Bromine monoxide (BrO) measurements made using a MAX-DOAS (Multi-AXis Differential Optical Absorption Spectroscopy) instrument in the austral summer of 2016/17 during the Antarctic Circumnavigation Expedition (ACE).

***** Dataset abstract *****

To achieve the objectives of the project, we installed a MAX-DOAS (Multi-AXis Differential Optical Absorption Spectroscopy) instrument on the vessel "Akademik Tryoshnikov". This instrument is based on the DOAS technique, which is used to measure trace gas concentrations in the atmosphere. The method consists of the analysis of the spectral absorption lines that each trace gas produces in the solar spectra. The DOAS technique uses the narrowband features that every trace gas has in their spectral absorption coefficients. This differential cross section is unique and acts like a fingerprint for the trace gases, allowing to differentiate between them and to estimate their concentrations (for further details see Platt and Stutz, 2008).

In the past decades, atmospheric chemists have come to realize that halogen species (like Cl, Br or I and their oxides ClO, BrO and IO) exert a powerful influence on the chemical composition of the troposphere and through that influence affect the evolution of pollutants, hence having a significant impact on climate. These reactive halogen species are potent oxidizers for organic and inorganic compounds throughout the troposphere. In particular, halogen cycles can act on several compounds (such as methane, ozone, particles...), all of which are climate forcing agents through direct and indirect radiative effects. Dynamic exchange of halogens between ocean, sea ice, snowpack and atmosphere is the main driver for the frequent occurrence of Ozone Depletion Events (ODEs) and Atmospheric Mercury Depletion Events (AMDEs) (Saiz-Lopez and von Glasow, 2012).

In this dataset we present the mixing ratio and vertical column density of bromine monoxide (BrO) recorded in the austral summer of 2016/2017 in the Southern Ocean and Atlantic Ocean, averaged over one-hour time periods.

***** Original data collection *****

The data was collected by a MAX-DOAS instrument, which collects scattered sunlight at different viewing angles. The instrument was installed on board to measure ambient trace gases. It was built in our scientific laboratory (Atmospheric Chemistry and Climate, AC2), and it comprises two parts. The first one is the scanning telescope system, which is placed outside on the second deck of the ship, with a clear view of the horizon. It consists of a weatherproof metal chamber that is located on top of a stabilization system (gimbal table) in order to counteract the ship movements. Moreover, a GPS was also installed in order to save the latitude and longitude of the ship during the circumnavigation.

Additionally, an inclinometer was also attached to the gimbal table to record the actual pitch and roll of the instrument with the purpose of correcting the viewing elevation angles afterwards. The

metal chamber has a light collector that receives scattered sunlight. The incoming light is focused by a lens (F = 200 mm, diameter of 50.8 mm) onto an optical fiber which has 19 individual quartz fibers. The optical fiber is then connected to the second part (indoor), which comprises a spectrometer (Princeton Instruments SP500i), a charge-coupled device detector (CCD camera Princeton Instruments Pixis 400B) and a computer. Once in the spectrometer, the light is diffracted and dispersed by a 600 groove/mm grating resulting in a spectral window of 90 nm. This indoor part is located in a temperature-controlled laboratory. The instrument electronic offset and dark current are subtracted from each spectrum. The exposure time is adjusted automatically depending on the sunlight intensity in order to optimize the signal to noise ratio.

Raw measurements of optical spectra of ambient trace gases from which this dataset is derived is available (Benavent et al., 2020; DOI: 10.5281/zenodo.3827443), alongside GPS and inclinometer data.

It should be noted that scattered sunlight measurements can be strongly affected by clouds, mainly due to multiple scattering effects that give rise to large uncertainties in the light path retrieval. For this reason, we installed a camera alongside the MAX-DOAS in order to take live pictures of the sky every 5 minutes to evaluate a cloud index, which goes from 0 (clear sky) to 10 (completely overcast). Only spectra with a cloud index below 4 are taken into account for further analysis.

Images from the webcam from which this dataset is derived are also available (Benavent et al., 2020; DOI: 10.5281/zenodo.3827445).

Data was collected using in-house software which is responsible for saving the data and keep the instrument running. Finally, the spectra were saved for both spectral regions (UV and VIS) in ASCII text files.

Before the campaign, we calibrated the wavelength of the spectrometer. The method we used to do it was measuring the positions of atomic emission lines (Hg-Ne lamp) of known wavelengths. The atomic emission lines could be treated as delta functions; the Princeton software adjusts the individual lamp emission lines as a Gaussian function to determine the centre position and it automatically corrects if there is some wavelength shift.

***** Data processing *****

Once the campaign was finished, we received the raw spectra in our laboratory in order to analyse IO. In order to do this, first we filtered the data by cloud index, it means that only spectra with a cloud index below 4 are taken into account for further analysis.

Absorption spectroscopy is a well-established tool for the analysis of atmospheric trace gases. It is based on the Lambert-Beer law, which describes the exponential attenuation of the light intensity

as it passes through a given sample that contains certain absorber species. This decay depends on the absorbers concentration and the light path:

$$I(\lambda, L) = I_0(\lambda) \times \exp\left(-\sum_i \int_0^L \sigma_i(\lambda)\rho_i(s)ds\right)$$

where $\sigma_i(\lambda)$ is the absorption cross-section of the absorber i, $\rho_i(s)$ represents its concentration along the light path and I_0 and I are the intensities before and after the considered absorption processes, respectively. In our case, I_0 is the Fraunhofer reference solar spectrum (with no atmospheric absorption) while I stands for the recorded, ground-based spectrum, with all the absorption and scattering processes included. The integral is done over the actual photon path and the results are added for every absorber (Plane and Saiz-Lopez, 2006).

The fit is carried out on the differential structures of the spectra (DOAS, Differential Optical Absorption Spectroscopy). The spectra were analysed using the QDOAS software version 3.2, developed at BIRA-IASB (see http://uv-vis.aeronomie.be/software/QDOAS/). The direct product of the DOAS method is the DSCD (Differential Slant Column Density), which is the concentration of a given absorber integrated along the effective light path relative to the amount of the same absorber in a measured reference spectrum. These DSCDs are the main input for the profile algorithms, which are able to characterise how gas concentrations are spatially distributed. The quality filters applied in this step are the following, we discarded:

- DSCDs with an absolute value lower than twice the estimated detection limit: lower residual (in optical density units) divided by the maximum value of the differential absorption cross section.
- DSCDs with a RMS of about 0.01 in optical density units or a relative uncertainty higher than 1.

Once we get the filtered DSCDs, we move to the RTM (Radiative Transfer Model) to convert the DSCDs into vertical profiles. We use bePRO to infer the vertical profile, developed at BIRA-IASB (Clémer et al., 2010). The calculation is based on the Optimal Estimation Method (OEM; Rodgers, 2000) and it consists of a two-step approach: first, the aerosol extinction vertical profiles are retrieved and then, once the aerosol influence in the irradiance attenuation is subtracted, the process can be repeated again for the trace gases. The final product of the process is the vertical concentration profile, along with its corresponding vertically integrated amount: Vertical Column Density (VCD).

The profiling tool simulates the atmosphere regarding different processes such as the aerosol loading, species composition, temperature and pressure profiles, and so on. This allows the determination of simulated DSCDs in a way that tries to optimize the difference with respect to each measured DSCDs scanning cycle. The long-term comparison between them is representative of the goodness of the adjustment.

***** Quality checking *****

Please see the data processing section for details about flags that were applied.

***** Standards *****

This dataset uses widely accepted standards for atmospheric sciences.

***** Further information for interpreting the data and using the dataset *****

Filters: Details of filters used within this dataset can be found in the data processing section.

Timescales: the data are averaged over a period of an hour, meaning that a certain value X at time 14:00 UTC is the average of all the values of the given variable between 13:30 and 14:29 UTC.

Interpolation: an interpolation to increase the time resolution of the data is not recommended, because our results are close to our detection limit. Moreover, there are several physical and chemical considerations to take into account. Therefore, we considered the interpolation to be too risky.

Aggregation to lower temporal resolution: the data can be averaged over a lower resolution grouping (i.e. daily, or every six hours…)

***** Dataset contents *****

- ace_bromine_monoxide_atmospheric_measurements.csv, data file, comma-separated values
- data_file_header.txt, metadata, text
- README.pdf, metadata, PDF/A-1a
- README.txt, metadata, text

***** Dataset contact *****

Alfonso Saiz-Lopez, Department of Atmospheric Chemistry and Climate, Spanish National Research Council (CSIC). ORCID: 0000-0002-0060-1581. Email: a.saiz@csic.es

***** Dataset license*****

This dataset of atmospheric bromine monoxide measurements from ACE is made available under the Creative Commons Attribution 4.0 International License (CC BY 4.0) whose full text can be found at https://creativecommons.org/licenses/by/4.0/

***** Dataset citation *****

Please cite this dataset as:

Benavent, N., Garcia-Nieto, D., Cuevas, C.A. and Saiz-Lopez, A. (2020). Bromine monoxide (BrO) measurements made using a MAX-DOAS (Multi-Axis Differential Optical Absorption Spectroscopy) instrument in the austral summer of 2016/17 during the Antarctic Circumnavigation Expedition (ACE). (Version 1.0) [Data set]. Zenodo.