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**BrO measurements
over the Eastern
North-Atlantic**

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BrO measurements over the Eastern North-Atlantic

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Abstract

The aim of the work presented here was to detect BrO in the marine boundary layer over the Eastern North-Atlantic by Multi AXis-Differential Optical Absorption Spectroscopy (MAX-DOAS) of scattered sunlight. With this technique, information about the concentration and the vertical profile of trace gases in the atmosphere can be gained. BrO can be formed in the marine atmosphere by degradation of biogenic organohalogenes or by oxidation of bromide in sea salt aerosol. BrO influences the chemistry in marine air in many ways, e.g. since it catalytically destroys ozone, changes the NO₂/NO-ratio as well as the OH/HO₂-ratio and oxidises DMS. However, the abundance and the significance of BrO in the marine atmosphere are not yet fully understood.

We report on data collected during a ship cruise, which took place along the West African Coast in February 2007, within the framework of the Surface Ocean Processes in the Anthropocene project (SOPRAN). Tropospheric BrO could be detected during this cruise at peak mixing ratios of (10.2±3.7) ppt at an assumed layer height of 1 km on 18 February 2007. Furthermore, it was found that the mean BrO concentrations increased when cruising close to the African Coast suggesting that at least part of the BrO might have originated from the African coast.

1 Introduction

The halogen compound bromine oxide (BrO) plays an important role in stratospheric chemistry (where it was first detected by Molina and Rowland, 1974) as well as in the troposphere, because of its ability to destroy ozone in a catalytic reaction cycle (e.g. von Glasow and Crutzen, 2007). In the troposphere, BrO was first positively identified in polar regions (e.g. Tuckermann et al., 1997), where it can lead to total ozone depletion (Barrie et al., 1988; Bottenheim et al., 1990). Furthermore, BrO is found, although at smaller concentrations, in the marine boundary layer (MBL) in mid-latitudes (e.g. Leser et al., 2003; Saiz-Lopez et al., 2004).

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Since the sources, the reactions, and the loss processes of BrO in the MBL are not yet completely understood, estimations of BrO concentrations have large uncertainties. Furthermore, investigations concerning this topic are rare, in particular over the open ocean. This work, therefore, describes BrO measurements in the MBL of the Eastern North Atlantic in February 2007, which were performed to gain more insights in the BrO abundance in this area.

Reactive bromine is released to the MBL by different processes. First by autocatalytic liberation from sea salt aerosols, from which Br₂ or BrCl can be released, yielding Br after photolysis (Fan and Jacob, 1992; Vogt et al., 1996).

Bromine can also be released from volatile organohalogens (like CHBr₃), which are emitted by marine algae and accumulate in the troposphere (e.g. Quack et al., 2004). The latter source is very strong near the coast or in upwelling region (see for example the recent measurements by Carpenter et al., 2009).

Organohalogens are also emitted by halophytes (e.g. Rhew et al., 2000), which are plants (e.g. mangroves in tropical regions) growing in areas with high salt concentrations like salt marshes, mangrove regions or seashores. However, their importance as source for halogens in the atmosphere is still unclear (Varner et al., 1999). The organohalogens emitted by marine algae or by halophytes can be photolysed or react with OH, thus forming bromine radicals. Bromine atoms in the troposphere are quickly oxidised by O₃ yielding BrO.

Dust plumes are another abiotic factor that might influence the release of halogen compounds in the marine boundary layer. It is widely accepted that dust provides an important reactive surface (Usher et al., 2003) and that there might be reactions of halogens on dust surfaces or releases of reactive halogen species from dust. However, the extent of its influence is not known yet. Also a liquid-phase reaction of HOBr (see below) with BrO can lead to the so-called “bromine explosion” (Platt and Lehrer, 1996; Wennberg, 1999), which derives its name from the exponentially increasing release of reactive bromine into the gasphase. This process appears to dominate in polar regions, but may also play a role elsewhere.

Reactive bromine species can have various influences on the chemistry in the boundary layer. It can destroy ozone, change the NO/NO₂ and the OH/HO₂ ratio or oxidise dimethylsulfide (DMS) (for a more detailed description see e.g. Simpson et al., 2007).

5 There are two ozone destroying cycles in the troposphere involving Br. In both cycles, Br is oxidised by O₃, which – in turn – can be reduced to Br in two different ways: first, BrO reacts with HO₂ to form HOBr. Next, the hypobromous acid is photolysed and recycles back Br and the hydroxyl radical. This cycle typically dominates when low bromine radical levels are present, as found in the MBL. The other ozone destroying
10 cycle is a self reaction or cross reaction of two halogen oxide molecules, but it plays only an important role at high BrO levels, e.g. in polar regions or over salt pans. More details can be found e.g. in von Glasow and Crutzen (2007).

Leser et al. (2003) were the first to directly detect bromine monoxide in the marine boundary layer in mid-latitudes. They found a maximum concentration of 2.4±2.1 ppt
15 (assuming a layer height of 1 km) north of the Canary Islands at 13° W and 30° to 37° N. Later, Saiz-Lopez et al. (2004) measured BrO by LP-DOAS at Mace Head, on the west coast of Ireland, with a maximum daytime concentration of 6.5 ppt. Further shipborne measurements at mid latitudes with a minimum daytime value of 3 ppt were made by Ibrahim (personal communication). These investigations were also undertaken close
20 to the Canary Islands. Very recent LP-DOAS BrO and IO measurements by Read et al. (2008) at Sao Vicente (Cape Verde Islands) also showed nearly continuous presence of daytime BrO in the tropical marine boundary layer.

The BrO measurement presented here were performed using the MAX-DOAS technique, as introduced by Hönninger and Platt (2002), during a cruise (P348) of the
25 German research vessel Poseidon from Gran Canaria via the Cape Verde Islands and back along the West African Coast to Gran Canaria (see Fig. 2). The cruise took place from 8 to 24 February 2007. The West African Coast is an interesting site for the investigation of BrO, since the biological activity is very high in this region. This is caused by the large upwelling region there and the strong dust impact from the Sa-

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hara Desert (e.g. Middleton and Goudie, 2001). Furthermore, the Mauritanian coast is nearby, where halophytes occur in a significant amount. Thus, air masses coming from there might contain organohalogenes emitted from these plants.

During the whole cruise, continuous measurements were undertaken to detect BrO in the MBL. Also iodine oxide was measured, the precursors of which are emitted mainly by algae. However, the IO level never exceeded the detection limit, which was estimated to (0.77 ± 0.55) ppt.

2 The measurements

We applied the MAX-DOAS technique, which analyses scattered sunlight at different elevation angles (the angles between the viewing direction and the horizontal direction). This implies, that light reaching the telescope at a smaller elevation angle has travelled a longer path through the investigated tropospheric trace gas layer (with a given vertical extension). Thus, information about the vertical distribution of tropospheric trace gases is obtained. The height of the layer and its trace gas concentration can be concluded from the measurements (Hönninger et al., 2004).

The data analysis yields slant column densities S (SCD), which are defined as the integrated concentration c along the light path L . The SCD is dependent on the length of the light path and thus on the number of scattering events in the atmosphere. Also the elevation angle α influences the magnitude of the SCD. Since L is difficult to determine, a more general dimension, the vertical column density V (VCD) is introduced. The VCD is defined as the concentration c integrated along the vertical height z and is independent from the line of sight and the actually observed light path.

S and V can be transferred into one another using the air mass factor A (AMF), which is the ratio of S and V , $A = \frac{S}{V}$. A takes into account the radiative transfer within the atmosphere and can be determined using radiative transfer models. In the here presented work the model McArtim (Deutschmann, 2008) was applied to calculate the air mass factors. Also the layer height h can be estimated using this model. The trace

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gas concentration c can then be derived through the relation $c=V/h$.

2.1 The instrument

The MAX-DOAS instrument consists of three separate telescopes, that are connected via quartz fibre bundles (7 fibres per bundle) to an Acton Spectra Pro 300 Imaging Spectrometer with an Andor CCD Camera (DV 420-OE). The 2-D – detector (1024 by 256 pixels) records the spectra of the three telescopes simultaneously. This is accomplished by illuminating a CCD chip with a fiber bundle from each telescope. (The radiation collected by each telescope illuminated 50 of the 256 rows of CCD-detector pixels.) For that purpose, the fiber endings are arranged in a column at the spectrometer entrance slit. The telescopes were placed on a gimbal mount, which compensates for the pitch and roll of the ship. The entire set up was mounted at the top deck. The line of sight of one telescope was in direction of the bow of the ship. In order to increase the total observed area, the two other telescopes had a slightly offset azimuth angle (about 20°) to the left or right of the centre telescope, respectively. Each of the three telescopes measured the same sequence of elevation angles (see below) shifted in phase to each other. Thus the time required to record one set of elevation angles was reduced and the total time resolution improved. Spectra were recorded in the ultraviolet/visible wavelength range from circa 330–460 nm. A more detailed description of the instrument can be found in Wagner et al. (2004).

2.2 Field measurements

The data were collected during the ship cruise P348 on board the research vessel “Poseidon”, within the framework of the Surface Ocean PRocesses in the ANthropocene project (SOPRAN) from 9 to 24 February 2007. During daylight hours continuous measurements were taken throughout the entire duration of the cruise. One measurement series (a set of 6 to 8 different elevation angles) took between 10 and 20 min, depending on the light conditions. The set of elevation angles used was modified several times

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in order to optimize the measurements. However, the angles 6°, 3°, 2° and 1°, which are most sensitive for tropospheric trace gases, were always included. The Fraunhofer reference spectra (FRS) were taken under a 80° elevation angle, since the light path under a 90° angle was blocked by a mast of the ship. Measurement interruptions occurred due to malfunctions of the instrument producing discontinuity in the data series lasting from half an hour to two hours.

2.3 Data analysis

The recorded spectra were analysed for BrO with the Differential Optical Absorption Spectroscopy method (Platt, 1994) using the software WinDOAS (vanRoosendaal and Fayt, 2001). Thereby, the characteristic absorption structures of the trace gases are used for their identification in the recorded spectra. A wavelength range from 346 nm to 359 nm was chosen, where the BrO absorption features are still significant, while at the same time the influence of overlapping absorption structures due to ozone is minimised. Furthermore a dark current and an offset spectrum were recorded at regular intervals to account for detector dark signal and electronic offset.

During the analysis process, in addition to the trace gas literature spectra several other spectra are fitted simultaneously to the logarithm of the measured spectra using the least-squares method (Stutz and Platt, 1996). These spectra are a Fraunhofer spectrum (FRS), a Ring spectrum, a polynomial, the corresponding trace gas spectra and an additive polynomial.

The FRS accounts for the solar Fraunhofer lines as well as for diode to diode variations. It was taken with the same measurement device at an 80° elevation angle (see above). The second order polynomial represents broad band structures and the constant additive polynomial was included to account for stray light in the spectrograph. The Ring spectrum (Grainger and Ring, 1962) accounts for the effect of rotational Raman scattering in the atmosphere, it was calculated from the respective FRS with DOASIS (Kraus, 2006). The trace gas reference spectra, which were considered in this wavelength range were a BrO spectrum by Wilmouth et al. (1999), a NO₂ spectrum at

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220 K and one at 294 K, both by Vandaele et al. (1998), an O₃ spectrum at 223 K and one at 273 K, both by Bogumil et al. (2003). An example of a BrO fit resulting in high BrO column densities (2.11×10^{14} molec/cm²) is shown in Fig. 1.

Since a FRS is included in the fit the analysis does not yield SCDs but rather “differential” slant column densities (DSCDs) for the fitted trace gases, $DSCD(\alpha) = S(\alpha) - S_{ref}(80^\circ)$, with α being the investigated elevation angle and $S_{ref}(80^\circ)$ the slant column density of the chosen FRS. Two methods to determine DSCDs were applied in the here presented work, which differ in the way the FRS is selected. In the first, the spectra of the entire day are analysed using a fixed FRS taken at noon of the same day. Thus, the stratospheric trace gas columns, which change over the course of the day, show up in the results of this analysis. These DSCDs are denoted dSCDs. The second method yields Δ SCDs, which are evaluated using the FRS closest in time to the respective measurement spectra (i.e. the measurement at $\alpha=80^\circ$ recorded as part of either the previous or the current set of elevation angles). This method has the advantage, that the stratospheric signal can largely be neglected, since the stratospheric BrO column changes during a single scanning sequence are very small (except for the early morning and late evening). The Δ SCDs values, therefore, essentially only reflect the tropospheric BrO signal.

2.4 Radiative transfer modelling

The dSCD values retrieved from the data analysis are compared with calculations of the radiative transfer model McArtim in order to determine the height h and the VCD of the BrO layer.

Two simulations were run eventually. In the first, the known height profile of the trace gas O₄ was used to estimate the aerosol profile present in the atmosphere, which is a strong influence factor to the optical properties of the atmosphere (e.g. Wagner et al., 2004). Thereby, O₄ air mass factors were modelled using arbitrary a priori aerosol profiles as input. These were compared to air mass factors, which were calculated from measured O₄ dSCD – also gained within the BrO data analysis – using the known

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vertical column density of O_4 , as described in more detail in Sinreich et al. (2005). The aerosol profile was changed until a good match between the modelled and calculated AMFs was obtained. In the second simulation run, which derived the BrO profile, the best fitting aerosol profile was used as fixed input. Assuming a layer with constant BrO concentration (defined as box profile) the height of this BrO layer could be yielded.

The following correlation was applied comparing simulated BrO AMFs with measured BrO SCDs:

$$\frac{\bar{S}(\alpha) - \bar{S}(80^\circ)}{\bar{S}(\beta) - \bar{S}(80^\circ)} = \frac{A(\alpha) - A(80^\circ)}{A(\beta) - A(80^\circ)}$$

where \bar{S} is the averaged dSCD for the investigated time period and α , β and 80° denote the respective elevation angle.

The height of the BrO layer was changed in the simulation until the simulation matched the measurement. The mean ratio between the BrO dSCDs and the modelled BrO dAMF yielded the BrO VCD.

In both simulations, the albedo over the ocean was assumed to be 0.02, the single scattering albedo 0.95 and the asymmetry parameter 0.68. The wavelength for the retrieval of the aerosol profile was 361 nm, and for the BrO profile 349 nm.

2.5 Error estimation

The overall errors of the given concentrations consist of different parts. First, there is a statistical error of the evaluated dSCDs, which is derived as described in Stutz and Platt (1996). It is also given by the used software WinDOAS.

The next error taken into consideration is a statistical Monte Carlo error from the used model McArtim. However, this error is rather small and can be neglected compared to the first mentioned error.

At last, there are errors due to uncertainties in the model assumptions, as for e.g. the aerosol profile and the appraisal of the height. These errors could not be determined quantitatively, and will therefore only be qualitatively discussed herein.

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3 Results

The summary of our results, the average over the daily mean BrO Δ SCDs recorded at 6° elevation angle of all three telescopes is indicated by bars in the map of the cruise shown in Fig. 2. The Δ SCDs recorded during the large early morning and evening solar zenith angles (higher than 70°) were excluded from Fig. 2, as they possibly include stratospheric contributions. Daily mean BrO Δ SCDs frequently exceeded 10^{13} molec/cm². It can be seen, that the mean BrO Δ SCDs were higher, when the ship was cruising along the Western Coast of Africa, close to the Mauritanian upwelling region.

The 6° elevation angle values were chosen since the SCDs did not further increase at smaller elevation angles as can be seen in Fig. 3, where mean BrO Δ SCD values are plotted as a function of the respective elevation angles. The reason for this behaviour might be the relatively high aerosol extinction close to the (water) surface, since the radiation is scattered very frequently there, and thus smaller (here smaller than 6°) elevation angles will not experience longer light paths anymore.

The BrO dSCD diurnal profiles (i.e. evaluations relative to a single noontime reference spectrum) showed the same characteristic “bath tube – shape” each day (see Fig. 4). This well known, characteristic shape is caused by the longer light path through the stratosphere in the morning and in the evening due to the higher solar zenith angles. Three sample days are shown in Fig. 4.

The highest tropospheric BrO slant column densities were detected on 18 February 2007 between 14:00 UTC and 16:00 UTC, as it is marked by an arrow in Fig. 4 and also marked with a yellow dot in Fig. 2. At this time, the ship was cruising in easterly direction, close to the Mauritanian upwelling region, at the geographical coordinates 18.0° N and 17.4° W to 18.0° N and 17.0° W, thus close to the Mauretanian upwelling region. 18 February 2007 was a clear and sunny day with the wind blowing from easterly direction, thus coming from the Mauritanian mainland.

Boundary layer BrO concentrations were calculated for this peak using the backward

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Monte Carlo radiative transfer model McArtim (Deutschmann, 2008). The dSCDs of O₄ and BrO from 14:00 UTC until 16:00 UTC were used as input.

For the aerosol profile retrieval, at first, a run without any aerosols was performed. However, this led to too high air mass factors for the smaller elevation angles. Thus, some box profiles with different heights and different exponentially decreasing profiles were tested.

The best fit of the simulation of the O₄ dSCDs was received using an exponentially decreasing aerosol profile with a scale height of 350 m and an extinction coefficient of 0.2 km⁻¹ at the ground. The calculated as well as some of the modelled profiles can be seen in Fig. 5.

As even the BrO dSCDs taken under a 20° elevation angle show enhanced values at the time of the peak (as can be seen in the left graph of Fig. 4), the BrO layer probably extended to relatively large altitudes (1–2 km). The most probable results yielded a vertical layer, that was a box profile with a height of 1 km. The value of the vertical column density, in accordance with this profile and the measured dSCD values, was determined as $(3.6 \pm 1.3) \times 10^{13}$ molec/cm². This corresponds to a BrO mixing ratio of 10.2 ± 3.7 ppt for the 1 km thick layer. However, it was not possible to determine the layer height unambiguously with the available information on meteorological conditions during the time of measurement. Supposing a layer height of 2 km, the mixing ratio would still have been 5.1 ± 1.8 ppt. Under extreme (and mostly unlikely) assumptions, with a layer height of 10 km, the measured BrO SCDs would be consistent with a mixing ratio of 3.0 ± 1.1 ppt. Nevertheless, the dSCDs during the peak event (as can be seen in Fig. 4) as well as the modelled AMFs were higher for smaller elevation angles, which are very strong indications for a tropospheric trace gas layer (see e.g. Wagner et al., 2007).

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4 Discussion

There were two remarkable events during this cruise. The first was the overall rise in the BrO slant column densities when travelling close to the African coast and the other the BrO peak seen on 18 February 2007.

5 The overall enhanced BrO levels can be caused by several reasons, which will be discussed in the following.

First, it could be due to the proximity to the Mauritania upwelling region (e.g. Hagen, 2001), where higher concentrations of halogen precursors are expected due to the high biological activity there.

10 Furthermore, it can be seen from Fig. 2, that the mean Δ SCDs of the 9, 10 and 23 of February 2008 are very low. At these days the ship was the furthest north during the cruise and thus furthest away from the upwelling region (see Fig. 2). The other days show, even though there is a daily variation, in general higher values. When considering, that the wind was mainly blowing from north-eastern direction, this BrO enhancement can then most probably be explained by contributions from the upwelling region plus bromine emissions originating from the African mainland and then being blown out to the ocean. The even more enhanced BrO levels close to the coast could then be caused by the the ship being located closer to the sources.

15 Furthermore, it is worth mentioning that elevated BrO SCDs were already measured before in the same region, by Leser et al. (2003) and by Ibrahim (personal communication). Thus, these results can be seen as indication, that in this region higher BrO concentrations can arise.

20 Also dust in the atmosphere might, as described in more detail in the introduction, in principle increase the levels of reactive halogen compounds in the atmosphere. Very high dust contents were found by Baker (personal communication) in air mass samples taken during this cruise. However, when comparing the time series of the dust levels evaluated by Baker and the BrO SCD values, no direct correlation (high dust and BrO values at the same time or high dust values followed by high BrO values) could be

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found between them. Therefore, it is not likely that aerosols were a major reason for the detected enhanced BrO values.

Halogen species coming from the Mauritanian salt lakes and from coastal mangrove trees can also be blown out to the open ocean, which might be another source for the measured enhancement. During the days where the ship was cruising along the African coast, the wind was mainly blowing from north-eastern direction. Thus, it came from the mainland, indicating that halogen species from there might have contributed to the measured high values. However, no direct correlation between the direction of the wind and the measured BrO values could be found.

During the BrO peak event observed on 18 February 2007 even the SCDs at a 20° elevation angle were significantly enhanced. This indicates elevated BrO levels up to several km altitude and thus, that the measured BrO might have travelled already some time in the surveyed air masses, where it could have had time to disperse vertically before reaching the ship. The source of the BrO peak might therefore be due to halogenated hydrocarbons emitted by tropical halophytes growing in Mauritania. Also organohalogens, emitted from algae close to the coast, might have contributed to the BrO peak event.

Such high levels of BrO should then lead to noticeable O₃ destruction: Taking the BrO+HO₂ reaction as the dominant and rate limiting process and assuming furthermore an HO₂ concentration of 10⁸ 1/cm³ would result in an ozone destruction rate of about 0.2 ppb per hour. This would approximately cut in half the O₃ lifetime in the marine background lower atmosphere.

5 Conclusions

Very high BrO mixing ratios (>10 ppt) could be measured in the lower troposphere over the Eastern North-Atlantic with the MultiAXis-Differential Optical Absorption Spectroscopy. The data were collected during February 2007 during a ship cruise on the research vessel Poseidon, as a part of the Surface Ocean PRocesses in the ANthro-

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pocene (SOPRAN) project. The peak BrO concentration was estimated, using radiative transfer models yielding a layer height of 1 km, to (10.2 ± 3.7) ppt. This is the most probable scenario, but the layer height could not be determined unambiguously. A higher layer would lead to somewhat smaller, but still remarkable BrO values, in particular keeping in mind that these elevated levels would prevail in a large fraction of the tropospheric column.

Furthermore, the overall concentrations increased when the ship was cruising close to the African Coast suggesting the upwelling region and the African mainland as a source of reactive bromine (or its precursors). No direct correlation between the BrO data and dust or wind data, also collected during the cruise, could be found. Thus, the measured elevated BrO values are probably caused by algae from the upwelling region close to the African coast or by mangroves growing at Mauritania, as the wind was most of the time blowing from the African mainland. These measured high levels of BrO should then have led to a quite noticeable decrease of O_3 .

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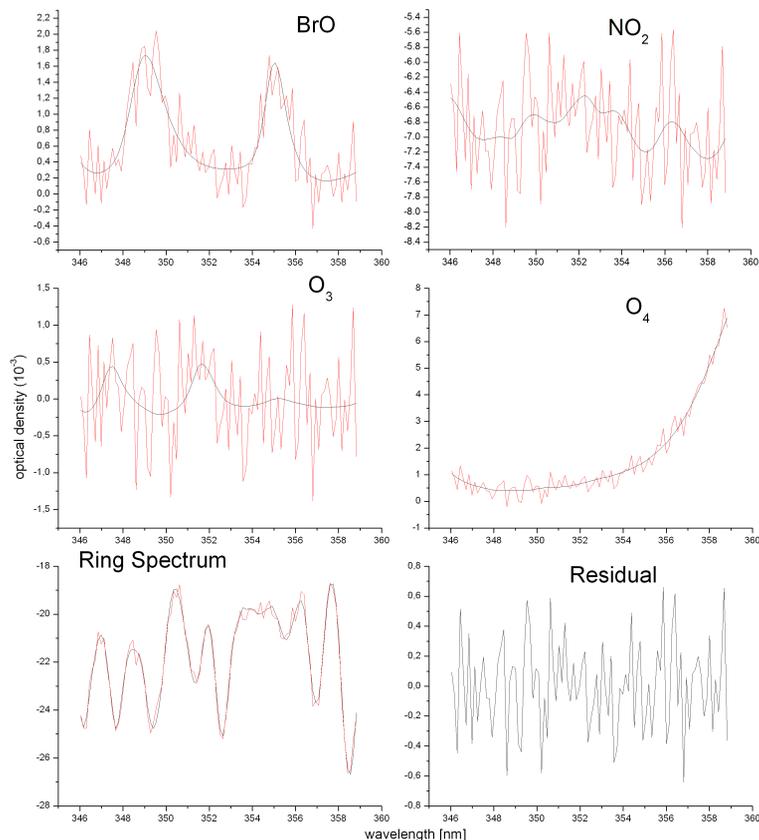


Fig. 1. An example of a WinDOAS fit for BrO for a spectrum with high BrO values at 6° elevation angle. It was taken on 18 February at 14:56 UTC. (The displayed optical densities are defined as the product of the slant column density and the respective cross section.) The resulting dSCDs are: $dSCD(\text{BrO})=2.11 \times 10^{14}$ molec/cm², $dSCD(\text{NO}_2)=-1.21 \times 10^{16}$ molec/cm², $dSCD(\text{O}_3)=2.49 \times 10^{18}$ molec/cm².

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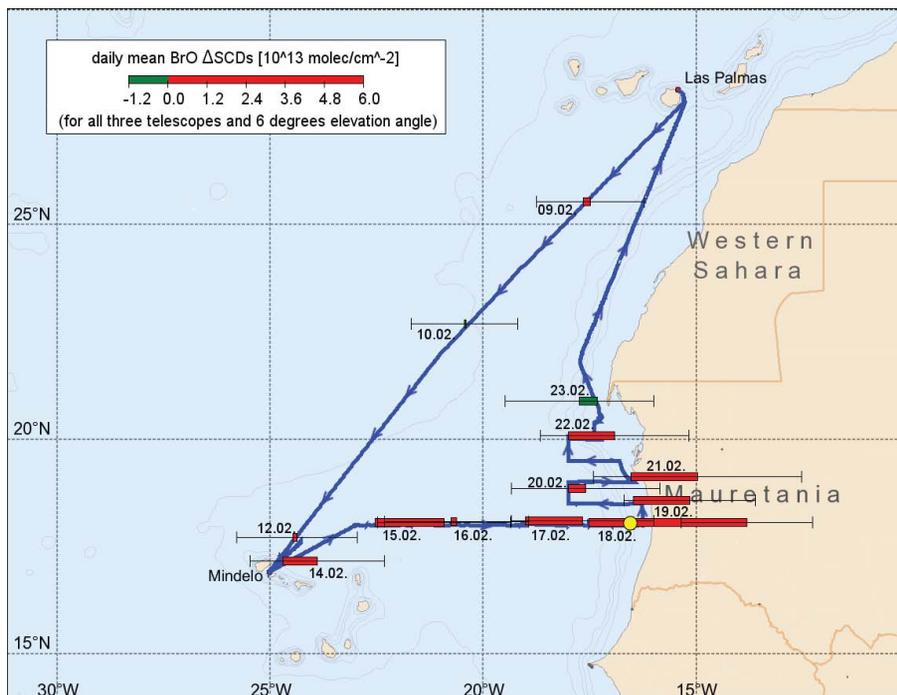


Fig. 2. The daily mean Δ SCD values of BrO of all three telescopes, taken at 6° elevation angles for the whole cruise are indicated by red bars, thin lines indicate the errors, which are the mean standard deviations. (Posidon, P348, 8 to 24 February 2007). The values increase, when the ship was cruising along the coast of Mauritania. The yellow circle indicates the location, where the tropospheric BrO peak on 18 February 2007 was measured. Each bar is plotted at the ship coordinates at 12:00 UTC of the respective day.

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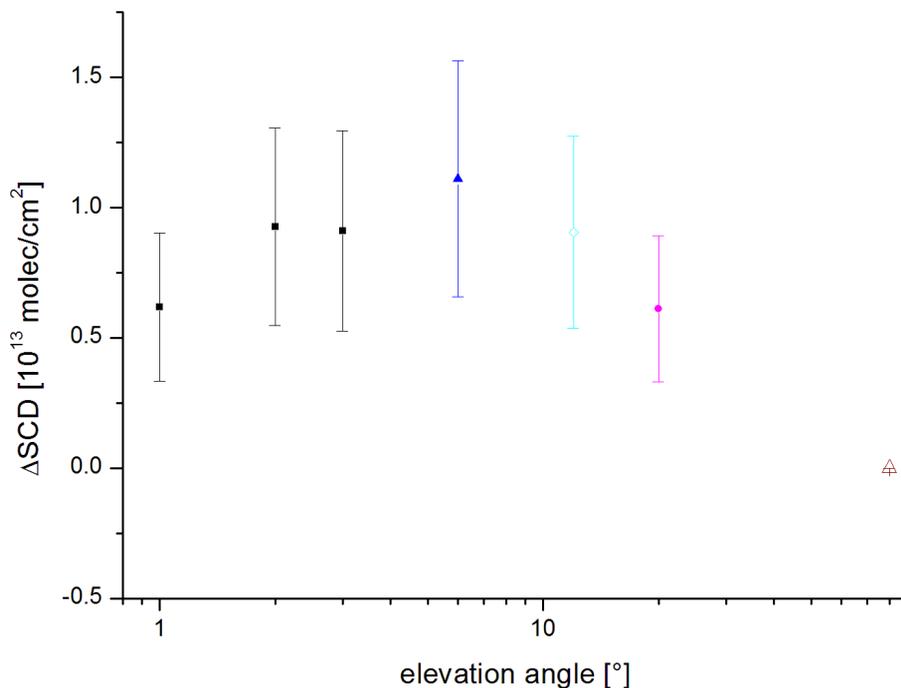


Fig. 3. Plot of the BrO Δ SCD values, (averaged from 14:00 UTC to 16:00 UTC) on 18 February as function of the MAX-DOAS elevation angles (on a logarithmic scale). The values do not rise anymore for angles smaller than 6°. (The value for the 80° angle is zero, because the spectra taken under this angle was used as the reference spectra.)

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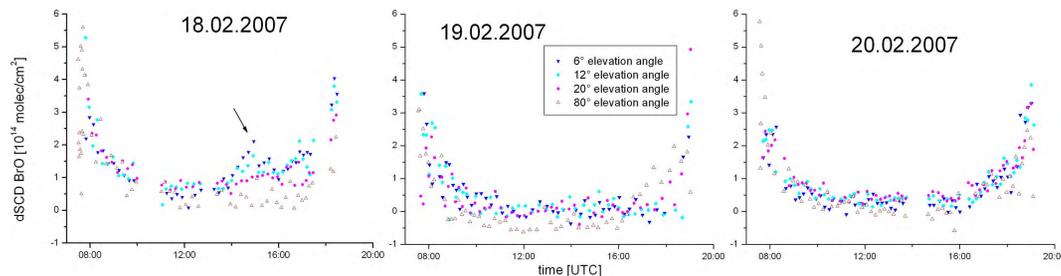


Fig. 4. The diurnal variation in the dSCDs of BrO on 18 to 20 February. The peak in the afternoon of 18 February (arrow) can be seen at the elevation angles 6° (the largest enhancement), 12° and 20°. It indicates tropospheric BrO.

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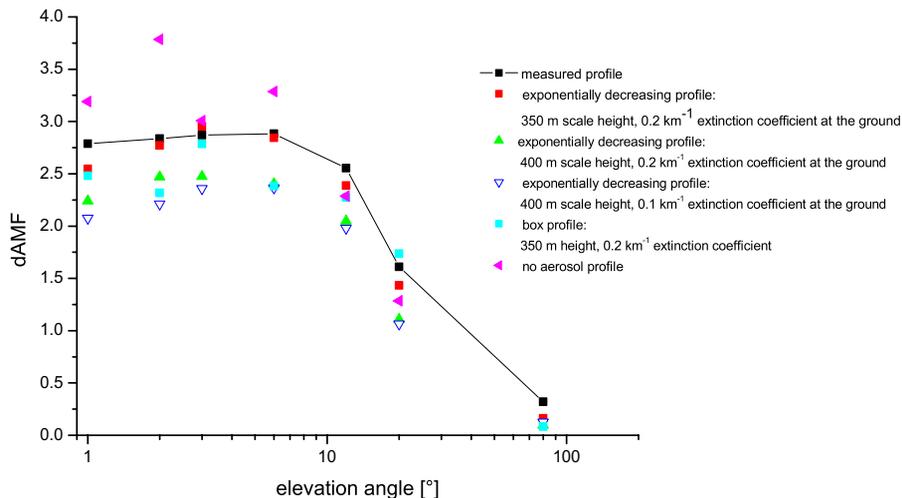


Fig. 5. The different elevation angles are plotted on a logarithmic scale versus the dAMFs for the measured (black line) and some modelled aerosol profiles. The exponentially decreasing aerosol profile with a scale height of 350 m and an extinction coefficient of 0.2 km^{-1} (red dots in the graph) was used as fixed input further on. It can be seen, that it represents the measured dAMFs quite well, especially for the smaller elevation angles.

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