Interactive comment on "Seasonal variation of tropospheric bromine monoxide over the Rann of Kutch salt marsh seen from space" by C. Hörmann et al.

Anonymous Referee #2
Received and published: 18 May 2016

We would like to thank Referee #2 for the detailed and helpful comments and suggestions he/she made to improve the quality and clarity of our manuscript.
For reference, the original comments (**black**) are always included below, followed by our response (**blue**). Modifications of the original manuscript (**green**) are indicated in **red**.

This manuscript describes measurements of BrO above the Rann of Kutch in India/Pakistan from satellite remote sensing. The work is interesting and well presented, although some use of English should be improved. The scope of the work fits in the journal.

General comments:

The manuscript describes potential albedo effects on the retrieval of tropospheric BrO and tries to argue that albedo is not a contributor to the enhanced BrO observed in this region. That discussion needs further consideration. It is clear from the albedo maps (Fig. 4) that the "white desert" of the Rann of Kutch is higher albedo than surroundings, or during Monsoon is similar to surroundings. The text description indicates that the albedo is lower during the time of the April/May peak, which is true in the sense that of the absolute albedo in the Rann compared to other times of year, but the albedo contrast between the Rann and surrounding areas appears largest during the Feb-May time period. Significantly, the albedo contrast between the Rann and surroundings during the monsoon is very small, so if albedo affects BrO retrieval, no differential albedo exists during the monsoon and no BrO enhancement would be expected. The method of removing a background surrounding the Rann (Eqn. 1 on page 6) is potentially sensitive to the differential albedo between the Rann region and the surroundings. Therefore, I would suggest plotting on Fig. 5 not the reflectivity in the Rann region, but instead the difference in reflectivity between the Rann and the "background" region used for removal of stratospheric BrO influence. At least by eye, this seems to have a pattern more like the BrO enhancement. However, it does appear that the winter season is different than springtime despite similar albedo difference (Rann minus surrounding background regions). That seasonal difference could be affected by stratospheric annual cycling and should be further considered.

The albedo indeed contributes to the BrO enhancement observed over the Rann area and is therefore considered for the radiative transfer calculations (Section 3.3). Nevertheless, the BrO distribution cannot be generally explained by the influence of the bright Rann surface as there is no clear correlation between the observed reflectivity and the BrO VCDs.
The referee correctly notes that the contrast between the Rann and the surroundings changes during the year, not only because of the varying absolute albedo of the salt marsh, but also because of that in the surrounding region. It is therefore very important to make sure that the "differential albedo" does not affect the polynomial stratospheric background correction and (in a worst case scenario) might lead to a spurious enhancement/decrement of the final retrieved BrO VCDs over the Rann.
To minimize this risk, an extensive area surrounding the Rann is used for the stratospheric background correction (18-30°N and 62-78°E; this essentially encompasses the whole area shown in the monthly BrO maps in Figure 3). The actual Rann area (22.5-25.5°N and 67.5-72.5°E) is completely

excluded from the 2D polynomial fit to make sure that the differential albedo between the Rann and the surrounding area doesn't affect this approach.
Following the suggestion of Referee #2 and to further demonstrate that the albedo contrast can not explain the BrO patterns, we normalized the reflectivity of the Rann region by the mean reflectivity in a nearby area (the reference area mentioned in Section 4.2: 22.5-25.5°N/62-67°E) for all months during the time period 2005-2014. To illustrate the change of contrast between Rann and surrounding areas, Figure X1 (right) shows the normalized reflectivity in longitudinal direction over the Great Rann (24°N latitude) along with the increasing BrO VCDs (left) during March-May 2005-2014 (colour coded in blue – March, red – April and black – May). While the BrO VCDs are already enhanced during March, peak in April and clearly decrease and shift towards East in May, it is still obvious from the normalized reflectivity that there is a continuous decrease of the Rann albedo at the same time (please note that the enhanced reflectivity at 67.5°E during May results from increasing cloud coverage at the western coast in the run-up to the monsoon season).

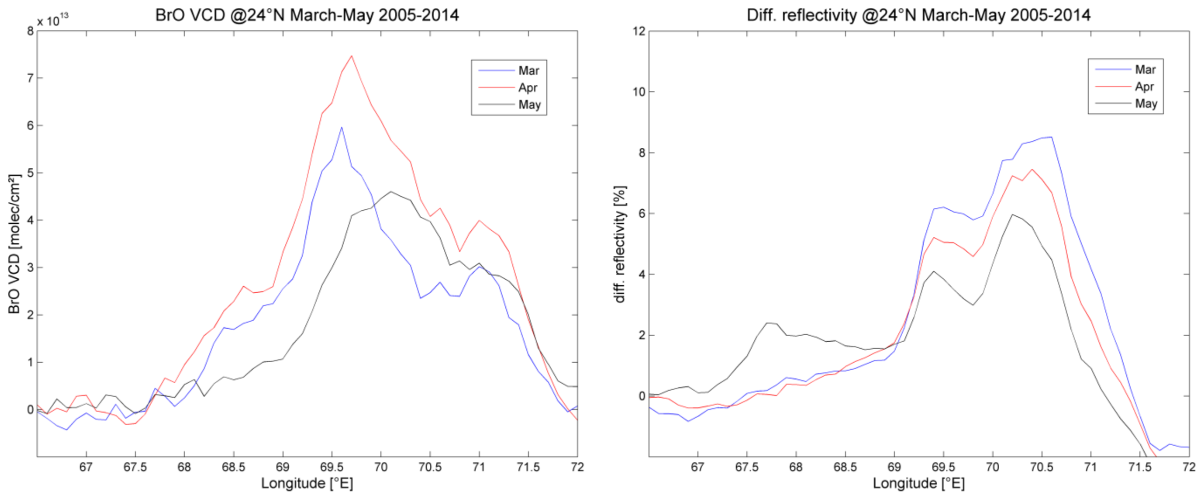

Fig X1: Mean BrO VCD (left panel) and differential reflectivity (right panel) in longitudinal direction over the Great Rann of Kutch at 24°N latitude for March-May (colour coded) 2005-2014.

During winter time (December-February), the differential reflectivity over the Rann (and therefore the contrast between the Indian Ocean and the salt marsh) is even higher, but shows only little variation (Fig. X2, right panel). The corresponding BrO VCDs are only slightly enhanced and also show very small variations, although the upcoming BrO increase seems to already start slowly in February (Fig. X2, left panel).

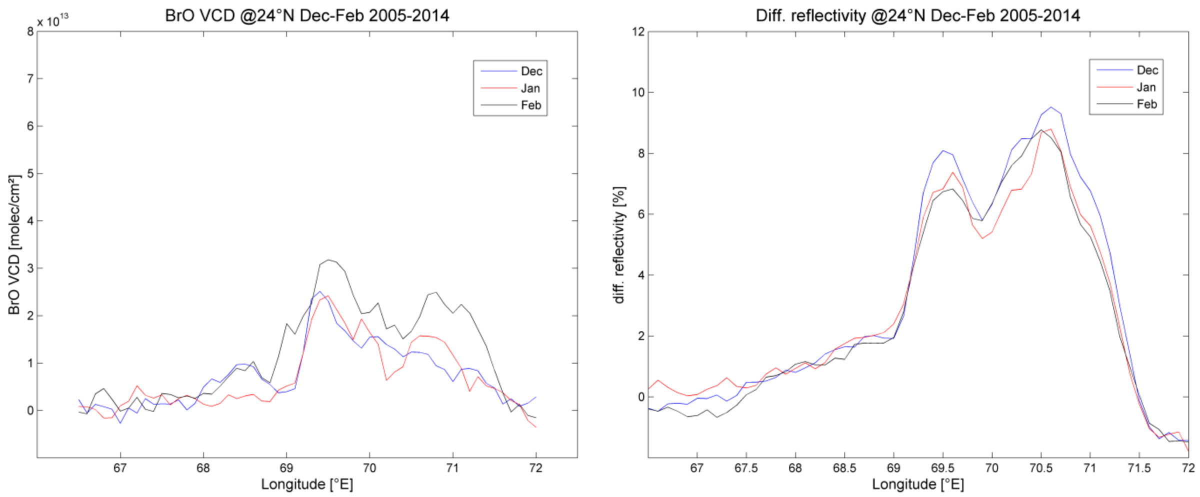

Fig. X2: Mean BrO VCD (left) and differential reflectivity (right) in longitudinal direction over the Great Rann of Kutch at 24°N latitude during December-February 2005-2014 (colour coded in blue – December, red – January and black – February).

Another important finding is that the spatial patterns of the reflectivity and the BrO VCDs are quite different, indicating that the observed enhanced tropospheric BrO VCDs are not a possible artefact caused by the albedo contrast.

We included the results of this accompanying study as an additional section in the Supplementary Material and added the following reference to Section 4.1 of the manuscript:
"While there is only little variation in the regional reflectivity within the Rann area over different months, the spatial distribution of BrO VCDs changes and even seems to progress into the eastern part of the Great Rann from March-May (see Supplementary Material for a more detailed investigation of these effects)."

The discussion of GOME-2 data and comparison to OMI is less well developed than other aspects of the work. A number of arguments are made, but none are really fully explored. For example, there is a discussion of the diurnal cycle of BrO that is indicated to potentially be the cause of lower BrO abundance at the time of GOME-2 overpass (morning) compared to OMI (early afternoon).

We agree with the referee that the discussion of this point is rather qualitative. The reason for this is that the GOME-2 cloud product is not very reliable over the bright surface of the Rann. However, the aim of this study was a relative comparison of both data sets (after they were processed in the same way). We made this more clear in the revised version of the manuscript (see also answer to Referee#1).

At most clean polar sites, BrO cycles are not highly diurnally varying, which is due to production of Br_2 in the prior evening and at night and rapid photolysis of this brown gas in the early morning. Therefore, the supposed cycle at least would differ from polar sites. A reference, Holla et al. (2015), is cited, which does indeed show a peaking of BrO later afternoon. However, the Holla et al. (2015) manuscript also shows NO_2 data that are enhanced through trapping of pollution NO_2 in the shallow nocturnal / early morning boundary layer. Levels of NO_2 above ≈1 nmol/mol appear to prevent production of high BrO levels. Therefore, the diurnal cycle at the Dead Sea may not be appropriate to the Rann of Kutch. In fact, the manuscript doesn't consider regional pollution, when it could have an effect on these data. Nearby Karachi has a population of ≈24 million people, and Ahmadabad is ≈7 million.

We like to thank the reviewer for the valuable note! It is true that the supposed BrO cycle at the Dead Sea in Holla et al. (2015) is often influenced by enhanced levels of NO_2 and therefore differs from those observed in clean polar sites and probably also at the Rann of Kutch. For the Dead Sea, Holla et al. (2015) found mutually exclusive enhanced BrO and NO_2 abundances in time and space, suggesting a conversion of NO_2 into $BrONO_2$ and therefore suppressing the *bromine explosion* during the early morning. This hypothesis was additionally supported by typically observed diurnal variations of the synoptic winds and meteorology.
In contrast to the Dead Sea area, satellite observations by both considered satellite instruments (OMI and GOME-2) over the Rann of Kutch only show a very localized NO_2 enhancement close to the cities of Karachi (≈ 300-400 km away) and Ahmadabad (≈ 200-300 km away) due to the short NO_2 lifetime of several hours. Close to the salt marsh, the observed tropospheric NO_2 VCDs are typically close to background levels. A possible influence of NO_2 at the Rann of Kutch can therefore expected to be much less important than over the Dead Sea basin. For corresponding tropospheric NO_2 maps for OMI and GOME-2, please visit e.g. the TEMIS website (available via http://www.temis.nl/airpollution/no2col/no2regioomimonth_v2.php).

We revised argument #3 of Section 4.5 as follows:

"3. One of the main chemical reasons for much lower BrO VCDs using GOME-2 might be that the measurements take place about 4 hours earlier when compared to OMI observations (≈ 9:30 vs. 13:30 LT). At the time of the morning overpass, the 'bromine explosion' mechanism has presumably not progressed very far, as solar irradiance is approximately 50% less than during OMI's afternoon overpass (according to ECMWF data) and the process is photolytically driven. Furthermore, O_3 is needed for the rapid build-up of BrO, which might be more easily available during the morning on the one hand, but may lead to differences in the spatial BrO distribution patterns for GOME-2 when compared to OMI. Observations at the Dead Sea (Israel) have shown that the largest BrO VCDs may show up close to noontime, if enhanced NO_x levels are generally present due to anthropogenic pollution (Holla et al., 2015). In contrast to the Dead Sea area, however, neither OMI nor GOME-2 observations show significantly enhanced NO_2 VCDs over the Rann of Kutch area, but only in the vicinity of the cities Karachi (≈ 300-400 km away) and Ahmadabad (≈ 200-300 km away). A possible influence of NO_2 at the Rann of Kutch is therefore assumed to be much less important than over the Dead Sea."

Other effects like boundary layer height, morning fog/clouds, etc. should be fully discussed and this section should be revised accordingly.

The possible effects of the BLH are briefly discussed on p.13, argument #4, while an influence of clouds (and/or morning fog) due to the different overflight time of the instruments could not be explained from MODIS and ECMWF data (as mentioned in Section 4.5). Furthermore, we are convinced that the best way to conduct such an analysis would be an extensive ground-based local measurement campaign, where the environmental parameters may be observed with much better temporal resolution during the day at the same time as the BrO (and possibly NO_2) column.
To emphasize this, we modified the end of Section 4.5 as follows:
"Although all of these effects probably contribute to the observed differences between OMI and GOME-2 observations, the reasons for these discrepancies are still a matter of further research. The best way to analyze the influence of ambient conditions on BrO formation would be an extensive ground-based measurement campaign. Such local observations would provide high temporal resolution data of meteorological parameters like wind speed and direction, relative humidity, boundary layer height, clouds (and morning fog) as well as a possible influence of anthropogenic pollution."

The boundary layer height is not treated consistently in this manuscript. In the section about GOME-2 data, 2km (GOME-2 overpass) and 3km (OMI overpass time) are quoted, but the Table 1 and AMF calculations appear to use a 1km ABL height, with alternatives of 0.4 and 2.0 km. This is not consistent and clearly from the sensitivity testing in Table 1, would change the peak BrO mixing ratio significantly.

The referee is right that (according to the ECMWF data) the boundary layer height during the overflight times of the satellite instruments is 2 and 3 km (GOME-2 and OMI), respectively, which may lead to differences of the BrO layer profile and therefore the true BrO VCD. However, the BrO VCDs in Section 4.5 are only calculated by using a geometrical AMF for both instruments (GOME-2 and OMI), which means that neither a specific BrO layer profile nor the boundary layer height is taken into account for the AMF calculation. A more sophisticated AMF calculation for the GOME-2/OMI section remains difficult due to problems with the GOME-2 operational cloud product (see former discussion), so we decided to only show a qualitative comparison of the data. However, a different treatment of GOME-2 and OMI data by assuming BrO layer heights of 2km respectively 3km would result in only about 15 % differences for the resulting BrO VCDs and cannot explain the GOME-2 BrO VCDs close to background level.
It is furthermore important to note that while it can be expected that a change of the boundary layer height may lead to changes of the BrO layer profile, the true BrO profile over the Rann remains unknown (the BrO layer doesn't necessarily need to fit the boundary layer height). The presumed

baseline scenario (homogeneous BrO layer between 0-1km) only represents a first guess of the true BrO profile, based on the assumption that BrO forms at the salt surface and is partly transported to higher altitudes. To indicate the large uncertainties of the derived BrO mixing ratios, Table 1 shows results for two other a priori BrO profiles. However, for an adequate estimation of the true BrO profile, results from local ground-based MAX-DOAS measurements are desirable.

To emphasize the assumptions made, we modified the manuscript as follows:

Section 3.3 (end): "It is furthermore important to note that the baseline scenario (assuming a homogeneous BrO layer between 0-1km) only represents a first guess of the true BrO profile, based on the assumption that BrO forms at the salt surface and is partly transported to higher altitudes. While the BrO profile can be expected to depend on the prevailing boundary layer height, the true profile over the Rann remains unknown (the BrO layer doesn't necessarily need to fill in the complete boundary layer). An estimate of the uncertainties caused by the a priori assumptions will be given in Section 4.2. For an adequate estimation of the true BrO profile, however, results from local ground-based MAX-DOAS measurements would be desirable in the future."

Section 4.5 (argument #4): "4. The boundary layer height during the GOME-2 overflight in April/May is significantly lower (≈ 2km) than for the OMI measurements (≈ 3km). As the BLH increases towards noon, BrO originating from the ground might be transported to higher altitudes where it could be more easily detected by the OMI as the instrument's sensitivity generally increases for elevated layers. Additionally, the increasing BLH might lead to an increased mixing-in of tropospheric O_3 from higher altitudes and thereby lead to further formation of BrO. It is important to note that the data shown in Figure 4 were only calculated by application of a geometrical AMF and therefore possible differences for the BLH and BrO profile are not taken into account. However, in the case of a homogeneous BrO layer filling in the complete boundary layer, corresponding radiative transfer effects would only result in about 15% differences for the resulting BrO VCDs and can therefore not explain the GOME-2 BrO VCDs close to background level."

The manuscript should indicate that this work is motivation for measuring BrO from the ground in this region to verify the space-borne observations. Although the region is clearly remote, it is not inaccessible, nor would measurements via simple MAX-DOAS systems be difficult. Verifying the presence or absence of this space-detected feature would significantly contribute to our ability to connect space-based measurements to ground truth.

We totally agree with the referee and modified the manuscript as specified in our answers to the previous comments.

A number of sections discuss that the Rann of Kutch "...is probably one of the strongest natural point sources of reactive bromine...", but there is no comparison of this source to other sources. Additionally, the manuscript indicates that there is "supposed to have significant impact on local and regional ozone chemistry", but there is no calculation showing that this impact is significant. It certainly "may" have an impact, but in the absence of some reference indicating significance, the wording appears inaccurate.

We agree with the referee that it is important to emphasize that there are still only few measurements of halogen formation over salt lakes worldwide. To our knowledge, these are the first reported observations of BrO over a salt lake (salt marsh) by a satellite instrument at all. However, there are at least two main points, why the Rann of Kutch is "…probably one of the strongest natural point sources of reactive bromine…" and halogen emissions from salt lakes may "…have significant impact on local and regional ozone chemistry":

1. By looking at global BrO maps using OMI data, the Rann of Kutch appears to be the only salt lake/marsh where a clear enhancement of the BrO column can be easily seen during several months from satellite measurements, even without correcting for the stratospheric background and excluding clouded data.

2. Although the actual BrO profile over the Rann of Kutch is unknown, a qualitative comparison to the BrO VCDs over the Dead Sea indicates that the BrO abundance over the Rann of Kutch is much larger than over the Dead Sea. So far, the largest BrO mixing ratios at a salt lake were reported from ground-based DOAS measurements at the Dead Sea (up to 220 ppt, as reported in Matveev et al., 2001 and Tas et al., 2005).
   It is nevertheless likely that the BrO VCDs over the Rann of Kutch (as well as the Dead Sea) are generally biased low because of spectral dilution due to the low spatial resolution of satellite instruments like OMI when compared to local ground-based measurements (compare to argument #1 of the GOME-2 discussion on p.13 of the revised manuscript).

Saiz-Lopez and von Glasow (2012) state that about 2.5% of the global land surface "*(…) is covered by saline soils, implying that halogen release might be relevant on a rather large part of the continents and not only over the comparatively small areas of salt lakes*". However, they also noted that "*A regional or global assessment of the relevance of halogen chemistry over salt lakes and saline soils is so far missing*". To further classify the significance of the BrO abundance in comparison to other salt lakes, local ground-based MAX-DOAS measurements are highly desirable (as mentioned several times before).

We added a short paragraph to Section 4.6 of the manuscript to strengthen the given statements as follows:

"It is interesting to note that the BrO VCDs found over the Dead Sea are generally much lower than those observed over the Rann of Kutch, although the above-mentioned ground-based measurements showed the highest BrO mixing ratios so far observed at a salt lake (up to 220 ppt). This finding indicates that the Rann of Kutch is likely one of the strongest natural point sources of reactive bromine compounds outside the polar regions. This argument is further strengthened by the fact that the Rann is the only salt lake/marsh, where a clear enhancement of the BrO column can be easily seen during several months from satellite measurements (even without correcting for the stratospheric background or excluding clouded data). However, BrO from other salt lakes (particularly smaller ones, like the Dead Sea) may generally not be identified as easily from the OMI data."

Specific comments:

page 1, line 11: indicate that the times are "respectively" done

page 1, line 13: replace "former" with "prior" done

page 1, line 15: reword "supposed to have a significant influence"

We reformulated the sentence: "*The measurements indicate that the Rann of Kutch salt marsh is one of the strongest natural point sources of reactive bromine compounds outside the polar regions.*"

page 1, line 19: Missing "von" from "von Glasow" done page 1, line 21: move "significantly" to after "troposphere" done

page 2, line 19: cut the word "ever" done

page 2, line 27: are both BrO and IO below 2 ppt? clarify

We reformulated the sentence as follows: "However, none of these measurements showed significantly enhanced BrO or iodine oxide (both less than 2 ppt or below the detection limit of the MAX-DOAS measurements)."

page 4, BrO retrieval: This section appears to indicate that Level 1 OMI data were reanalysed by this group rather than use of the OMI BrO product (OMBRO). Can this be made more clear, and the specific sources of the data from OMI data streams should be described fully. If this calculation differs significantly from OMBRO, that should be noted – why was OMBRO not used?

Our group has a long-standing experience in spectral retrievals of satellite observations, and was one of the first to analyse BrO from satellite. Thus in this study we applied our own algorithm for the analysis of the satellite data (OMI and GOME-2). As shown in the reply to Referee #1, almost the same results are obtained if the OMBRO product is used. We added this information to the text:

The spectral data of both satellite instruments were analysed at MPI-C for BrO column densities by using the Differential Optical Absorption Spectroscopy (DOAS) technique….
The OMI BrO retrieval follows the general settings of the GOME-2 retrieval: Level 1 data (online provided by the Goddard Earth Sciences Data & Information Services center, NASA) were analysed using a wavelength range from 336--360 nm, including 4 adjacent BrO absorption bands.

page 6, line 15: This section is not fully clear. Why are slant columns of BrO (S*_trop) being calculated? Which "geometrical AMF"? Doesn't a geometrical AMF assume that the reflector is the Earth's surface, while the actual tropospheric return may be from clouds / fogs / aerosol light scattering?

A geometrical AMF indeed assumes that the detected sunlight directly traversed the complete atmosphere and is reflected by the Earth's surface alone. However, if the main absorber can be assumed to be mainly present in the stratosphere, the geometrical AMF is a viable approximation for the actual AMF. In the manuscript, the geometrical AMF is solely used for an initial calculation of the main effect of the satellite's measurement geometry and the stratospheric BrO background correction. Please additionally see our answer to Referee #1.
We made this point now more clear in the manuscript.

page 6, Radiative transfer section. This seems like it should use at least 2km layer

Please see comments above

page 6, line 28: "...and briefly described in Carn..." done

page 7, line 25: Effects of local pollution may be affected by wind direction

Please see comments above

page 8, line 18: should say "...not a strong..." done

page 12, after line 16: should discuss potential of morning fog and/or NO2

Please see comments above

page 13, line 1,2: boundary layer height inconsistent with modeling.

Please see comments above

page 13, line 28: why is Salar de Uyuni being discussed here?

Salar de Uyuni is the largest salt flat in the world and clearly enhanced BrO column densities have been detected by ground-based DOAS measurements in the past. It is briefly mentioned to make clear why other large salt lakes/marshes may not be easily observed by satellites using the DOAS technique due to spectral effects over high and bright surfaces.
We added this information to the manuscript.

page 14, line 11: clarify "supposed to"

Please see comments above

page 15, line 14: Wasn't OMAEROG also used, as well as either some level 1 OMI data or OMBRO (unclear).

We added the missing information to the Acknowledgement

page 22, caption says "adapted from Fund, W."? Typo?

Changed to "adapted from World Wildlife Fund:..."