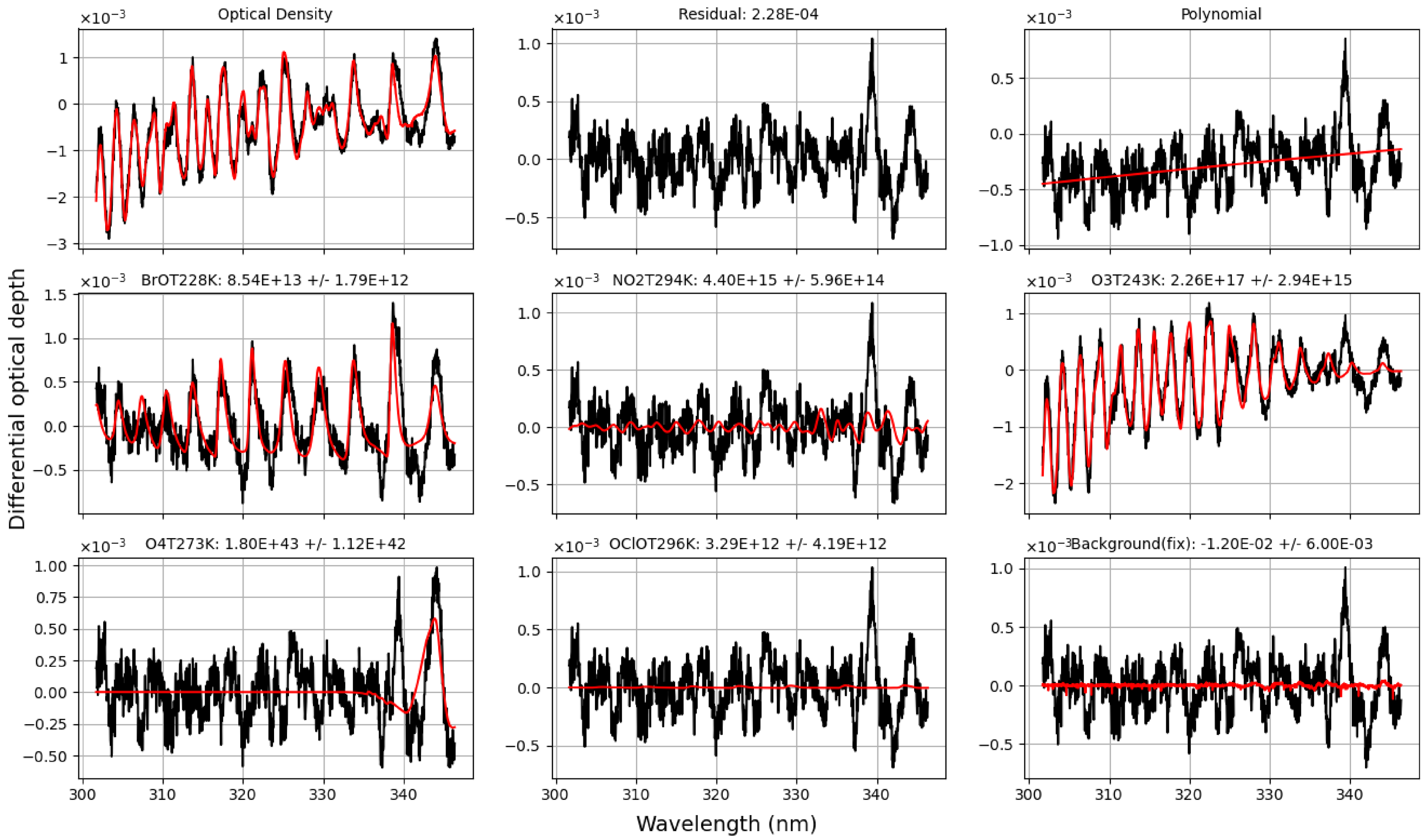
Continue with next spectral window

EGU General Assembly 2024

EGU24-3149

Link to Abstract

Correspondance:
b.lauster@mpic.de



Fit settings	
Fitting interval	301.7 - 346.4 nm (**UV-I**; left) 332.5 - 357.5 nm (**UV-II**; bottom)
High-pass filter	4000 iterations
Polynomial	3rd degree
Shift/Stretch	Applied to spectrum wavelengths
Fitted cross-sections	See fit examples

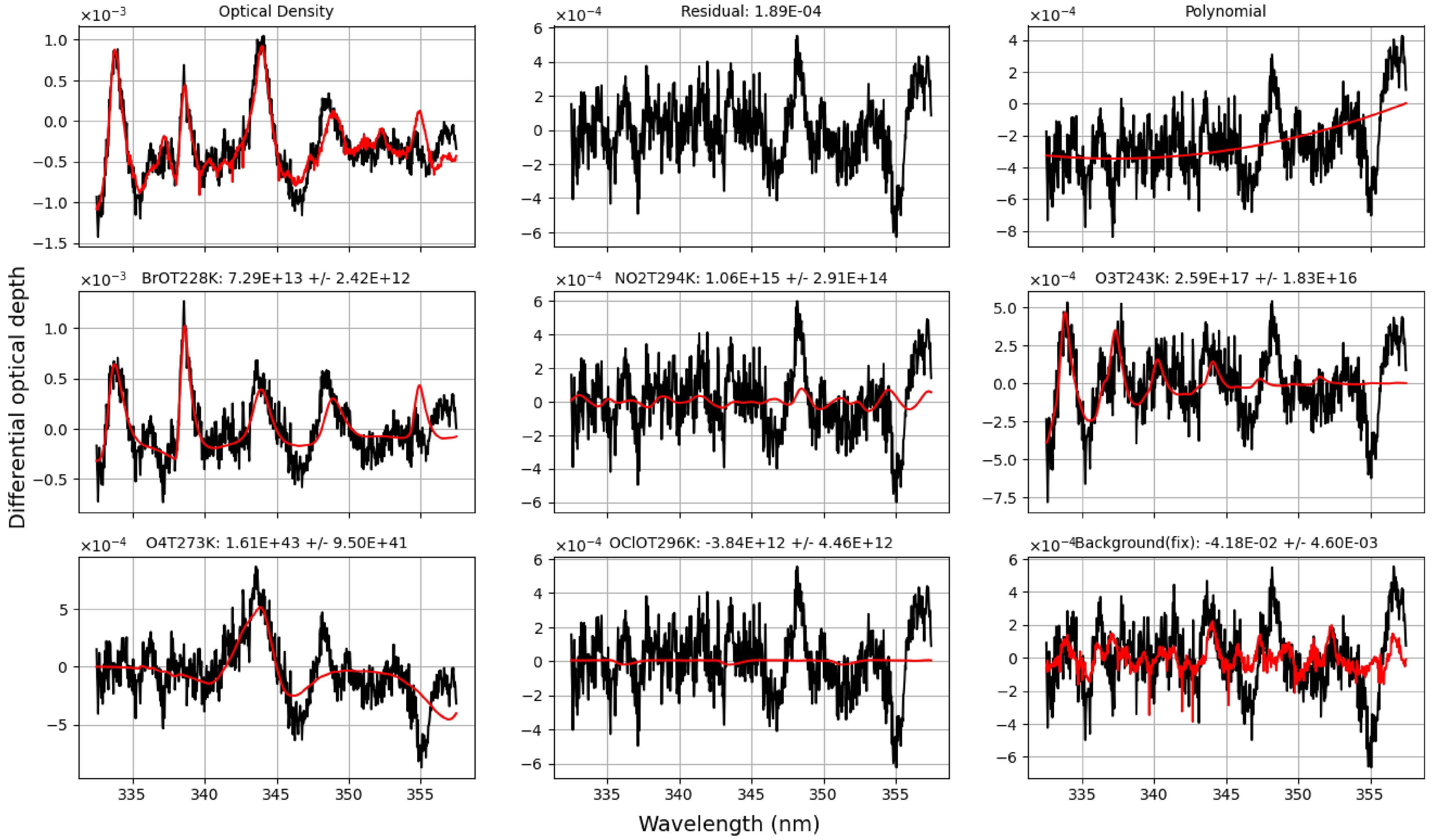
- Spectra are analysed using **heiDOAS** (Python-based fitting routine on the basis of the Levenberg-Marquardt algorithm)
- High-pass filtering accounts for broad-band spectral structures
- Additionally fitting a background spectrum accounts for further instrumental effects / temporal variations
- Small residual / RMS indicates good fit quality

↑

2024-03-29 05:16:22 to 05:25:20 UTC (UV-I)

2024-03-29 04:16:36 to 04:22:48 UTC (UV-II) →

Note that the optical density panel depicts the high-pass filtered ratio of the measured atmospheric spectrum and its respective reference spectrum.

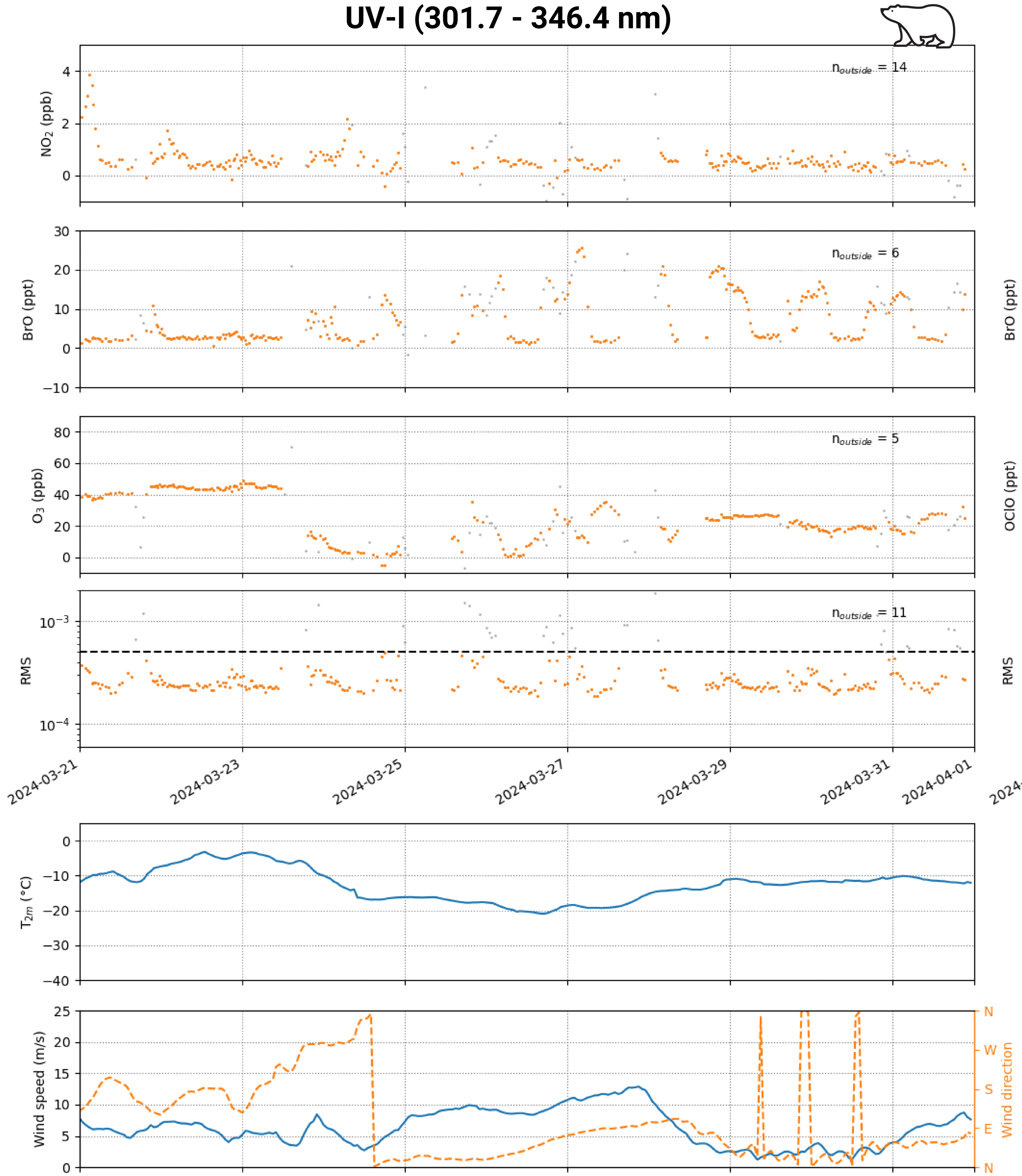


← Shown are fit examples of the UV-I and UV-II spectral windows. Each panel depicts the fitted cross-section (red) and the fit plus the residuum (black). The panel titels name the trace gas species, the temperature at which the cross-section was measured and the retrieved column in molec/cm^2.

As can be seen, still some systematic residual structures remain. These are subject of ongoing investigations in order to further improve the quality of the results.

Correspondance:
b.lauster@mpic.de

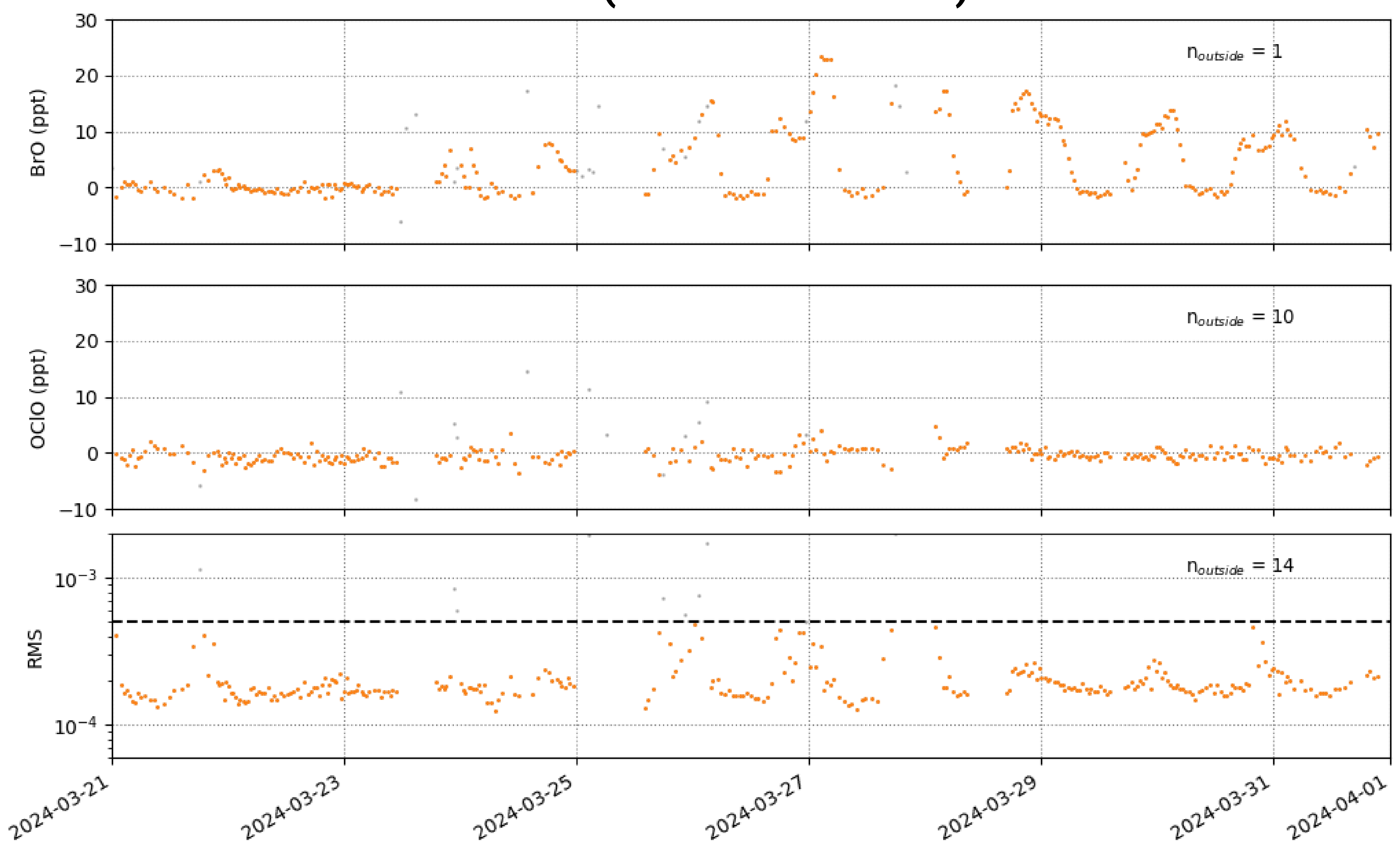
UV-I (301.7 - 346.4 nm)



Conversion of trace gas columns (SCD_i) to mixing ratios (x_i) using the light path length (L) and assuming *standard air* (273 K, 1013 hPa):

$$x_i = \frac{SCD_i\,[\mathrm{molec\,cm^{-2}}]}{\rho_V[\mathrm{cm^{-3}}]\times L\,[\mathrm{cm}]} \quad \text{with} \quad \rho_V = 2.69\times10^{19}\ \mathrm{cm^{-3}}$$

UV-II (332.5 - 357.5 nm)



These time series show preliminary results and work is ongoing to improve the data quality and to carry out further trace gas analyses.

$n_{outside}$ is the number of data points outside the plot ranges.

Meteorologica data are taken from ERA5 (Hersbach et al., 2023).

- Good agreement for retrievals of both spectral windows (compare BrO panels)
- Enhanced BrO abundances sometimes, but not always coincide with reduction in ozone

⇨ Indication for complexity of halogen chemistry

- OClO (and ClO – not shown) are up to now mostly below the detection limit

⇨ ClO > 100 ppt were measured in Antarctia by the same instrument (Nasse, 2019) and one particular aim is to see whether similar ClO episodes also occur in the Arctic

- Episodes with elevated BrO are only observed when the air originates from the Arctic ocean

Our study aims at a better understanding reactive halogen chemistry in the Arctic. For this, long-term measurements are conducted at Utqiaġvik (Barrow), Alaska, and following aspects studied:

⇨ Optimisation of LP-DOAS data analysis

⇨ Investigation of reactive halogen chemistry and ODEs with respect to meteorological conditions, and the importance of the different halogen species (chlorine ⬄ bromine ⬄ iodine), as well as upper limits of further trace gases (e.g., Br_2, I_2, …)

⇨ Comparison to MAX-DOAS measurements (i.e. trace gas profiles)

⇨ Comparison to satellite retrievals and models

EGU General Assembly 2024

EGU24-3149

Correspondance: b.lauster@mpic.de

Link to Abstract

ACKNOWLEDGEMENTS

We thank Cody Johnson, Charles Shutt and UIC Science for logistic and technical support throughout the initial setup and future work. Also, we acknowledge Jan-Marcus Nasse and the workshop of IUP Heidelberg for the thorough construction of the LP-DOAS instrument.

REFERENCES

Hersbach, H., Bell, B., Berrisford, P., Biavati, G., Horányi, A., Muñoz Sabater, J., Nicolas, J., Peubey, C., Radu, R., Rozum, I., Schepers, D., Simmons, A., Soci, C., Dee, D., Thépaut, J-N. (2023): ERA5 hourly data on single levels from 1940 to present. Copernicus Climate Change Service (C3S) Climate Data Store (CDS), DOI: 10.24381/cds.adbb2d47 (Accessed on 09-04-2024)

Nasse, J.-M.: Halogens in the coastal boundary layer of Antarctica, PhD thesis, Universität Heidelberg, Heidelberg, Germany, https://doi.org/10.11588/HEIDOK.00026489, 2019.

Platt, U. and Stutz, J.: Differential Optical Absorption Spectroscopy: Principles and Applications, Springer Science & Business Media, Berlin, Heidelberg, Germany, 2008.

Saiz-Lopez, A. and von Glasow, R.: Reactive halogen chemistry in the troposphere, Chemical Society Reviews, 41, 6448, https://doi.org/10.1039/c2cs35208g, 2012.

Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., Frieß, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., and Wolff, E.: Halogens and their role in polar boundary-layer ozone depletion, Atmospheric Chemistry and Physics, 7, 4375–4418, https://doi.org/10.5194/acp-7-4375-2007, 2007.

Simpson,W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and von Glasow, R.: Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, Chemical Reviews, 115, 4035–4062, https://doi.org/10.1021/cr5006638, 2015.