We would like to thank the reviewer for providing helpful comments and suggestions for improvement of the paper. We believe that they enhance the scientific value of our contribution. In the following, we discuss the questions and suggestions and give a point by point response.

General comments

A central hypothesis of this study is that the transition from multi-year to first year sea ice in the Arctic ocean affects the distribution, number and intensity of bromine explosion events and thus Arctic tropospheric BrO. The potential mechanism(s) behind should be made a bit clearer in the Introduction and the discussion of results should be made under these assumptions. To be more specific: Multi-year ice that has survived at least one melt cycle has less bulk salinity compared to first year sea ice. The increase in first-year sea ice could potentially favour bromine explosion events by providing more sea salt bromine.

To test this hypothesis, relating first year sea ice area with (excess) tropospheric BrO, as done in Fig. 11 is very useful and the implications of this relation should be stated accordingly. The correlation between first year sea ice area and BrO seems to be significant (by looking at Fig.11, I couldn't find a statistical test for significance) although of course not perfect. How much this relation explains (in terms of variance, trend, shift in geographic distribution) should be stated clearly, together with its limitations. Phrases like "linked in a complex way" (end of abstract and in the Conclusions) without explaining what the "complex way" is hide more than they reveal.

There may be other factors how sea ice age impact on tropospheric BrO e.g. through a reduction in sea ice thickness. So while for the point above the distinction between first year and multi-year ice is most important (and the distinction between say 5 or 6 year old ice is not so important), for other factors the actual age may be critical. Please be specific in the discussion and in the presentation. Example 1: the colour scale in Fig. 9 makes it difficult to clearly identify if the majority of the ice in recent years is first year ice or 2 year old ice. Example 2: the age trend in Fig. 13: Even a relatively small trend may have resulted in a shift from multi-year to first year ice over the years. Try to be specific in the discussion of the implications.

Currently, although the Arctic sea ice extent is decreasing, the more saline first year ice grows at the expense of multiyear ice. This is affecting the number and magnitude of bromine explosions occurring. The criticism is that there is no clear conclusion on the relationship between tropospheric BrO and first year ice conditions. In response your comment, we have rephrased parts of the abstract, the introduction, the main text and the summary, (e.g. the moderate correlation coefficient of 0.32 between the two quantities during polar springs is now given on the abstract). With the help of maps in Fig. 9 and time-series in Fig. 11, we have pointed out that changing sea ice conditions do not explain all the changes of the observed tropospheric BrO. This is because the appearance of bromine explosions depends on other parameters as well (air temperature, wind speeds, cyclone activity).

We have performed a hypothesis test of the significance of the correlation coefficient as you suggested, based on the null hypothesis that there is no correlation between tropospheric BrO

and first year ice. The null hypothesis was rejected, meaning that the correlation between tropospheric BrO and first year ice is significant. The color scale in Fig. 9 was optimized in a way that first year ice is distinguishable from multiyear ice. Values from 1 to 2 are colored blue, while multi-year ice (2 years and above) is denoted with green and other colors. So everything blue in the maps of Figure 9 means that there was at least one first year ice grid box during the polar spring average. Also, in Fig. 13, we tried to explain better the point, which you have made by adding another sub-plot in the figure, which shows the trend of the occurrences of first year ice. We infer from it that the trend of occurrences of first year ice has increased in some areas where also an increase of tropospheric BrO occurred (i.e. east of Greenland), but also decreased in some others (i.e. in the Canadian Archipelago, where BrO also increased). In summary, we explain that sea ice age influences tropospheric BrO but, given that the correlations between first year ice and daily tropospheric BrO are moderate, does not fully account for the changes of the tropospheric BrO column dataset.

Section 3.1 contains a general description of the DOAS method used to retrieve the BrO SCDs. I am not sure if a general description of the DOAS method is needed here, but in its current form there are too many mistakes and omissions to make it useful (specific points below). Please carefully check.

With respect to your comments for the DOAS section, we have followed the specific comments (indicated below):

Specific comments

P1,L11: First sentence of abstract is a bit disconnected here. Would be better in the Introduction. More generally I feel that at many places (in the abstract and elsewhere in the manuscript) "Arctic Amplification" could better be replaced by "Arctic warming" because what matters in this context is the warming, not so much the amplification (although this may be seen as pettifoggery).

We removed the first sentence. We have also replaced in all places (except in the introduction where we describe the term “Arctic Amplification”) the term “Arctic Amplification” with “Arctic warming”.

P1, L15: “e.g. Hg”: any other metals?

Bromine molecules can also react with lead, forming $PbBr_2$. However $PbBr_2$ is insoluble.

P1, L15: “22 year”: suggestion: name range of years already here

Rephrased to: “22 year (1996 to 2017)”

P1,L19/20: “magnitude of BrO: : :of about 1.5%/year”: what exactly increases with 1.5%/year? Tropospheric columns? Please be specific.

Rephrased to: “We determined an increasing trend of about 1.5% of the tropospheric BrO VCDs per year during polar spring”.

P1, L25: It is true that the understanding of Arctic Amplification is inadequate, but a few citations on Arctic Amplification may be useful. E.g. Pithan and Mauritsen, Nature Geosc., 2014.

Added two more references (Pithan and Mauritsen, 2014, Stjern et al, 2019), which discuss the response of Arctic Amplification to individual climate drivers and to temperature feedbacks.

P1, L24/25: "loss of sea ice" and "reduction of ice extent" are of course not independent. Maybe say loss of ice resulting in reduction of ice extent, thickness and reduced fraction of multi-year ice?

Corrected the sentence to: “… are the loss of ice, resulting in reduction of ice extent, thickness and a reduced fraction of multi-year ice (Stroeve et al., 2012) and the increasing rate of loss of the Greenland ice cap (Mouginot et al., 2019)”.

P2, L10: “over 30 years ago”

Added

P2, L12: introduce “O3” when first used as “ozone (O3)”

Done

P2, L13: I think this point should be made a bit clearer: O3 and OH are decreasing, but bromine radicals instead could act as oxidising agents. Are there references how the oxidising capacity overall changes?

Indeed, on short timescales, bromine radicals can contribute to the formation of OH. However, on longer timescales, the depletion of ozone caused by bromine compounds reduces the production of OH. Added a reference (Stone et al, 2018), which suggests that the long-term effect of bromine radicals prevails. Also, added one reference on the global tropospheric OH distribution (Lelieveld et al., 2016), which suggests that the secondary sources of OH (i.e. recycling in radical reaction chains), play a more important role in global OH distribution.

P2, L21: wicket sentence

Rephrased to: “However, there is the general consensus that the potential sources of BrO plumes are (a) rich in sea salts and relatively cold (conditions occurring in potential frost flowers regions; Rankin et al., 2002; Kaleschke et al., 2004; Sander et al., 2006), (b) surfaces covered with liquid or frozen brine (Sander et al., 2006), (c) associated with blowing snow (Yang et al., 2008; Blechschmidt et al., 2016; Frey et al., 2019), (d) surface snow packs (Pratt et al., 2013; Peterson et al., 2018) and young salty sea ice regions (Wagner et al., 2001; Simpson et al., 2007; Peterson et al., 2016).”

P3, R4,R8: should that be "->" instead of "="?

Changed to ⇌

P3, L19: Closing bracket missing.

Added

P3, L19: This idea needs a bit more explanation: Transport of BrO plumes over large distance by deposition and reactivation due to release from snow pack and blowing snow?

Rephrased to: "It was shown that BrO plumes can be transported far from their initial formation areas, as high wind speeds associated with cyclones (Begoin et al., 2010; Zhao et al., 2015; Blechschmidt et al., 2016) can transfer them together with blowing snow (Giordano et al., 2018)".

P3, L24: "Polar Regions" -> "polar regions" (at many places in the manuscript)

Replaced by "polar regions" as suggested

P3, L24: "hostile" for what or whom? In spite of difficulties numerous studies have performed in-situ measurements or ground-based DOAS measurements in the Arctic. Satellite measurements are not "unique".

Changed the sentences containing the problematic words to: "The polar regions are some of the most remote places on the planet. Consequently, satellite remote sensing is a suitable method to study bromine chemistry in the Arctic."

P3, L33: It is good to provide context by citing previous studies, but better cite what has been learned rather only what has been done.

We have rephrased the whole section, now mentioning also the findings of each publication: "The relationship between BrO release and young sea ice was also discussed (Wagner et al., 2001), where it was indicated that large BrO concentrations are found over or near sea ice on the Caspian Sea. Van Roozendael et al. (2004) compared SCIAMACHY observations of Arctic BrO to GOME data, showing satisfactory agreement between the two different sensors. Theys et al. (2011) compared tropospheric BrO columns derived from GOME-2A to a chemical transport model, showing consistency with the release mechanisms of bromine. Sihler et al. (2012) compared GOME-2 BrO columns to ground-based measurements in the Arctic, demonstrating good agreement between the retrievals. Seo et al. (2019a) presented the first BrO retrievals from the TROPOMI instrument, showing high-resolution bromine explosion cases with low fitting errors".

P4, L2: "them" = "BrO explosion events" ?

Replaced as suggested

P4, L10: at some stage you should mention that first year sea ice is more saline than multi-year ice

Rephrased the sentence to: “Changes in meteorological parameters, e.g. increasing air temperature (Serreze and Barry, 2011), decreasing mean sea level pressure over northeastern America and increasing pressure over Eurasia (Ogawa et al., 2018; McCusker et al., 2016), increase in cyclone frequency and intensity (Akperov et al., 2019), stronger surface winds (Mioduszewski et al., 2018) and changes in sea ice conditions (e.g. reduced sea ice extent; Stroeve et al., 2012), increased first year sea ice fraction (and consequently salinity), and therefore decreased sea ice thickness (Richter-Menge et al., 2017) occur due to Arctic warming.”. Also included one sentence in the introduction: “The reduced multi-year ice is being replaced by first year ice, which is in addition more saline. (Galley et al., 2016)” (P1, L30).

P4, L26: remove word “results”

Removed

P5, L9: This statement is too general. There were other satellite instruments before GOME, depending on what you mean by "many" and "key trace gases"

Rephrased the sentence to: “GOME was the first satellite instrument, which was able to measure key tropospheric gases which have weaker absorption lines than ozone: examples are NO2, BrO, HCHO and SO2”.

P5, L16: what is the difference between "near IR" and "short wave IR"?

Although the spectral limits of the terms near IR and short wave IR are not SI standardized, near-infrared radiation usually implies a spectral wavelength region from 0.75 to 1.4 μm, while short-wavelength infrared implies the spectral region from 1.4 to 3 μm. Shortwave IR is sometimes defined as 0.76 to 2 μm. The sentence has been changed to: “... allowing the observation of many trace gases in the near infrared (0.75 to 1.4 μm) and short wave infrared (1.4 to 3 μm) spectral wavelength regions”.

P6, L5: throughput mentioned twice

Corrected

P6, L9: This sentence seems odd. "Long changing polymers" -> “long chained polymers"?

Changed to “long chain polymers”

P7, Eq.1: In eq.(1) the concentration of the gas j is missing.

We define the concentration in this study as the number density of the trace gas j with concentration ρ (in molec cm^{-3}). This, when multiplied by the length of the light path s (in

meters), gives the column amount or column (in molec cm^{-2}) of the trace gas j. We have rewritten Equation 1 as follows:

$$I = I_o\, e^{-\int \sum_{j=1}^{J} \{\sigma_j(\lambda)\rho_j\} ds}$$

Also, we have rephrased the text below to: "where I is the measured intensity of the electromagnetic radiation, I_o is the initial intensity, J is the total number of absorbing trace gases, j denotes a particular trace gas (e.g. BrO), $\sigma(\lambda)$ is the cross section of the absorber at wavelength λ, ρ the concentration of the trace gas".

P7, L14: really ABSORPTION cross sections or SCATTERING cross sections?

Changed to scattering cross sections

P7, L31: is a "four degree" polynomial a polynomial of fourth-order, i.e. with five degrees of freedom? Please be specific and consistent to avoid confusion.

Changed to fourth-order polynomial

P8, Eq.5: There is something wrong with eq. (5). The sum should be under the root. And not on the LHS.

Corrected

P8, L16: Latitudes and longitudes need to be specified more consistently. E.g. "- 180_E" should be "180_W" and "-50.0_S" should be "50_S". If you use east and west longitudes please avoid "235_E to 270_E" and use instead "90_W to 125_W".

Changed to "the Arctic from 70.0^o N to 85.0^o N latitude, 180^o W to 180^o E longitudes) and for the Pacific reference region (50.0^o S to 10.0^o N latitude and 90.0^o W to 125.0^o W longitude).".

P10, L1: Please mention this drift already in the instrument overview in Section 2.

Moved to section 2.4

P11, L2: This first sentence does not make much sense and is redundant.

The sentence has been changed to: "NO_2 and O_3 columns from satellite retrievals and tropopause height from meteorological reanalysis data are used for deriving the tropospheric BrO component from the retrieval (stratospheric separation)."

P13, L13: what is the meaning of the word "high" here?

Removed from the sentence

P13, L15: you can remove "due to Arctic Amplification" here. See also my general comment on Arctic Amplification.

Removed

P14, L10: There are also real stratospheric BrO trends due to changes in anthropogenic emissions!

The sentence has been changed to: "The stratospheric BrO VCDs show a small upward trend from 1995 to 2001 and a slight decrease afterwards, which are in agreement with measurements of stratospheric BrO from Harestua station (Hendrick et al., 2008)."

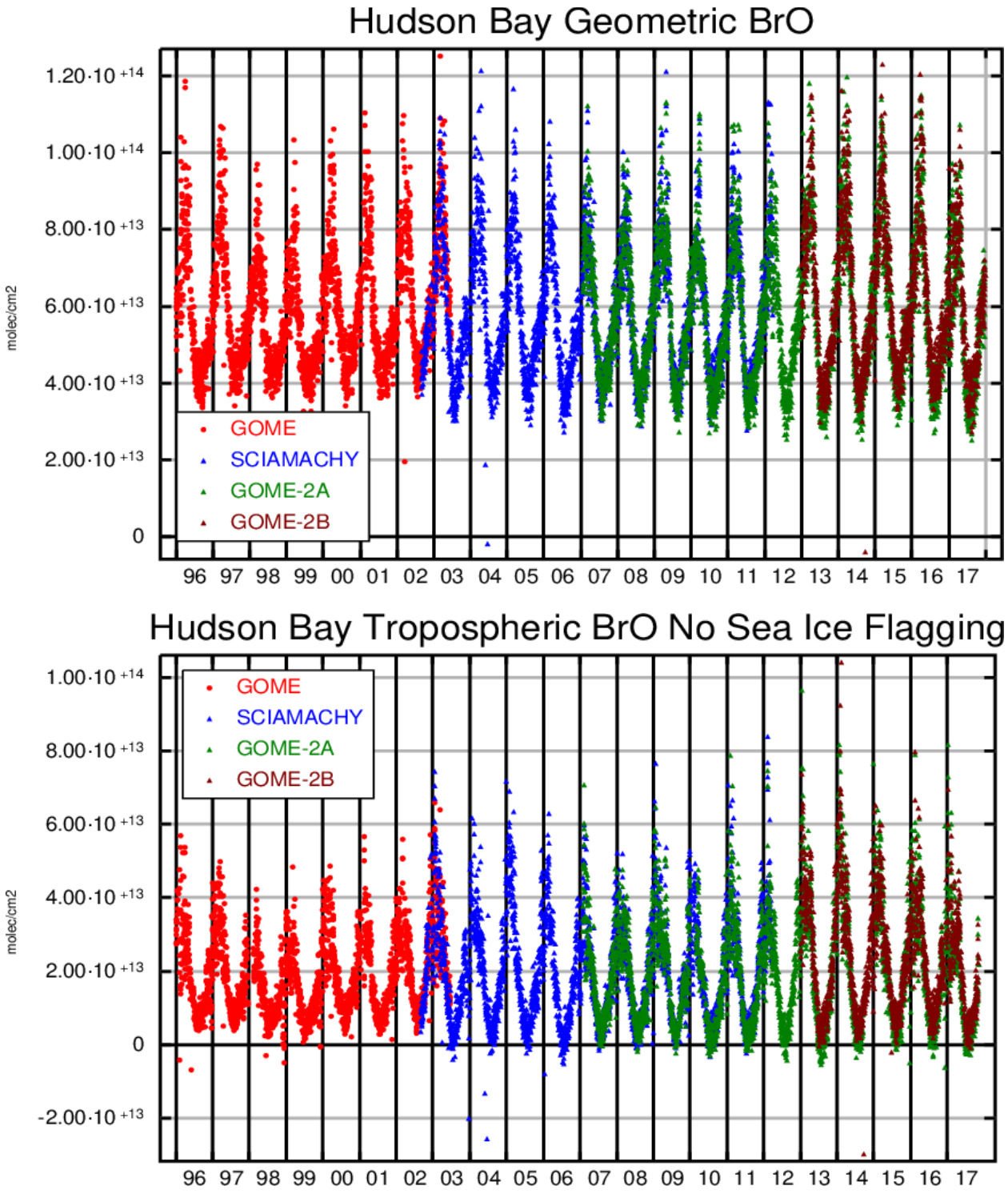
P15, L1: I don't think you need to explain that temperatures in summer are higher because of increased solar insolation (it does not matter in this context), but you could specify in which month the maximum temperature and in which month the sea ice minimum are reached.
Changed to: "During July and August, the temperature reaches its maximum. In September, the minimum sea ice extent is observed."

P15, L7: Looking at the spatial distribution may tell if there are (few and/or small) areas of bromine explosion in September or only a gradual increase in the background. Would it make sense to include somewhere also maps with BrO in autumn?

During September, the sea ice coverage is very low, so it would not make sense to include September maps of tropospheric BrO in the manuscript. However, we have checked September maps of tropospheric BrO and concluded that the small increase observed is mainly a background increase, as we cannot see clearly localized BrO explosion events.

P22, L4: "in the early years, most of the BrO is found in the region of the Barents and Kara Sea": I am confused. Richter et al. (1998) show largest BrO enhancements in March 1997 over the Canadian Archipelago, Hudson Bay and north-west of Greenland.

Richter et al showed specific days of total BrO vertical column densities. Although the Hudson Bay is a well known BrO hotspot, we decided to perform our analysis only over latitudes > 70^0 N, as the proportion of sea ice covered areas and the fraction of pixels for which tropospheric BrO VCDs can be retrieved is larger there. Retrieved tropospheric BrO columns are more accurate for latitudes > 70^0 N, as the tropospheric air mass factor that we use considers a 0.9 surface reflectivity.
We have analyzed retrievals over Hudson Bay, and we are attaching figures of geometric and tropospheric BrO VCDs (similar to Figure 3 of the paper, with a land mask applied):



We see a less pronounced trend for BrO VCDs over the Hudson Bay, in comparison with the Arctic region, as defined in the manuscript (latitudes > 70^{o})

P24, Fig11: I don't fully understand what are the points shown in the right hand side panels? Related to this: what is the correlation coefficients for the data shown in the time series on the

left hand side? The same as given in the right hand side plots? Did you check if the correlations are significant? (By eye, the correlation between Arctic MAM mean BrO and 1st year ice extent in Fig. 11a seems significant.)

Every point in the right panel scatter plots represents one polar spring day (the average tropospheric BrO VCD for this day is plotted against first year sea ice extent in the top right panel, the area with tropospheric BrO VCD above the threshold is plotted against first year sea ice extent in the bottom right). The time-series on the left side are the polar spring averages of the scatter plots. The correlation is positive but moderate for the top right scatter plot. We have performed a hypothesis test to verify the significance of the correlation coefficient and found that the correlation is significant (p value lower than 0.05). We added this information to the text of the paper. Also, we have calculated the correlation coefficient of the annual time-series (the blue and red curve shown in the left sub-figures). The correlation coefficient between polar spring averages of tropospheric BrO and first year ice extent corresponding to the top left sub-figure is 0.62, while the correlation between areas of polar spring averages of tropospheric BrO VCDs > 7 x 10^{13} molec cm^{-2} and first year ice is 0.46. However, we believe that the correlation coefficients obtained from the daily scatter plots are more meaningful and represent the actual relationship of tropospheric BrO and first year ice extent more accurately.

P24, L11: the phrase "fresh" ice is misleading, as first year ice has a higher salinity, i.e.is not "fresh"

Changed to “and more first or young sea ice is formed each winter period”

P24, L15: What is the correlation coefficient? (See comment above.) A rigorous statistical analysis is more useful than the “anecdotal evidence” given in the following sentences.

The correlation coefficients for the two scatter plots are presented inside the plots (denoted with r). The results of the significance test has been added to the text.

P25, L4-7: I find these sentences confusing. My impression from Fig. 11a is that there is a positive correlation between first year sea ice and BrO, although this is clearly not the only factor. But then you say this agrees with Choi et al. who found even a negative correlation? I would say this is in contrast to Choi et al. and part of this difference may be attributed to a possible degradation of the OMI instrument?

Although the correlation between tropospheric BrO and first year ice is positive from the scatter plot, we see that it is not strong, as many days with high tropospheric BrO columns occur with moderate first year ice extent (around 4.5x10^{6} km^{2}). From the time-series, we see in many years an opposite evolution (one quantity increases, while the other decreases, for example 2008 and 2015). The text was rephrased, especially in the section where we compare to Choi et al, to: “This finding is in contrast to the results by Choi et al. (2018), where an analysis of BrO VCD retrieved from OMI was performed. They found a correlation coefficient of -0.32 between first year ice extent and tropospheric bromine explosion frequency. The negative sign is attributed to a decrease of tropospheric BrO VCDs over the latter years of the trend analysis. The differences

to Choi et al. (2018) may be explained by a degradation of the OMI instrument (Kroon et al., 2011).".

P25, L22: Please specify the value of the autocorrelation used. What exactly is the meaning of the "period M"? Generally I am not convinced that the trend model with harmonics is an ideal choice as you don't have data during winter. For calculating trends in individual months as in Table 4 the harmonics are not needed at all.

An autocorrelation value of 0.2 was used. The period M is the 22 years of the entire dataset. The reason why we used this approach is that, although the winter columns are missing, we still see a profound seasonality in our dataset. However, when we calculated the monthly trends in table 4, this approach was not used (added in the text).

P25, Table 4: It is a bit unusual to have the units in a column, instead of in the header.

Added the unit information to the title and in the header of the figure

P28, L10: First paragraph of Summary is redundant, largely repeats introduction

Rephrased – removed most parts of the first paragraph

P29, L7: did you show that the correlation in Fig. 11a is not significant?

We have performed a hypothesis test on the significance of the correlation coefficient. The correlation is significant and we have added it in the text.

P29, L18: This statement on temperatures in 2016 is too vague. You could mention here that you have not considered changes in temperature and this may be another factor affecting tropospheric BrO to be investigated in future studies.

Rephrased to "The appearance of plumes of tropospheric BrO VCD and their intensity are influenced by several meteorological drivers (air temperature, sea level pressure, wind speeds and cyclones) and the amounts of blowing snow (Blechschmidt et al., 2016; Seo et al., 2019b). Further investigations are required to understand the evolution of tropospheric BrO and its dependence on these drivers of tropospheric BrO release."

P30, Author contributions: Sounds a bit strange that not all authors are named for their contributions here (not even for "providing insight and knowledge").

Rephrased to: "I. Bougoudis undertook the retrieval of BrO from the different satellite instruments, collected and processed the sea ice age data, performed the analysis and prepared the paper. This study was initiated by J.P. Burrows and A.-M. Blechschmidt. The research presented was supervised by A.-M. Blechschmidt, A. Richter and J.P. Burrows. A.-M. Blechschmidt and N. Theys provided the stratospheric separation. A.-M. Blechschmidt, A. Richter, S. Seo, N. Theys and J.P. Burrows provided input with respect to BrO issues of relevance. A. Richter developed software which was used for processing and analysing the BrO

data. A. Rinke provided input on sea ice and trend analyses. All authors contributed to the writing of the paper.”.

P31: Barrie and Platt listed twice

Corrected

P32: Claas listed twice.

Corrected.

P32, L23: something is missing here

Inserted the missing reference

P33: Fickert listed twice

Corrected

We thank the reviewer for providing the helpful and critical comments and suggestions about the paper. We believe that they enhance the scientific value and accuracy of the manuscript. In the following, we discuss the questions and suggestions and provide point by point responses.

General comment

"The paper is well written overall. However, there lacks clear take home messages, i.e. how does this work significantly advance our knowledge. I would like to come away with more than the relationship is 'complex'. I would like quantification of the first year sea-ice extent and Arctic amplification on BrO explosion events as these have been nicely explored in this paper, but the clarity of conclusions drawn reduces the potential significance and usefulness of this work. Below I detail edits throughout the paper with my major concern being around the significance of this work, and how it could be used to advance model, observation comparisons going forward, so that predictions of the implications for the oxidative capacity of the Arctic (and therefore also the Antarctic) can be explored in climate simulations".

We have re-written the abstract, introduction and conclusion sections, in order to clearly state the importance of the current study and removed the general statement that the relation between tropospheric BrO VCDs and sea ice is complex. We observe changes in tropospheric BrO plumes in recent years. These changes can be linked non-linearly to changes in sea ice age and extent that are also occurring. This is now pointed out in the manuscript. We provide the correlation coefficient between first year ice extent and tropospheric BrO in the abstract, in order to clarify and quantify the relation from the beginning. Furthermore, we have added a significance test between the two quantities, in order to clarify, that although their correlation (based on the magnitude of the correlation coefficient) is moderate, it is significant. Also, we have included another subplot in Figure 13, where we show the trend of first year ice occurrences. In this way, our conclusions on the impact of first year ice on the recent increased formations of tropospheric BrO plumes are more solid. In the conclusion, we have erased the repetitions and kept only the take-home messages: The 1.5% increase of tropospheric BrO during polar springs and its moderate correlation of 0.32 to the first year ice extent evolution. Also, we discuss potential future significance and usage of work. The dataset that we retrieved can be integrated in chemical transport models, in order to be used as validation of simulations on the impact of bromine explosions on O_3 loss and potential OH changes.

With respect to your detailed edits, we have followed the specific comments (indicated below):

Specific comments

Page 1, line 12: Sentence needs revising: Every polar spring BrO explosions occur, which are a series of chemical reactions that release bromine molecules to the troposphere over sea ice covered regions.

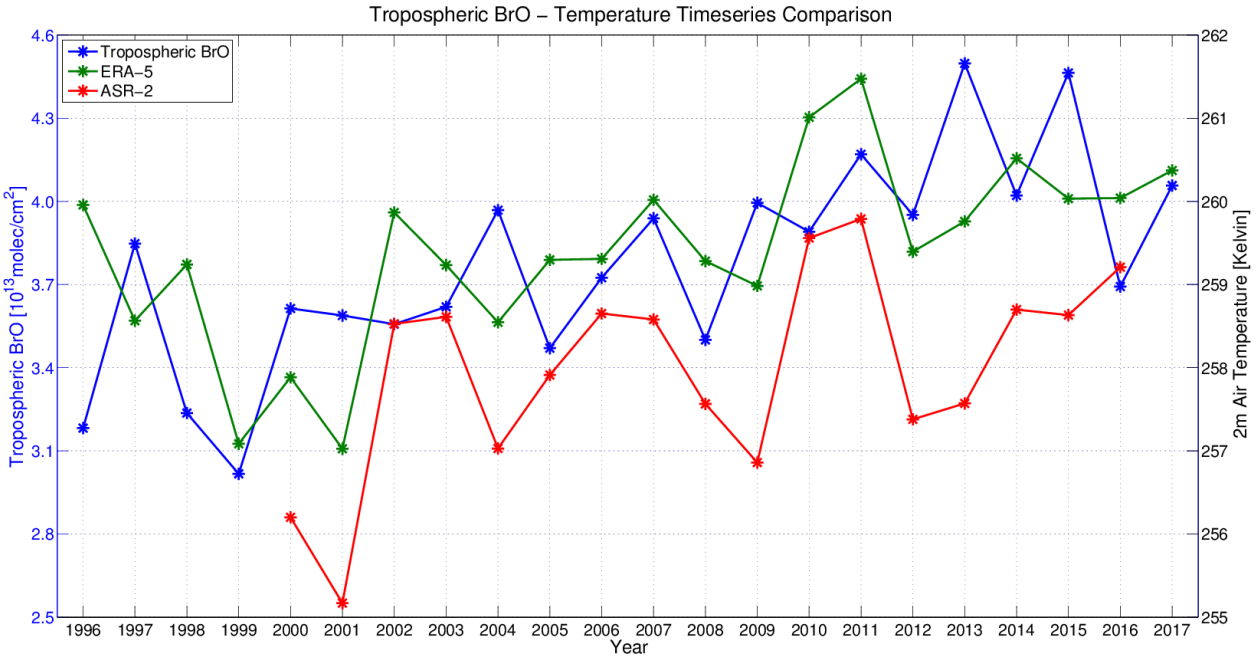
Thank you for pointing to this sentence. We rephrased the sentence to ". Every polar spring, phenomena called bromine explosions occur over sea ice. These bromine explosions comprise photochemical heterogeneous chain reactions that release bromine molecules, Br2, to the troposphere and lead to tropospheric plumes of bromine monoxide, BrO."

Page 1, line 16: Name the four satellite experiments

Added (GOME, SCIAMACHY, GOME-2A and GOME-2B)

Page 1, line 20: and elsewhere: 1.5% per year – since there is a focus in the abstract on Arctic Amplification – could this response be expressed also per degree of warming experienced?

This is an interesting suggestion. However, the non-linear connection of tropospheric BrO plumes with their driving mechanisms (as also indicated in the paper, the comparisons of tropospheric BrO and sea ice age can be seen in some cases, but not in all), and the deep interactions between the mechanisms themselves, make the specification of the effect of the warming of the air temperature on bromine explosions and the trends appearing in the time-series a difficult task. We therefore prefer not to add a statement such as "BrO increased by 5% per K warming" as this would suggest a linear relationship, which in our opinion does not exist. However, we are attaching here the time-series of tropospheric BrO and 2m Arctic air temperature, from 2 reanalysis datasets (ECMWF ERA-5 (Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horányi, A., Muñoz-Sabater, J., et al. (2020). The ERA5 global reanalysis. Quarterly Journal of the Royal Meteorological Society, 146(730), 1999–2049. https://doi.org/10.1002/qj.3803), downloaded from the following website: https://www.ecmwf.int/en/forecasts/datasets/reanalysis-datasets/era5, and WRF Arctic System Reanalysis version 2 (Bromwich, D. H., Wilson, A. B., Bai, L., Liu, Z., Barlage, M., Shih, C.-F., et al. (2018). The Arctic System Reanalysis, Version 2. Bulletin of the American Meteorological Society, 99(4), 805–828. https://doi.org/10.1175/BAMS-D-16-0215.1), downloaded from: https://rda.ucar.edu/datasets/ds631.1/).



Page 1, line 22: Specify how linked (stating that it is complex is very general)

We have rephrased the text, stating that the link (based on the magnitude of the correlation coefficient) is moderate. “We infer from comparisons and correlations with sea ice age data that the reported changes in the extent and magnitude of tropospheric BrO VCDs are moderately related to the increase of first-year ice extent in the Arctic north of 70^{o} N, with a correlation coefficient of 0.32.”.

Page 1, line 24: Arctic temperature please qualify as surface air or sea-surface temperature?

Changed it to: “surface air temperature”

Page 2, line 6: here and elsewhere please remove hyphen in ecosystem

Removed it throughout the text

Page 2, line 11: 1990 and 1997 don’t represent 3 decades worth of studies, a 2010s review paper reference more appropriate here

Added a reference by Saiz-Lopez and von Glasow, 2012

Page 2, line 14: insert but : : : OH are reduced, but the reactions of: : :

Inserted as suggested

Page 2, line 17: the “Bromine explosion” closing speech mark needs format correction

Corrected

Page 2, line 20: citing a 2009 paper when discussing controversy is problematic, as modelling efforts recently have integrated simple and effective parameterisations, based on both frost flower and blowing snow mechanisms i.e. (Falk & Sinnhuber, 2018) or some other more recent reference would be appropriate here to discuss exactly what controversary still exists.

The exact level of impact of each parameter (such as blowing snow, wind speeds, air temperature) on the formation of enhanced BrO plumes is still unknown. This is what we meant with controversy. Added citation to Falk & Sinnhuber (2018), Huang et al. (2020), Seo et al. (2019). We have rephrased the text to: “Although there are studies which try to model BrO plumes from their driving mechanisms (Falk and Sinnhuber, 2018; Seo et al., 2019b; Huang et al., 2020), the exact level of impact of each parameter on the formation of enhanced tropospheric BrO is uncertain.

R1 – hv should be hï ¸ A˝oï˘A ˇ aï˘A´lthese should be defined in the text).

We are sorry but we could not figure out exactly what the reviewer wrote. However, we have defined hv as solar radiation in the text. All the other species in the chemical reactions are described in the section below the reactions.

Page 3 line 7: bromine atoms rapidly remove (switch from remove rapidly)

Rephrased as suggested

Page 3 line 20: it's = its

Corrected

Page 3, line 23: favor bromine explosion conditions. Again, there is more recent (and quantitative) modelling efforts.

Here we are mostly presenting studies which indicate the relation of tropospheric BrO to driving mechanisms, not modeling efforts. We added citations from Yang et al, (2020) and Fernandez et al, (2019), regarding recent efforts on BrO modeling.

Page 3, line 17: remove second comma

Removed (Page 4, line 17)

Page 5, line 23: on – was the data from Metop-C useable in theory, if so why wasn't it used in your study?

Metop-C was launched in autumn 2018, but the first data were received during spring of 2019. It therefore does not contribute to the investigated time period (1996 to 2017).

Page 6, Table 1: in GOME-2A line 40 x 40 (remove capitalisation from X)

Removed

Page 6, line 9: and elsewhere – Sun should be capitalised throughout

Changed throughout the paper

Page 9, line 5: insert comma: autumn, when the solar: : :

Inserted

Page 11, line 2 (whole paragraph needs reworking): For the NO2 and O3 column satellite retrievals, the tropopause height : : : is used: : :.

This has been rephrased to "NO_2 and O_3 columns from satellite retrievals and tropopause height from meteorological reanalysis data are used for extracting the tropospheric BrO component from the retrieval (stratospheric separation). Sea ice data (age and type) obtained by satellite remote sensing was used in order to identify regions with sea ice cover and hence high surface reflectivity, which is required for the retrieval of tropospheric BrO in this tudy and for data interpretation in relation to bromine sources."

Page 11 Line 4: reflectivity, which is required: : :

Corrected

Page 13, line 11: change the degree sign from a zero to a circle

Changed throughout the whole text

Figure 5: – please show 1 sigma errors in the VCD retrievals as well as interannual variability with error bars on these plots in order for us to be able to determine agreement significance.

The purpose of Figure 5 is to provide seasonal cycles for geometric, stratospheric and tropospheric BrO time-series, for each instrument. For each sensor we averaged the data over the individual months of the corresponding operation period. Therefore, and since we can see from Figure 3 that for some years we have higher columns than for others (e.g. 2013 to 2017, the GOME-2B operation period compared to 1996 to 2003, the GOME operating period), the agreement between the sensors is hence not the focus of Figure 5 and differences because of the different averaging time periods are expected.

Section 4.2: by selecting only for high BrO over sea-ice areas you are only capturing the genesis and not necessarily determining the implications of the combined oxidative capacity and changes in cyclonic activity. Much of the interesting implications of warming and BrO will happen outside of areas which are over sea-ice. I'm unclear why the only BrO over sea-ice was a necessary criteria?

We chose to work exclusively on sea ice covered regions because the tropospheric air mass factor that we use in the computation of tropospheric columns considers a surface reflectivity of 0.9. As a result, our tropospheric columns can be considered accurate only above bright surfaces. Over dark surfaces such as the ocean, the sensitivity of the satellite measurements to boundary-layer BrO is unfortunately low.

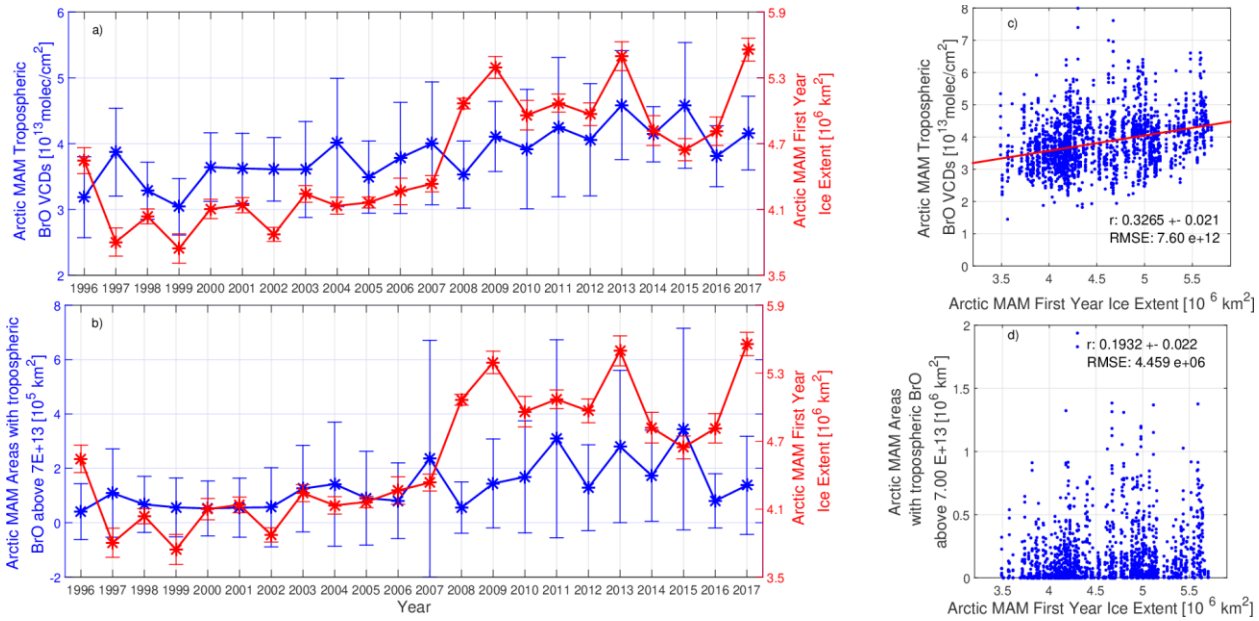
Figure 9: – please try to get onto one page, use horizontal colorbars perhaps?

Figure 9 has been fitted to one page.

Page 22, line 16. And Figure 11: Stating that the relationship between sea-ice area and BrO explosion is complex is unsubstantiated by a useful plot. I would like to see the first year sea-ice area versus average BrO column plot (or BrO explosion area). Figure 11d goes some of the way to providing this but I suggest that an annual number be provided i.e. those produced in 11 a and b (with variability range errorbars for both axes) could be more useful than using every data point above the threshold as is done currently. Figure 11d trend line is arbitrary and should be removed (unless the annual number provides support for a linear relationship). Some metric representation of annual cyclonic activity or amplification amplitude would be valuable too on this plot – i.e. providing an annual cyclonic index in color and some index for Arctic

amplification temperature with size may help to disentangle the story for us. This way we would be able to determine whether a parameterization that would be useful to test models could be derived for this 'complex' relationship.

Removed "complex" in this line and throughout the text (see reply above), being more precise on describing the relationship between tropospheric BrO and sea ice age (for example, adding a sensitivity test). Figure 11a shows the first year sea-ice versus average BrO columns plot (as you suggested). No threshold is applied in this sub-plot. Also, we have removed the trend line from Figure 11d. We have added 1σ uncertainties for the correlation coefficients of the two scatter plots. We calculated the correlation coefficients for the annual time-series of tropospheric BrO and first year ice as well. However, we believe that the ones from the daily scatter plots (as shown in the manuscript) are more informative and describe the relationship between the two quantities more accurately. We have added the variability range error bars for both axes and show the Figure here:



Page 25, line 4: VD -> VCD.

Changed

Figure 11: a-d labels missing.

Added the labels

Page 27, figure 12: How can trends over 1 year be considered significant or reliable with only a few points? I assume the annual cycle is removed for this plot (otherwise like a sine curve, you would get a trend just due to that). I'm really unclear about what figure 12 is showing, given it only is discussed briefly and doesn't add to the papers aims/conclusions. As the minimum time to detect a trend is not provided, I think this plot and the discussion can be removed.

Figure 12 provides information on the variability of the trend of tropospheric BrO VCDs for different starting years (x-axis) and ending years (y-axis). As the value of the calculated trend depends on the averaging time period, the Figure provides a visualization of the consistency of the observed BrO increases and how they changed over time. For almost all time periods over 5 years and more, positive trends occur. As the reviewer correctly pointed out, trends over very short time periods are less significant. The annual cycle for the trends is removed by starting and ending at the same time of the year (i.e. end of March). However, as the reviewer pointed out, trends over short periods are dominated by inter-annual variability.

Figure 13: over what time period is the trend calculated? Provide this in the caption.

Added. The trends are calculated over a 22 year period (1996 to 2017).

Page 29 line 5: the BrO explosion -> Bro explosion events.

Changed as suggested

Page 29: when discussing trends state over what period they are determined.

The information on the time period has been added.

Long-term Time-series of Arctic Tropospheric BrO derived from UV-VIS Satellite Remote Sensing and its Relation to First Year Sea Ice

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Abstract. ~~Arctic Amplification describes the rapid increase of the air temperature in the past three decades in the Arctic, which impacts on physicochemical conditions, the ecosystem and biogeochemistry.~~ Every polar spring, ~~the BrO explosion, a series of chemical~~phenomena called bromine explosions occur over sea ice. These bromine explosions comprise photochemical heterogeneous chain reactions that release bromine molecules, Br_2, to the troposphere ~~occurs over sea ice covered regions~~and lead to tropospheric plumes of bromine monoxide, BrO. This autocatalytic mechanism depletes ozone, O_3, in the boundary layer and ~~tropospheric ozone,~~ troposphere, and thereby changes the oxidizing capacity of the atmosphere ~~and facilitates the~~. The phenomenon also leads to accelerated deposition of metals (e.g. Hg). In this study, we present a 22 year (1996 to 2017) consolidated and consistent tropospheric BrO dataset north of 70° N, derived from four different UV-VIS satellite instruments ~~and investigate the BrO evolution under the impact of Arctic Amplification.~~(GOME, SCIAMACHY, GOME-2A and GOME-2B). The retrieval data products from the different sensors are compared during periods of overlap and show good agreement (correlations of 0.82 – 0.98 between the sensors). ~~By studying the sensor~~From our merged time-series of tropospheric BrO vertical column densities~~,~~ (VCDs), we ~~find~~infer changes in the bromine explosions and thus an increase in the extent and magnitude of tropospheric BrO ~~explosion events under~~plumes during the ~~impact~~period of Arctic warming~~with~~. We determined an ~~upward~~increasing trend of about 1.5% of the tropospheric BrO VCDs per year during polar springs. ~~Furthermore, the areas where BrO plumes frequently appear have changed, extending over larger regions in the Arctic during more recent years. Comparison to~~ We infer from comparisons and correlations with sea ice age data ~~suggests~~ that the reported changes in the extent and magnitude of tropospheric BrO VCDs are moderately related to the increase of first-year ice extent in the Arctic north of 70° N, with a correlation coefficient of 0.32. However, the BrO plumes and thus bromine explosions, show significant variability, which also depends, apart from sea ice, on meteorological conditions.

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1 Introduction

Arctic surface air temperature has risen at twice the rate of the global mean over the past three decades. This phenomenon is called Arctic Amplification (Serreze and Barry, 2011) and our understanding of ~~the processes leading to this phenomenon is~~ its causes is inadequate~~.~~ (Pithan and Mauritsen, 2014; Stjern et al., 2019). Important consequences of the rapidly increasing temperature in the Arctic are the loss of ~~sea~~ ice, ~~the~~resulting in reduction of ~~the sea~~ ice extent, thickness and a reduced fraction of multi-year ice (Stroeve et al., 2012) and the increasing rate of loss of the Greenland ice cap (Mouginot et al., 2019). The reduced multi-year ice is being replaced by first year ice, which is in addition more saline. (Galley et al., 2016). Both the maximum and the minimum yearly sea ice extent began to be noticeably smaller over a decade ago. The minimum sea ice extent**,** which occurs usually in September, reached its record low in 2012 (Yang and Magnusdottir, 2018). The yearly maximum sea ice extent, which occurs every March, ~~shrinks~~is shrinking at a significant rate (Serreze and Meier, 2018). The thickness of sea ice has declined dramatically in recent years as the portion of thick multi-year ice decreases (Richter-Menge et al., 2017). Sea ice is replaced by open ocean, which being darker, reduces surface reflectivity in the Arctic. As a result, more of the incoming solar radiation is absorbed by the ocean and its biosphere (e.g. phytoplankton). Consequently, the temperature of the ocean and the air in the boundary layer increases, creating a positive feedback loop. This is one of the most pronounced effects ~~associated with~~occurring during Arctic Amplification (Hansen et al., 1997; Kirtman et al., 2013). These evolving conditions impact on many other physical, chemical and biological processes, as well as the ~~eco system~~ecosystem in the Arctic.

Bromine monoxide (BrO) plays a significant role in the atmospheric chemistry of the Arctic. During polar springtime, episodes of strongly enhanced amounts of BrO have been observed in the boundary layer (Barrie and Platt, 1997). The formation of these intense plumes of BrO results in tropospheric ozone depletion. Tropospheric ozone depletion and the link to halogen chemistry events was first discovered over 30 years ago (Barrie et al., 1988) and has been the subject of many studies and research campaigns over the past three decades (Toohey et al., 1990; Tuckermann et al., 1997; ~~Toohey et al., 1990; Tuckermann et al., 1997).~~Saiz-Lopez and Glasow, 2012). The release of reactive halogens and the decrease in ozone (O_3) impacts on the oxidizing capacity of the troposphere. The photolysis of O_3 in the UV-B leads to the formation of the most important tropospheric oxidising agent, the hydroxyl radical, OH~~.~~ (Lelieveld et al., 2016). Although bromine radicals can contribute to the formation of OH on short timescales, the destruction of ozone caused by reactive bromine lowers the OH concentrations and is more profound (Stone et al., 2018). While in plumes of tropospheric BrO, the oxidising agents O_3 and OH are reduced, the reactions of BrO play also other important roles in atmospheric chemistry. For example, BrO efficiently reacts with elemental mercury. This oxidation initiates a process whereby deposition of mercury, Hg, to snow and ice increases. This results in Hg entering the food chain (Lu et al., 2001; Schroeder et al., 1998). The rapid and sudden appearance of BrO plumes over the ~~Polar Regions~~polar regions has been called the ~~"~~"bromine explosion" (Barrie and Platt, 1997; Platt and Lehrer, 1997). It is explained by an autocatalytic multiphase chemical cycle, which occurs on cold saline surfaces (Fan and Jacob, 1992; Sander and Crutzen, 1996). ~~The~~Although there are studies which try to model BrO plumes

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from their driving mechanisms (Falk and Sinnhuber, 2018; Seo et al., 2019b; Huang et al., 2020), the exact level of impact of each parameter on the formation of enhanced tropospheric BrO is uncertain. However, there is the general consensus that the potential sources of BrO plumes are (a) rich in sea salts and relatively cold (conditions occurring in potential frost flowers regions; Rankin et al., 2002; Kaleschke et al., 2004; Sander et al., 2006), (b) surfaces covered with liquid or frozen brine (Sander et al., 2006), (c) associated with blowing snow (Yang et al., 2008; Blechschmidt et al., 2016; Frey et al., 2019), (d) surface snow packs (Pratt et al., 2013; Peterson et al., 2018) and young salty sea ice regions (Wagner et al., 2001; Simpson et al., 2007; Peterson et al., 2016). A pH lower than 6.5 is required for efficient bromine activation (Fickert et al., 1999; Halfacre et al., 2019).

Organic sources of BrO, such as oceanic ~~bromocarbons~~organobromine compounds, have also been discussed in the literature (Salawitch et al., 2006, and references therein) but ~~the~~their relatively long lifetimes result in a slow release of Br throughout the Arctic troposphere or beyond and are currently not considered to explain ~~observations~~a significant part of the bromine ~~explosions~~explosion mechanism. Starting with molecular bromine in the gas phase, the sequence of autocatalytic chain reactions describing the bromine explosion reactions can be written in its simplest form as:

$Br_2 + hv\ (350\ nm < \lambda < 500\ nm) \rightarrow 2Br$ (R1)

$2(Br + O_3 \rightarrow BrO + O_2)$ (R2)

$2(BrO + HO_2 \rightarrow HOBr + O_2)$ (R3)

$2(HOBr_{(g)} \rightleftharpoons HOBr_{(aq)})$ (R4)

$2(HOBr_{(aq)} + Br^-_{(aq)} + H^+_{(aq)} \rightarrow Br_{2(g)} + H_2O_{(aq)})$ (R5)

Net: $2O_3 + 2HO_2 + 2Br^-_{(aq)} + 2\ H^+_{(aq)} \rightarrow 4O_2 + 2H_2O + Br_2$

In short, the autocatalytic multiphase chain reaction releases molecular bromine, Br_2, to be photolysed by solar radiation (hv) (R1). The resulting bromine atoms ~~remove~~ rapidly remove tropospheric O_3 (R2). The resultant BrO reacts with HO_2 to form HOBr (R3). This enters the aqueous phase or quasi liquid layers on cold brine or snow and ice~~,~~ (R4), where it reacts with halogen ions to release Br_2 to the atmosphere (R5). The efficiency of such a chain reaction depends on the chain length in the atmosphere. ~~This depends on~~ The ratio of the relative rate of chain propagation ~~and~~to chain termination reactions of the chain carriers, i.e. the Br and BrO, determines the chain length. The bromine explosion slows through the depletion of O_3 in the air mass, or through reactions of Br or BrO with formaldehyde or NO_2:

$Br + HCHO \rightarrow HBr + HCO$ (R6)

$BrO + NO_2 + M \rightarrow BrONO_2 + M$ (R7)

$BrONO_{2(g)} \rightleftharpoons BrONO_{2(aq)}$ (R8)

~~There~~In addition there are ~~also~~ cycles involving chlorine ions, also initiating ~~a~~the release of BrCl which leads to further catalytic loss of O_3. The involved reactions are explained in more detail elsewhere (e.g. Simpson et al., 2007; Sander et al., 2006).

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It was shown that BrO plumes can be transported far from their initial formation areas, ~~due to release from snow packs (Peterson et al., 2018) and blowing snow (Giordano et al., 2018) favored by~~as high wind speeds associated with cyclones (Begoin et al., 2010; Zhao et al., 2015; Blechschmidt et al., 2016~~.~~) can transfer them together with blowing snow (Giordano et al., 2018). Peterson et al. (2017) studied the vertical transport of BrO and ~~it's~~its recycling on aerosol particles, stating that BrO can be sustained, reformed and transferred on aerosols. Using a qualitative model, Jones et al. (2009) have shown~~,~~ that both a stable boundary layer with very low near surface wind speed conditions, as well as an unstable boundary layer with high wind speed conditions increase the number of reactants in the air and hence favor the bromine explosion. There are also several studies which tried to model tropospheric BrO plumes. Yang et al., (2020) used both a chemistry transport and a chemistry climate model to model tropospheric BrO, and compared the outputs with satellite columns and ground-based measurements. Fernandez et al., (2019) provided four years of polar spring comparisons between GOME-2A instrument columns and model runs, for the Arctic and Antarctic, having implemented polar halogen chemistry into the CAM-Chem model.

The ~~Polar Regions~~polar regions are some of the most remote ~~and hostile~~ places on the planet. Consequently, satellite remote sensing is a ~~unique~~suitable method to study bromine chemistry in the Arctic. Richter et al. (1998) and Wagner and Platt (1998) were the first studies on satellite observations of BrO plumes in ~~Polar~~polar regions, using the GOME instrument (Richter et al., 1998; Wagner and Platt, 1998; Burrows et al., 1999). Based on observations from the same instrument, Hollwedel et al. (2003) derived a six year time-series of Arctic and Antarctic total vertical column densities (VCDs) of BrO. This was the first scientific effort to study the evolution of BrO in the ~~Polar~~polar regions. The transport of BrO plumes, which represents a photo-stationary state with production and loss processes and their capability of depleting ozone, far away from the initial release area was studied with satellite remote sensing (Ridley et al., 2007; Begoin et al., 2010). The relationship between BrO release and young sea ice was also discussed (Wagner et al., 2001), where it was indicated that BrO concentrations are always found over or near sea ice on the Caspian Sea. Van Roozendael et al. (2004) used SCIAMACHY observations for Arctic BrO and compared them to GOME data, showing satisfactory agreement between the two different sensors. Theys et al. (2011) compared tropospheric BrO columns derived from GOME-2A to a chemical transport model, showing consistency with the release mechanisms of bromine. Sihler et al. (2012) compared GOME-2 BrO columns to ground-based measurements in the Arctic, demonstrating good agreement between them. Seo et al. (2019a) presented the first BrO retrievals from the TROPOMI instrument, showing high-resolution BrO cases with low fitting errors. Studies have also used satellite remote sensing, to link ~~them~~Bromine explosion events to their sources and triggering meteorological conditions~~, in order~~ to better understand this complex and significant phenomenon. For instance, Choi et al. (2018), Begoin et al. (2010), Toyota et al. (2011) and Jones et al. (2009) investigated links between tropospheric BrO and blowing snow. Blechschmidt et al. (2016) investigated a ~~BrO~~Bromine explosion event using GOME-2A and associated its long lifetime with continuous release of bromine molecules from blowing snow along the front of a polar cyclone.

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~~Major changes~~Changes in meteorological parameters, e.g. increasing air temperature (Serreze and Barry, 2011), decreasing mean sea level pressure over northeastern America and increasing pressure over Eurasia (Ogawa et al., 2018; McCusker et al., 2016), increase in cyclone frequency and intensity (Akperov et al., 2019), stronger surface winds (Mioduszewski et al., 2018) and changes in sea ice conditions (e.g. reduced sea ice extent; Stroeve et al., 2012), increased first year sea ice fraction (and consequently salinity), and therefore decreased sea ice thickness (Richter-Menge et al., 2017~~))~~) occur due to Arctic warming. It is therefore likely that the intensity, frequency and spatial distribution of bromine explosions in the Arctic are changing. These changes can potentially impact on the O_3 abundances and on the oxidant OH at high latitudes. Consequently, the objectives of this study are a) to derive the first consolidated and consistent long-term Arctic tropospheric BrO dataset using satellite remote sensing and b) to investigate and understand changes or trends in BrO and the relation to changes in sea ice, based on the new dataset. As described above, an earlier effort was carried out by Hollwedel et al. (2003), but they did not extract the tropospheric BrO column from their 6 year GOME dataset. ~~Moreover,~~ Choi et al., (2018) used an 11 year Arctic tropospheric BrO dataset from the OMI instrument~~,~~., and investigated the link to ~~young~~first year sea ice and sea salt aerosols released from blowing snow. However, the OMI sensor suffers from instrumental degradation, known as row anomaly (Class et al., 2010). In our study, we use measurements from four ultraviolet - visible satellite instruments to derive tropospheric VCDs of BrO over the Arctic, covering a time-span of 22 years, starting with GOME observations in 1996 and ending with GOME-2A and GOME-2B in 2017. We first retrieve BrO slant column densities (SCDs) for each instrument and then separate tropospheric VCDs from stratospheric BrO amounts.

This remainder of this paper is structured as follows: in section 2, a short technical description of the instruments used in this study is presented. In section 3, the methods applied for retrieving geometric and tropospheric BrO columns from the satellite sensors and the additional datasets used for stratospheric separation and sea ice flagging of tropospheric BrO are introduced. In section 4, an analysis ~~results~~ of the long-term data is presented, including time-series and maps of tropospheric BrO VCDs and comparisons with sea ice age and a statistical analysis of possible trends of tropospheric BrO VCDs. The paper ends with a summary and conclusions (section 5).

2 Instruments

The technical attributes of the satellite sensors that are used, together with information about instrumental degradation are described in the following. A short summary of characteristics of the sensors is given in Table 1.

2.1 GOME

The GOME (Global Ozone Monitoring Experiment) (Burrows et al., 1999) instrument was launched in 1995 on ERS-2. It was a nadir viewing scanning spectrometer, observing solar back-scattered radiation upwelling from the Earth's surface and atmosphere. It measured continuously in four spectral channels from 240 to 790 nm, with a spectral resolution between 0.2 and 0.4 nm. For 27 days per month, the spatial resolution of the forward scans was 40x320 km^2, and the swath 960 km. For

approximately 3 days per month, the instrument operated in narrow swath mode with a swath width of 240 km and ground scenes having a spatial resolution of 40x80 km^2. ERS-2 was in a ~~sun~~Sun synchronous orbit with a 10:30 local time equator overpass in the descending node. GOME was the first satellite instrument, which was able to measurement key tropospheric gases which have weaker absorption lines than ozone: examples are being NO_2, BrO, HCHO and SO_2 (Burrows et al., 1999). The instrument was launched in July 1995 and lost its global coverage in 2003, due to data rate limitation (the ~~onboard~~on board storage capability of the instrument was disabled and as a result data could only be transmitted directly to ground stations) (Bracher et al., 2005).

2.2 SCIAMACHY

SCIAMACHY (SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY) (Bovensmann et al., 1999; Burrows et al., 1995) was a satellite spectrometer ~~onboard~~on board Envisat. It was launched into space in 2002. The main advantage of SCIAMACHY compared to GOME was its broader spectral coverage, ranging from 210 nm to 2380 nm, allowing the observation of many trace gases in the near infrared (0.75 to 1.4 µm) and short wave infrared (1.4 to 3 µm) spectral regions. SCIAMACHY's spectral resolution was 0.2 nm to 0.5 nm, and its spatial resolution in the spectral region used for BrO retrievals was 30x60 km^2, with a 960 km swath width in nadir. The overpass of Envisat over the equator was at 10:00 local time. SCIAMACHY observed the Earth in nadir, limb and occultation geometries, providing a wealth of trace gas data on the atmosphere from the surface to the upper atmosphere (Bovensmann et al., 1999). In April 2012, Envisat lost contact with the ground station and as a result, the mission ~~had to be~~was terminated.

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2.3 GOME-2

The series of GOME-2 (Global Ozone Monitoring Experiment–2) (Callies et al., 2000) instruments were developed as the successors of GOME. There are currently three instruments in orbit, one launched ~~onboard~~on board Metop-A in 2006, one on Metop-B in 2012, and one on Metop-C in 2018. Here, we use data from GOME-2A and GOME-2B. All GOME-2 instruments share the same attributes and sense the Earth's backscattered radiance and ~~extraterrestrial~~extra terrestrial solar irradiance in the ultraviolet and visible part of the spectrum (240 nm to 790 nm). They have a spectral resolution between 0.2 nm and 0.4 nm, while the footprint size is 80x40 km^2 and a much wider swath (1920 km) than the previous instruments. GOME-2A changed its swath to 960 km and footprint to 40x40 km^2 in June 2013. The GOME-2 instruments are crossing the equator at 09:30 local time (Callies et al., 2000). All three instruments are currently in operation.

Table 1: Attributes of the satellite instruments used in this study

Instrument	Platform	Period	Footprint	Equatorial Overpass	Swath
GOME	ERS-2	1996 – 2003	320x40 km^2	10.30 LT	960 km

SCIAMACHY	Envisat	2002 – 2012	30x60 km^2	10.00 LT	960 km
GOME-2A	MetOp – A	2007 – present	80x40 km^2 ~~40X40~~40x40 km^2 (since June 2013)	09.30 LT	1920 km 960 km (since June 2013)
GOME-2B	MetOp – B	2012 – present	80x40 km^2	09.30 LT	1920 km

2.4 Instrumental Degradation

~~Many space~~ Space-borne optical instruments often suffer from a decrease in throughput in the ultraviolet spectral region, which arises from the deposition of absorbing layers on the optical surfaces such as mirrors, lenses or gratings. This results in a variety of effects such as loss of throughput and changing etalons in the instrument. The quality of the retrieved BrO data, which is produced from the weak absorption signal in the UV region, is influenced by these degradations. The GOME, SCIAMACHY and GOME-2 teams identify any degradation in the reflectances and correct where appropriate and possible. For example organic compounds and water, emitted by the spacecraft, are photochemically transformed by UV-B and vacuum UV from the ~~sun~~Sun and most likely form long ~~changing~~chain polymers, which have low vapour pressure and are adsorbed on the mirrors. In this context, Snel (2000~~),~~) showed that the GOME sensor experienced degradation in all wavelength regions but in particular in the UV, consistent with degradation of the scan mirror. Krijger et al. (2007~~),~~) compared the degradation of GOME to SCIAMACHY with respect to the reflectivity. Dikty et al. (2011~~),~~) investigated the impact of GOME-2A throughput loss on various time-series of trace gases. Most of the major degradation effects on the sensors are identified and documented in literature and where possible accounted for (Munro et al., 2016; Garcia et al., 2016). In addition, GOME-2A recently moved into a drifting in orbit and there are periods during which solar measurements are no longer feasible.

3 Methods

In this section, the methodology used to retrieve BrO SCDS from the satellite measurements and to obtain tropospheric BrO VCDs and datasets used in this study are described.

3.1 Retrieval of BrO slant column densities

Similar to previous studies on atmospheric BrO from hyperspectral satellite remote sensing observations in the solar spectral regions, the retrieval algorithm ~~is based on~~uses the differential optical absorption spectroscopy (DOAS) method (Platt and Perner, 1983; Burrows et al., 2011). DOAS ~~is an application of~~evolves from the Beer and Lambert law, which describes the attenuation of electromagnetic radiation in a medium:

$$I = I_o \, e^{-\int (\sum_{j=1}^{J} \sigma_j(\lambda)\rho_j) ds} e^{-\int \sum_{j=1}^{J} \{\sigma_j(\lambda)\rho_j\} ds}$$

Eq. (1), where I is the measured intensity of the electromagnetic radiation, I_o is the initial intensity, J is the total number of

trace gases absorbing, j denotes a particular trace gas (e.g. BrO), σ(λ) is the cross section of the absorber at wavelength λ, ρ the concentration of the trace gas ~~and s the length of~~. The integral is taken along the light path s.

The ~~main idea of the DOAS method is, that the~~ atmospheric ~~amount~~absorption of ~~the~~ trace gases of interest can be retrieved by using knowledge of their characteristic spectral fingerprints. This is ~~done~~achieved by separating the extinction signal into a low frequency and a high frequency part. The low frequency part is treated as a closure term and is fitted by a low order polynomial. The higher frequency term contains the absorption structures of the trace gases. The final output of the retrieval is the slant column density of the trace gas, i.e. the density of the trace gas, integrated along the light path (Platt and Stutz, 2008):

$$SCD_j = \int \rho_j(s)ds \quad \text{Eq. (2~~),~~)}$$

~~For cloud free conditions, the~~The radiance upwelling at the top of the atmosphere is ~~described~~approximated at a given wavelength by:

$$I(\lambda) = \text{~~}cI_0\alpha(\lambda)I_o(\lambda)\ e^{-\int\sum_{j=1}^{J}\{\sigma_j SCD_j - \sigma Ray(\lambda)SCD(Ray) - \sigma Mie(\lambda)SCD(Mie)\}ds}e^{-\int\sum_{j=1}^{J}\{\sigma_j(\lambda)SCD_j + \sigma_{Ray}(\lambda)SCD(Ray) + \sigma_{Mie}(\lambda)SCD(Mie)\}ds} \quad \text{Eq. (3),}$$

where ~~c~~α is the scattering efficiency, SCD_j the slant column density of the gas with index j, $\sigma_{Ray}(\lambda)$ and $\sigma_{Mie}(\lambda)$ are the ~~absorption~~scattering cross sections of Rayleigh ~~scatterers~~scattering molecules (e.g. primarily air molecules, molecular nitrogen N_2 and oxygen, O_2) and Mie ~~scatterers~~scattering particles (e.g. aerosol particles), SCD(Ray) and SCD(Mie) are the corresponding slant columns of Rayleigh and Mie scatterers. ~~The~~As Rayleigh and Mie ~~terms in Equation 2 are the low frequency broad band features and~~scattering efficiency varies smoothly with wavelength, they can be approximated by ~~a polynomial~~low order polynomials. This results in the following approximation:

$$ln\frac{I_o(\lambda)}{I(\lambda)} = \text{~~}\sum_j\{\sigma_j(\lambda)SCD_j(\lambda)\} - \sum_p\{\sigma_p\lambda^p\}\text{~~}\sum_j \sigma_j(\lambda)SCD_j - \sum_p b_p\lambda^p \quad \text{Eq. (4~~)~~)}$$

, where b_p are the coefficients of the polynomial. Variants on Eq. (4) are also employed to fit the spectra. To retrieve accurate BrO SCDs, an optimal selection of the spectral window, which maximises the information content with respect to the BrO absorption, and the selection of corresponding cross sections of other trace gases absorbing in the same spectral window is the first step. We chose to use temperature dependent cross sections of ozone (dominant absorber in the UV) by Serdyuchenko et al. (2014) at 223 and 243 Kelvin and a BrO cross section (Fleischmann et al., 2004) at 223 Kelvin. In addition, a pseudo cross section is used for simulating the filling-in of Fraunhofer lines by Raman scattering known as the Ring effect (Vountas et al., 1998), and another pseudo cross section, which deals with the issue of poor spectral sampling (Chance et al., 2005), was ~~added~~included in the fitting for all instruments. The high spectral resolution absorption cross sections were convolved by the slit function of each instrument. The ~~reason for~~impact of using ~~these cross sections is that~~

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~~our study is dedicated to BrO released in the Arctic region. Tests were made for~~ different combinations of trace ~~gases~~gas absorptions on the fit of BrO SCD was investigated. It was found that the omission of the explicit fitting of NO_2 and SO_2 has a minimal impact on the fit of the BrO SCD~~: the~~ north of 70° N. The differences in BrO SCD between fits with and without NO_2 or SO_2 in the selected spectral ranges were typically less than 1% of the BrO SCD. ~~Therefore,~~Consequently, we decided to use only the cross sections of the dominant absorber O_3 in this region~~,~~ and of the trace gas of interest itself, BrO ~~were added. Also, a four degree polynomial was used, as the~~in the non-linear least squares SCD fitting. The differences between fits of BrO SCD using fourth and fifth order polynomials were small ~~on the BrO SCDs, while~~and the quality of the fit improved ~~greatly~~significantly from a third to fourth degree polynomial fit. These results led to the selection of the use of the 4th order polynomial in our retrieval. The selection of parameters used in this study is appropriate for BrO columns in the region north of 70° N.

As BrO is a relatively weak absorber, small changes in the input parameters~~,~~ and especially of the fitting window of the retrieval~~, can~~ lead to large changes in the quality of the fit. Although there are many good practices developed for the DOAS fitting window selection for an absorber (e.g. it must include at least two absorption peaks from the trace gas of interest, no large Fraunhofer lines, small interference from other species etc.), there is no precise and agreed methodology to determine the optimal selection. ~~As a result~~Consequently, different spectral fitting windows for BrO retrievals have been used in previous studies. For example, Richter et al., (1998), used a 345 - 359nm wavelength region for GOME, Afe et al., (2004), used a 336 - 347 nm fitting window for SCIAMACHY, while Theys et al., (2009) used a 336 to 359 nm fitting window for GOME-2A. Each of the sensors has slightly different instrumental characteristics, and each of them shows different degradation behaviour. Consequently, we chose ~~different~~the optimal spectral fitting window for each of the sensors ~~that result in~~using the following set of selection criteria: a) ~~a low~~smallest root mean ~~squared~~square error (~~RMS~~RMSE) of the fit, b) ~~a reduced~~minimal trend of BrO SCDs over a clear Pacific reference region, where no strong trend in BrO is expected and c) good agreement between retrievals from the different sensors for periods ~~with more than one instrument in operation.~~of overlapping measurements. The ~~RMS~~RMSE of the fit in absolute units is defined as:

$$RMSE = \sqrt{\sum_{i=1}^{N} \frac{\left(ln\left(\frac{I_0(\lambda_i)}{I(\lambda_i)}\right) - \sum_J \sigma_j(\lambda_i) SCD_j - P(\lambda_i)\right)^2}{N}} \quad \text{Eq. (5),}$$

where N is the number of ~~wavelengths~~spectral points and P(λ) the low order ~~polynomial~~polynomial. The ~~RMS has been evaluated for~~RMSE was averaged over all the scenes in the region of interest (i.e. the Arctic from 70.0° N to 85.0° N latitude, ~~-180°E~~180° W to ~~180°E~~180° E longitudes) and for the Pacific reference region ~~(-~~(50.0~~°S~~0° S to 10.0~~°N~~0° N latitude and ~~235.0°E~~90.0° W to ~~270.0°E~~125.0° W longitude).

Figure 1 shows the SCDs of BrO over the Pacific reference region and the ~~RMS~~RMSE of the fit for the Arctic and Pacific regions.

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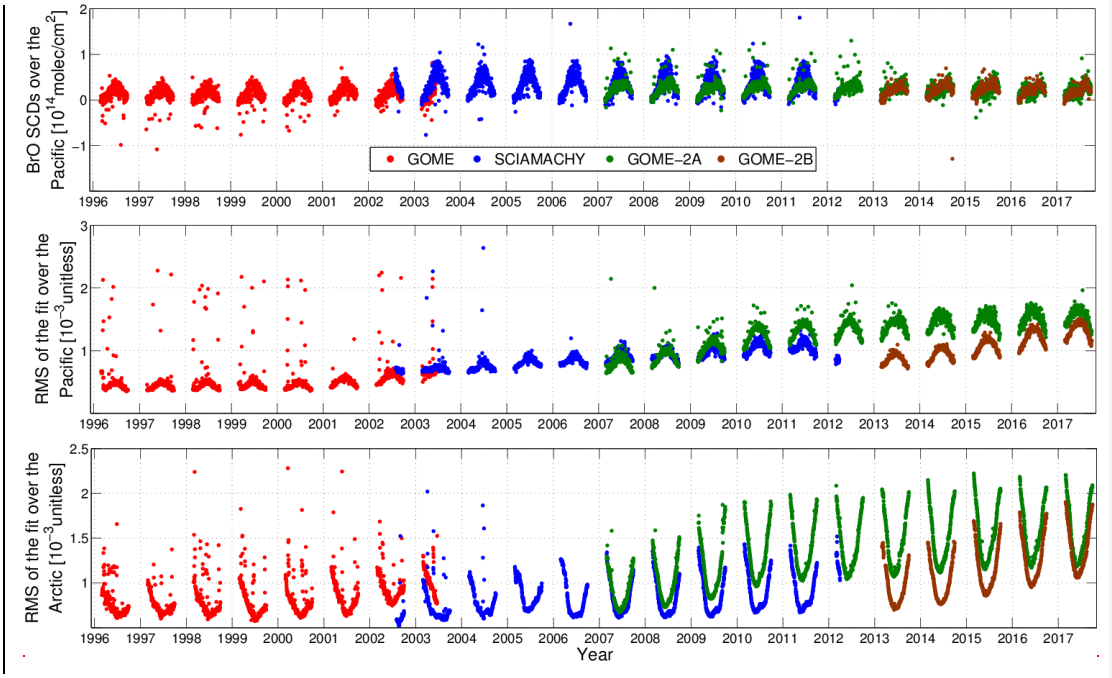
BrO SCDs over the Pacific [10^14 molec/cm^2]
GOME
SCIAMACHY
GOME−2A
GOME−2B
RMS of the fit over the Pacific [10^−3 unitless]
RMS of the fit over the Arctic [10^−3 unitless]
Year

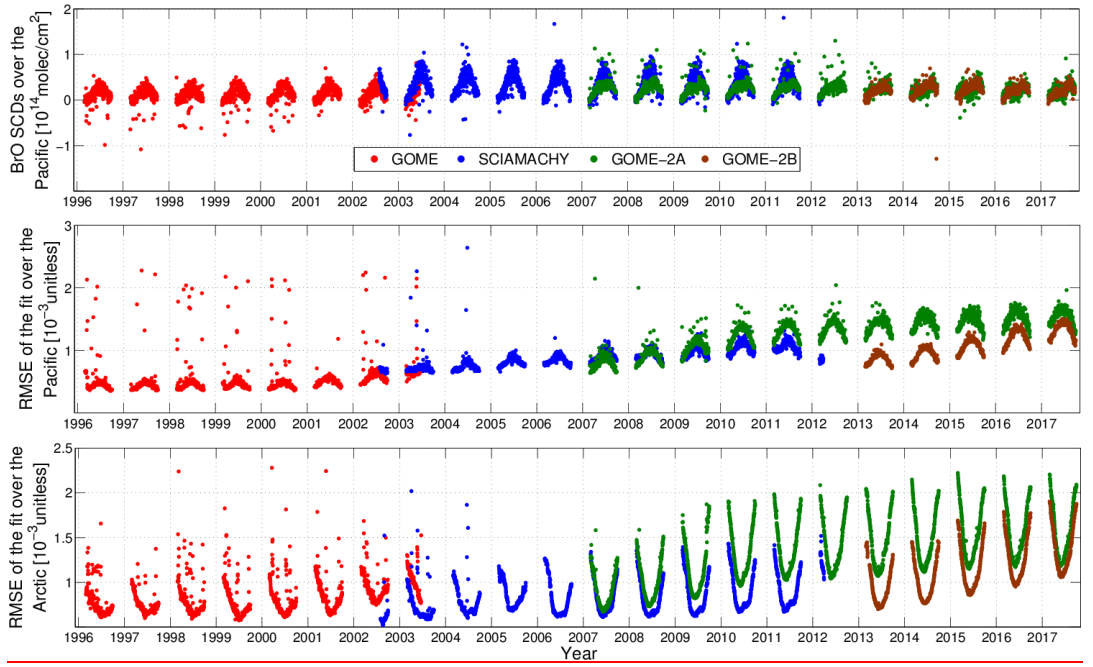

Figure 1: Time-series of a) SCDs of BrO [molec/cm^2] over the Pacific, b) fitting ~~RMS~~RMSE over the Pacific and c) fitting ~~RMS~~RMSE over the Arctic. GOME data is shown in red, SCIAMACHY in blue, GOME-2A in green and GOME-2B in brown colour.

The annual cycle in the fitting ~~RMS~~RMSE for the Arctic results from changes in the ~~sun's~~Sun's position and its impact on the upwelling radiance. In spring and autumn, when the solar zenith angle is larger, the scattering and attenuation increases, and as a result, the radiance signal is low. In the Arctic, SCIAMACHY has the lowest fitting ~~RMS~~RMSE of all instruments. GOME-2A shows a rapid increase in ~~RMS until~~RMSE up to 2009~~,~~ and a smaller upward trend in the following years. A similar systematic increase in ~~RMS~~RMSE occurs for GOME-2B. The ~~RMS~~RMSE for the Pacific region shows a similar behaviour for GOME-2A and GOME-2B, as both increase strongly with time. GOME appears to have lower ~~RMS~~RMSE values on average than the GOME-2A and GOME-2B instruments, presumably because of the lower spatial resolution, but the ~~RMS~~RMSE shows large variability. Generally, daily mean ~~RMS~~RMSE values are below 2.0x10^{-3}, for all instruments. There is no clear trend in the SCD of BrO over the Pacific region for any of the instruments.

The use of a reference area over the Pacific as background spectrum is an alternative to the use of solar irradiance measurements, which removes systematic errors arising from interfering instrumental structures in the solar irradiance measurements. The region of the Pacific is selected because of its relatively small annual cycle of BrO -(Richter et al., 2002). In this way, the quality of the fit improves greatly as problems in the radiances mainly cancel out. ~~This also has other~~

~~benefits. For example, GOME-2A is currently drifting in orbit and there are periods during which solar measurements can no longer be carried out.~~ Consequently, the Pacific background spectrum has been used instead of the Sun background spectrum for all instruments in the present study. Although trends over the clean Pacific background region resulting from instrumental degradation were minimised, residual trends had to be accounted for. This has been achieved by applying an additional Pacific correction to each instrument separately. The normalization method computes the average BrO SCD in a small Pacific area ($0.0^o \pm 10.0^o$ latitude, $180.0^o \pm 20.0^o$ longitude) and then subtracts this average from every pixel of the BrO SCD. To compensate the negative bias imposed by the method, a constant offset of ~~$7x10^{13}$ molec~~ $7x10^{13}$ molec/cm^2 was added for every day (Richter et al, 2002; Sihler et al., 2012). This correction tackles offset errors that are occurring for weak absorbers, and are due to instrumental degradation (Alvarado et al., 2014).

The empirically determined ~~set~~sets of parameters used in the ~~fitting of~~ BrO ~~in the spectral windows~~retrievals are reported in Tables 2 and 3.

Table 2: Parameter selection for all instruments

Parameters	Cross sections - Application Selection
Ozone, O_3	(Serdyuchenko et al., 2014), 223K and 243K
BrO	(Fleischmann et al., 2004), 228 K
Ring effect	Ring cross section calculated by SCIATRAN model
Under sampling correction	Yes
Fraunhofer ~~atlas~~lines	Chance and Kurucz (Chance et al., 2010)
Background spectrum	Pacific area ~~(~~(50.0°S to 10.0°N lat., ~~235~~90.0°W to ~~270~~125.0°W lon.)
Degree of the polynomial	4^{th}

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Table 3: Fitting windows used for the different instruments

Instrument	Fitting Window [nm]

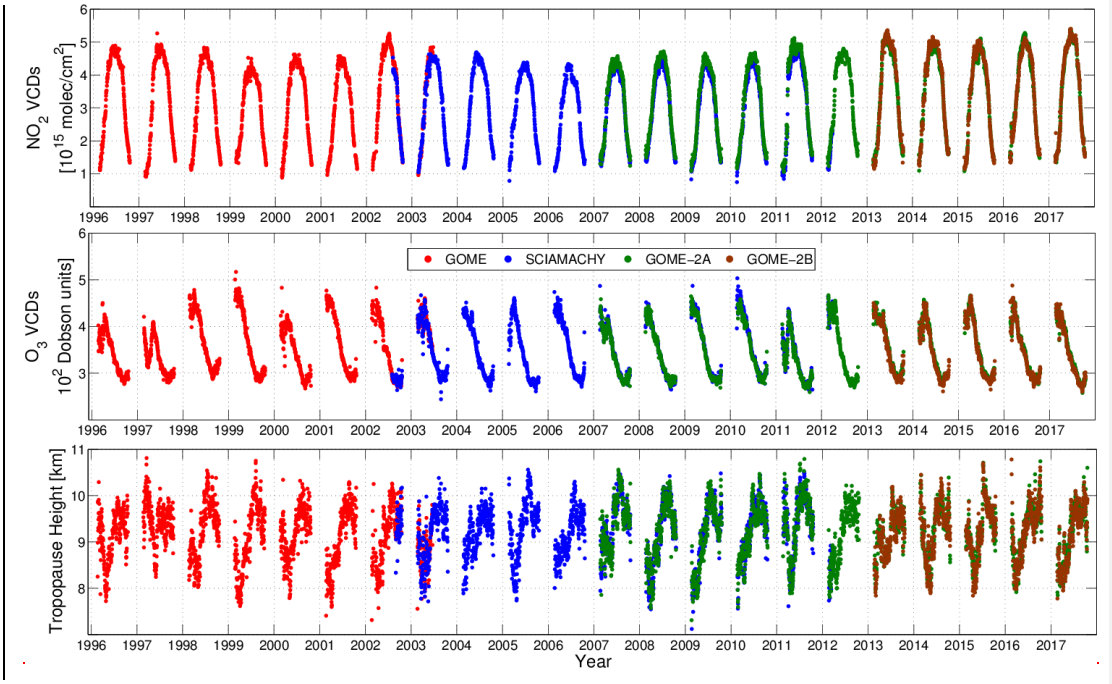
GOME	336.8 - 358
SCIAMACHY	336 - 347
GOME-2A	337.5 - 357
GOME-2B	338 - 360

3.2 Tropospheric BrO vertical column densities and datasets

NO_2 and O_3 ~~column~~columns from satellite retrievals~~,~~ and tropopause height from meteorological reanalysis data are used for extracting the tropospheric BrO component from the retrieval (stratospheric separation). Sea ice data (age and type) obtained by satellite remote sensing was used in order to identify regions with sea ice cover and hence high surface reflectivity, which is required for the retrieval of tropospheric BrO in this study and for data interpretation in relation to bromine sources.

3.2.1 Stratospheric Separation

In order to derive the tropospheric BrO VCD from the retrieved SCD of BrO, the method of Theys et al. (2009) was used. Briefly, this method ~~is based on~~uses a stratospheric BrO climatology, derived with the BASCOE model (Errera and Fonteyn, 2001) and requires year, latitude, tropopause height, O_3 and NO_2 columns as input. This approach has been applied successfully in previous studies (e.g. Begoin et al., 2010; Theys et al., 2011; Blechschmidt et al., 2016; Choi et al., 2018). In the present study, satellite ~~derived~~retrieved O_3 VCDs from Weber et al. (2013), stratospheric NO_2 VCDs from the QA4ECV project (Boersma et al., 2017), and from the Tropospheric Emission Monitoring Internet Service (TEMIS), (Boersma et al., 2004) and tropopause heights ~~derived~~retrieved from NCEP reanalysis (Kalnay et al., 1996) data were used as input. In Theys et al. (2009), a correction factor was applied, to account for the long-term reduction of bromine emissions in the stratosphere. This factor was based on ground based zenith-sky measurements of BrO over Harestua (Hendrick et al., 2008). In the present study, this factor was excluded, as the long-term development of stratospheric BrO VCDs of the model without applying the correction factor comes to a closer qualitative agreement with updated measurements of BrO over Harestua (from F. Hendrick, BIRA-IASB, personal communication). The time-series of NO_2, O_3 and tropopause height are shown in Figure 2:


NO2 VCDs
[10^15 molec/cm^2]
O3 VCDs
10^2 Dobson units]
Tropopause Height [km]
GOME
SCIAMACHY
GOME−2A
GOME−2B
1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017
Year

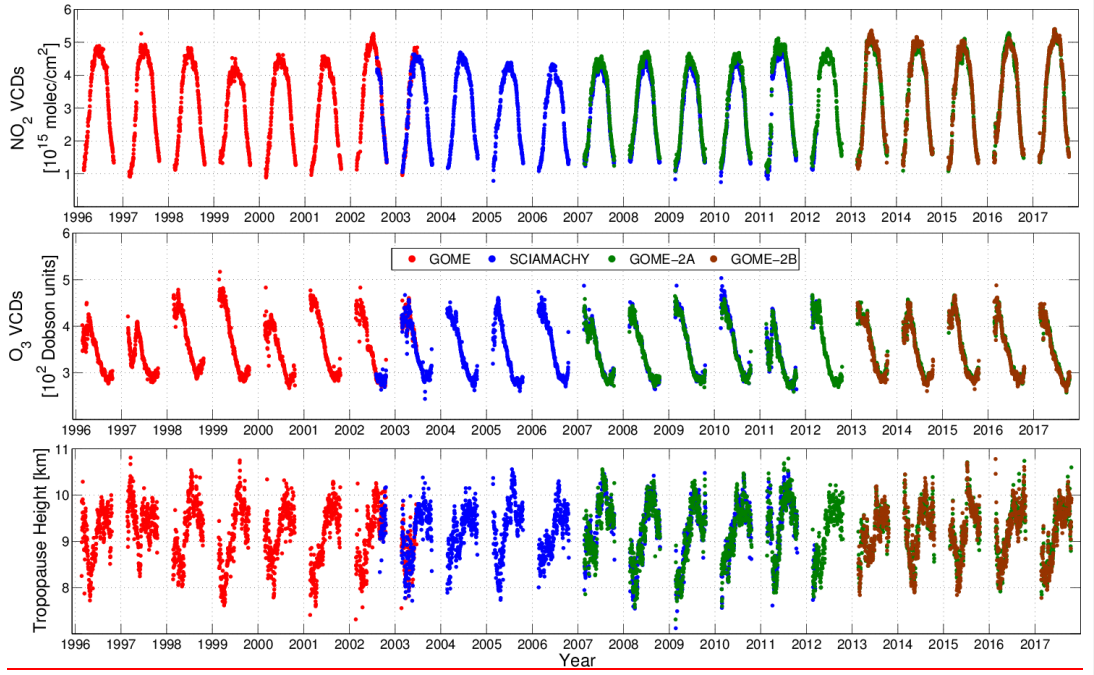


Figure 2: Time-series of daily averaged input data over the Arctic used for deriving stratospheric BrO VCDs: a) stratospheric NO_2 VCDs [molecules/cm^2] from QA4ECV (GOME, SCIAMACHY and GOME-2A) and TEMIS (GOME-2B), b) O_3 VCDs [DU] from Weber et al. (2013) and c) tropopause height [km] from NCEP reanalysis data. Data for the GOME instrument is coloured in red, SCIAMACHY in blue, GOME-2A in green and GOME-2B in brown. All three time-series show daily averages over the Arctic region (>~~70°N~~70° N).

The following formula (Theys et al., 2009) is used to derive the tropospheric VCD of BrO:

$$VCD_{tropo} = (SCD_{total} - VCD_{strato} \times AMF_{strato}) / AMF_{tropo} \quad \text{Eq. (6),}$$

where SCD_{total} is the slant column of BrO retrieved by the DOAS method, VCD_{strato} corresponds to the stratospheric BrO VCD ~~derived~~retrieved from the Theys et al., (2009) climatology, AMF_{strato} is a stratospheric air mass factor, AMF_{tropo} is a tropospheric air mass factor. For the latter, as in Begoin et al. (2010) and Blechschmidt et al. (2016), a surface albedo of 0.9 has been assumed above sea ice and that all tropospheric BrO is well mixed within the boundary layer extending to 400m altitude. Note that the stratospheric BrO VCD column is independent of the BrO SCD ~~derived from the DOAS retrieval described in section 3.1 and settings therein~~ and only depends on the Theys et al. (2009) climatology and its inputs.

3.2.2 Sea Ice

In order to study the connection between tropospheric BrO and sea ice under the impact of Arctic warming, long term sea ice data (starting from 1996) is required in this study. In addition, since the tropospheric AMF applied for the retrieval of tropospheric BrO (see previous section) assumes a surface albedo of 0.9, the sea ice data was used to remove data with no sea ice cover from the BrO data. For this purpose, the sea ice age dataset from Tschudi et al. (2019) was used. It is retrieved from different passive microwave satellite remote sensing instruments and has a very high spatial resolution of 12.5x12.5 km^2, while its temporal resolution is 7 days.

4 Results

~~In this study, the focus is the long term analysis of BrO columns during the period from March until September. This period has the best coverage by the UV-VIS satellite remote passive sensors at high latitudes.~~ The passive remote sensing spectrometers GOME, SCIAMACHY, GOME-2A & GOME-2B measure the upwelling reflectance at the top of the atmosphere. The months of October to February have few or no observations due to polar night in the target latitudes~~.~~ north of 70.0° N. The largest solar zenith angle (SZA) used is 80 degrees. The long term analysis of BrO columns was performed during the period from March until September, from 1996 to 2017. This period has the best coverage by the UV-VIS satellite remote passive sensors at high latitudes. The analysis is restricted to data northwards of 70.~~0~~°0° N, which is referred ~~to~~ as the Arctic~~ here~~. This region was chosen because the source regions ~~for BrO explosion events~~of bromine explosions and thus plumes of elevated BrO are known to be associated with regions of ~~high~~ sea ice cover. We present the derived BrO VCD time-series for the Arctic region, together with corresponding annual cycles, scatter plots and map plots in section 4.1. The tropospheric BrO is ~~compared to~~correlated with sea ice coverage and age in section 4.2, to investigate the impact of changing sea ice conditions~~ due to Arctic Amplification~~ on BrO amounts in the Arctic's troposphere. Finally, a trend analysis of tropospheric BrO is performed, together with a check for statistical significance of the trends (section 4.3).

4.1 Comparison between the BrO columns ~~derived~~retrieved from different sensors

The geometric BrO VCD is ~~derived~~retrieved by dividing the BrO SCD with a simple stratospheric AMF, which takes into account the scattering at the surface but ignores the impact of scattering within the atmosphere. Consequently, it necessarily differs from the sum of the tropospheric and stratospheric column. Daily values of the geometric, stratospheric and tropospheric VCDs of BrO over the Arctic region are shown in Figure 3.

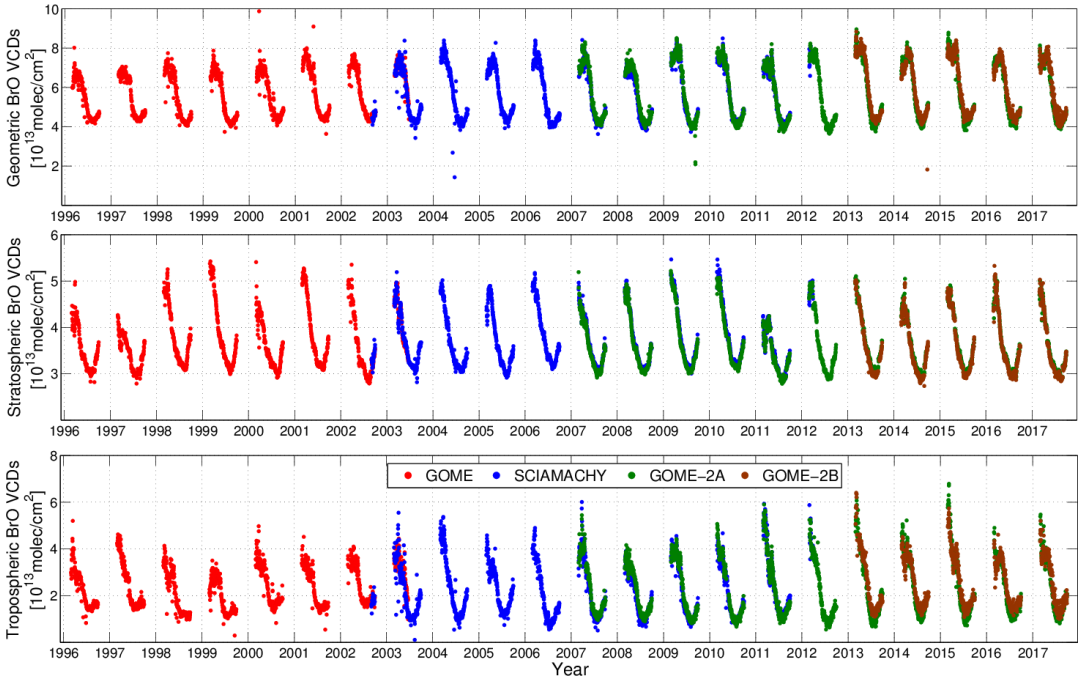


Figure 3: Long-term BrO time-series over the Arctic region: a) daily geometric BrO VCDs [10^{13} molec/cm^2], b) daily stratospheric BrO VCDs [10^{13} molec/cm^2] and c) daily tropospheric BrO VCDs [10^{13} molec/cm^2]. All figures show daily averages ≥ 70.0°N latitude. GOME data is coloured in red, SCIAMACHY in blue, GOME-2A in green and GOME-2B in brown.

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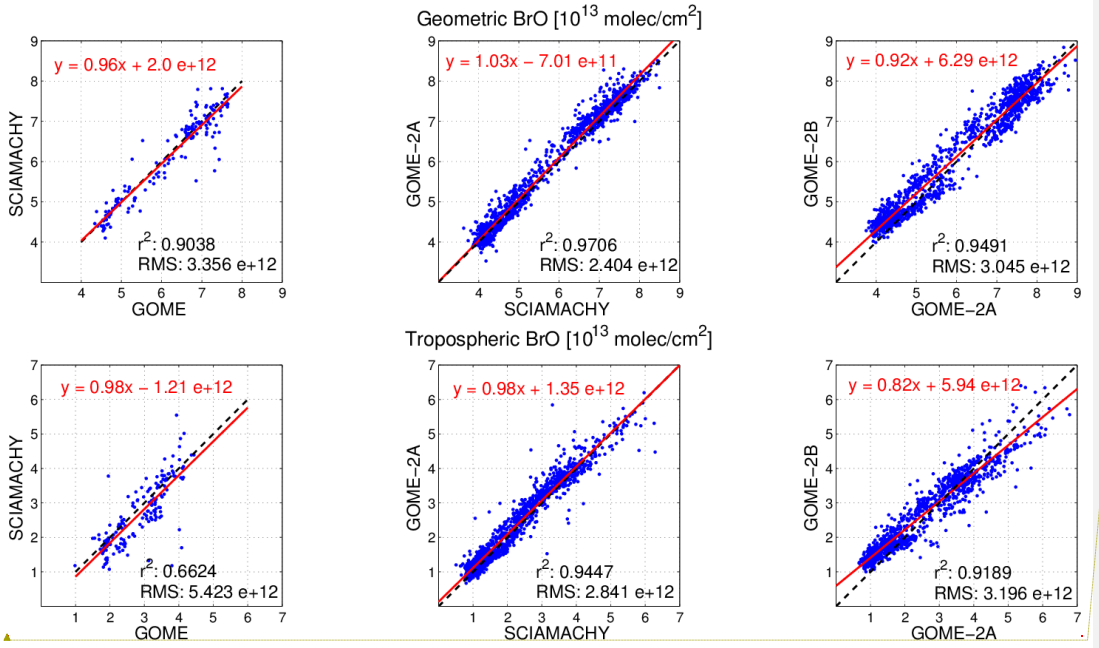
The geometric VCD accounts for the expected differences ~~from~~between the different viewing geometries of the satellite sensors to a good first order. ~~Qualitatively, there~~ There is good agreement during periods of overlapping measurements e.g. between the retrieved geometric BrO VCD from GOME and SCIAMACHY (from August 2002 to June 2003), SCIAMACHY and GOME-2A (from March 2007 to March 2012) and finally GOME-2A and GOME-2B (from March 2013 to September 2017). A quantitative comparison is provided below. The stratospheric BrO VCDs show a small upward trend from 1995 to 2001 and a slight decrease afterwards ~~as a result of changes in O_3, NO_2 and tropopause height.~~, which are in agreement with measurements of stratospheric BrO from Harestua station (Hendrick et al., 2008).

The comparison of tropospheric BrO VCDs time-series during the periods of overlap between the different instruments ~~show~~shows a similar level of agreement to that ~~for~~of the geometric VCDs. The seasonality of the tropospheric time-series is also similar to the geometric one. We attribute this seasonality to be in large a result of the inorganic release of ~~bromine associated with~~Br_2 and BrCl from sources, which depend on sea ice and meteorological parameters. As described in the introduction, in polar spring, the combination of low ~~temperatures~~temperature conditions on first year sea ice, ~~presumably~~

having sufficient brine, triggers the release of ~~Br in~~Br_2 and BrCl into the ~~atmosphere~~troposphere. This ~~occurs dominantly~~condition prevails in spring~~. During polar summers and early autumn,~~, moving slowly northwards with the ~~sea ice extent~~ solar zenith angle. During July and August, the temperature reaches ~~the yearly minimum and the temperature~~ its maximum~~, because of the increased solar insolation.~~. In September, the minimum sea ice extent is observed. The release of organo-bromine compounds from the ~~ocean~~oceanic biosphere is hence expected to be highest in summer and early autumn. This provides a biogenic source of bromine, but the oxidation of organic bromine containing compounds is relatively slow compared to the release of BrO from ~~BrO~~bromine explosion events. During summer and early autumn, tropospheric BrO VCDs reach their minimum values of the year. A small increase is observed in each September. The origin of this increase is not yet identified. Potential candidate explanations include inaccuracies in the stratospheric BrO VCDs calculation or potentially lower temperature accelerating the inorganic release of bromine from brine without reaching the threshold for explosion.

We identify peaks in the tropospheric BrO VCDs time-series: 2007, 2013 and 2015 are the years with the highest tropospheric BrO VCDs in polar spring. Hollwedel et al. (2003) investigated the period from 1996 to 2001. Despite the different settings and cross sections used in the retrieval, their geometric VCDs have similar magnitudes and patterns to those presented here (i.e. they increase from 1997 to 1998 and then decrease from 1999 to 2000). It is also interesting to compare the results from this study with those from Choi et al. (2018). They used the operational product of the OMI instrument (from 2005 to 2015) and the same stratospheric separation method as applied here. In agreement with our findings, Choi et al. (2018) found a peak in tropospheric BrO VCDs in 2007. However, the OMI dataset does not show the same increase as the SCIAMACHY and GOME-2A data in later years. The origin of this difference is not identified. It may be due in part to the strong row anomaly affecting the OMI data product (Class et al., 2010).

Figure 4 shows scatter plots of geometric and tropospheric VCDs, for the three overlapping time periods of the instruments.



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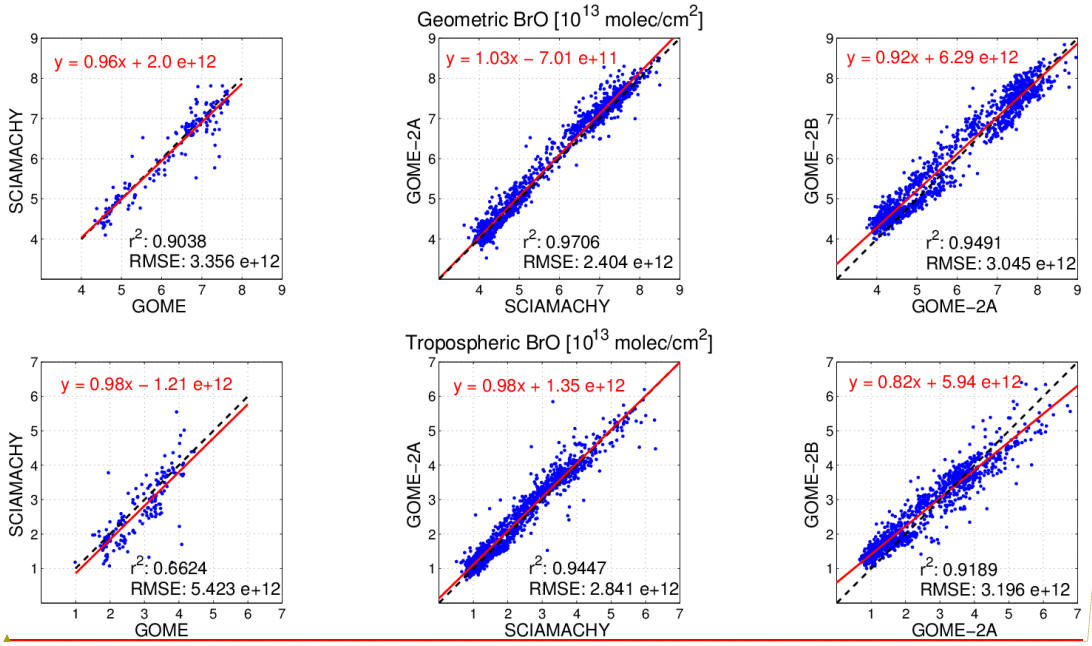

Figure 4: Scatter plots of geometric BrO VCDs (upper row), and tropospheric BrO VCDs (lower row) for (left) GOME against SCIAMACHY (August 2002 to June 2003), (middle) SCIAMACHY against GOME-2A (March 2007 to March 2012) and (right) GOME-2A against GOME-2B (March 2013 to September 2017). The dashed black line in each scatter plot is the reference line, the red one is the linear regression line. The Pearson correlation coefficient (squared, r^2), the ~~RMS~~RMSE and the y function of the regression line are also given. The units for all scatter plots are [10^{13} molecules/cm^2].

The best agreement is found between SCIAMACHY and GOME-2A, both for the geometric and the tropospheric VCDs, while the ~~least good~~ agreement is ~~found~~poorer between GOME and SCIAMACHY (this ~~can be~~is attributed to the comparably short overlapping period between these sensors).

Climatological seasonal cycles (averages over the whole period of retrievals of geometric, stratospheric and tropospheric VCDs) for each instrument are shown in Figure 5.

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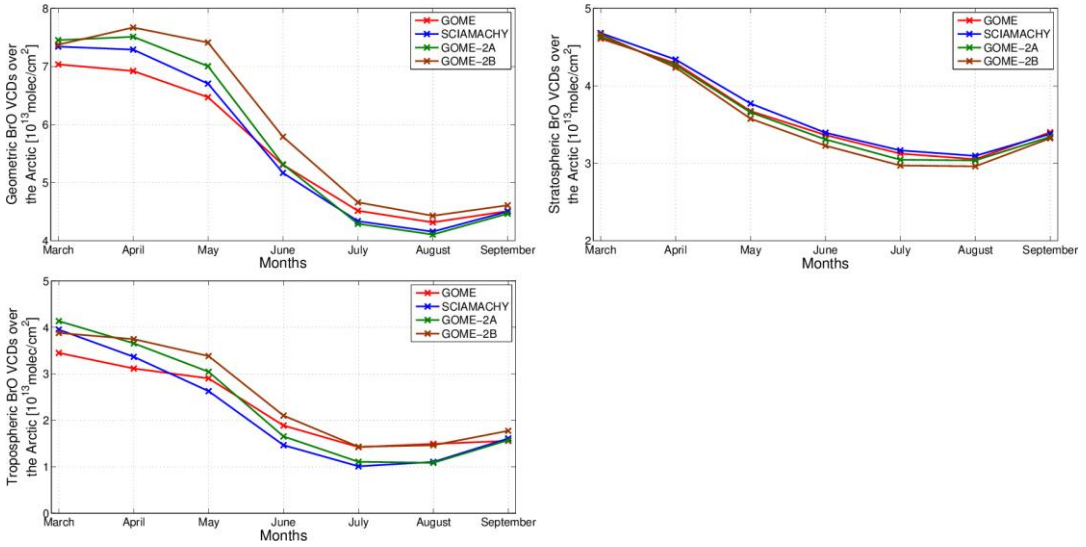
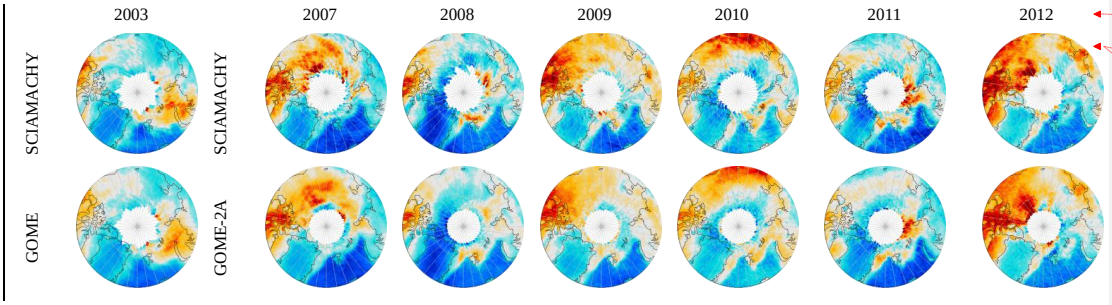


Figure 5: Climatological seasonal cycles of a) geometric BrO VCDs [10^{13} molec/cm^2], b) Stratospheric BrO VCDs [10^{13} molec/cm^2], and c) Tropospheric BrO VCDs [10^{13} molec/cm^2] over the Arctic for GOME (red), SCIAMACHY (blue), GOME-2A (green) and GOME-2B (brown).

The annual cycles of the geometric and the tropospheric VCDs time-series are similar in shape. The largest VCDs occur for all instruments in polar spring (March to May), followed by a strong decrease from May to June. In spring, GOME-2B VCDs are slightly larger, while GOME columns are slightly lower than data from the other instruments for the geometric VCDs. In summer and early autumn GOME VCDs are higher. For the tropospheric VCDs, the differences between the instruments become smaller.

Figure 6 shows average maps of geometric VCDs of BrO over the Arctic for the overlapping periods of the sensors.



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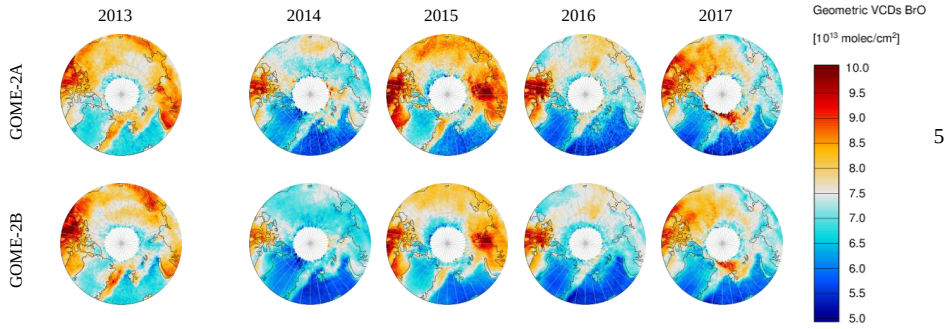
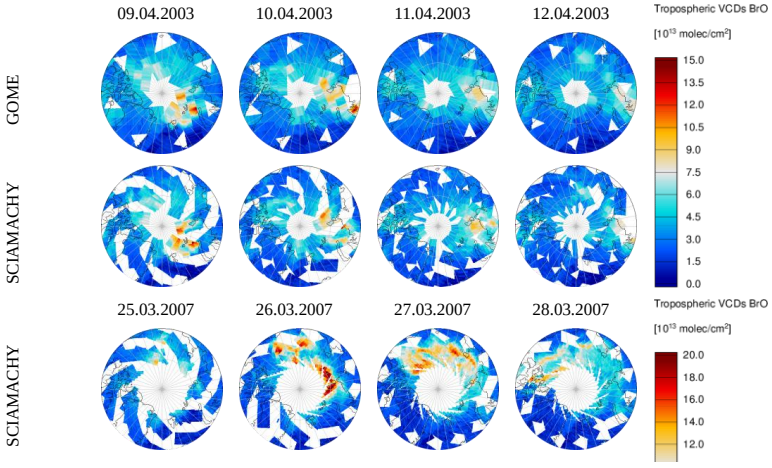


Figure 6: Monthly mean for March of geometric BrO VCDs [10^{13} molec/cm^2], in the Arctic region. Rows indicate different instruments, while columns different years~~, corresponding to~~ of overlapping periods of ~~instruments~~measurements.

~~We see that for most years, high~~Retrieved geometric BrO VCDs occur in similar ~~areas (~~locations and are of similar magnitude~~) for~~ from the different instruments. A qualitative comparison of geometric BrO VCDs between this study and the one by Hollwedel et al. (2003) ~~has been performed, showing again~~shows good agreement, with plumes of BrO being of similar magnitude and appearing over the same ~~regions~~locations.

Figure 7 shows ~~selected~~ the evolution of tropospheric BrO VCD maps over the Arctic ~~for particular BrO~~over 4 days of selected bromine explosion events, one event for each overlap period of the different sets of sensors. ~~For every event, we present 4 days, where BrO was released and transported in the Arctic troposphere.~~



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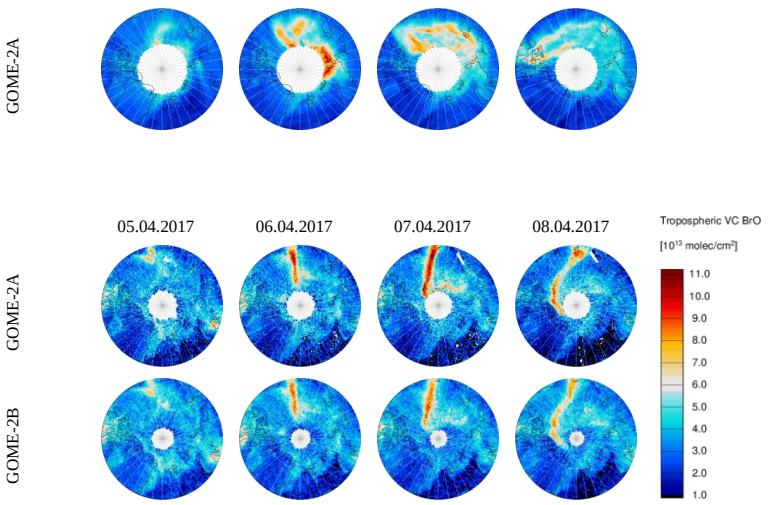

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Figure 7: Examples of ~~BrO~~bromine explosion events over the Arctic region for overlapping measurement periods between the sensors. Rows refer to the different instruments, whereas columns refer to the dates. For each case, four daily average maps of tropospheric BrO VCD [10^{13} molec/cm^2] -are shown.

~~BrO~~Bromine explosion events are characterised by high values of tropospheric BrO VCDs, which occur every polar spring. The agreement between the tropospheric BrO VCDs retrieved from the different sensors is good, as shown above. BrO plumes appear over the same areas and have similar magnitudes for each bromine explosion case. The times of observations are similar but not identical and ~~as yet,~~ we have not identified evidence of this ~~impacting~~influencing the comparison of tropospheric BrO VCDs. The sensors also observe the transport of plumes of BrO by cyclones away from the initial release area (e.g. the 2007 case shown in Figure 5, investigated in more detail by Begoin et al., 2010~~) is also observed by the sensors.~~). Hence, the track of cyclones transporting BrO plumes is expected to influence longer-term averaged BrO maps.

4.2 Arctic Tropospheric BrO and its ~~Relation~~relationship to Sea Ice

In this section, the evolution of tropospheric BrO and its relation to sea ice is presented. More specifically, the relationship between first year ice and tropospheric BrO is investigated. Since an albedo of 0.9 was assumed in the tropospheric AMF, a sea ice based ground scene flagging of our tropospheric BrO dataset was performed. In this way, only BrO observations above sea ice are analysed. BrO plumes are also transported over the ocean, but in this study, we focus on the plumes created by bromine explosions over sea ice. As described in section 4.1, the individual BrO VCDs time-series from the four sensors are highly consistent and the remaining inconsistencies are small. Hence, a merged tropospheric BrO dataset over sea ice was ~~derived~~retrieved, by ~~simply~~ averaging the overlapping days between the sensors. The merged tropospheric VCDs BrO dataset is shown in Figure 8 together with the results from the individual sensors and the time-series of sea ice extent from Tschudi et al. (2019).

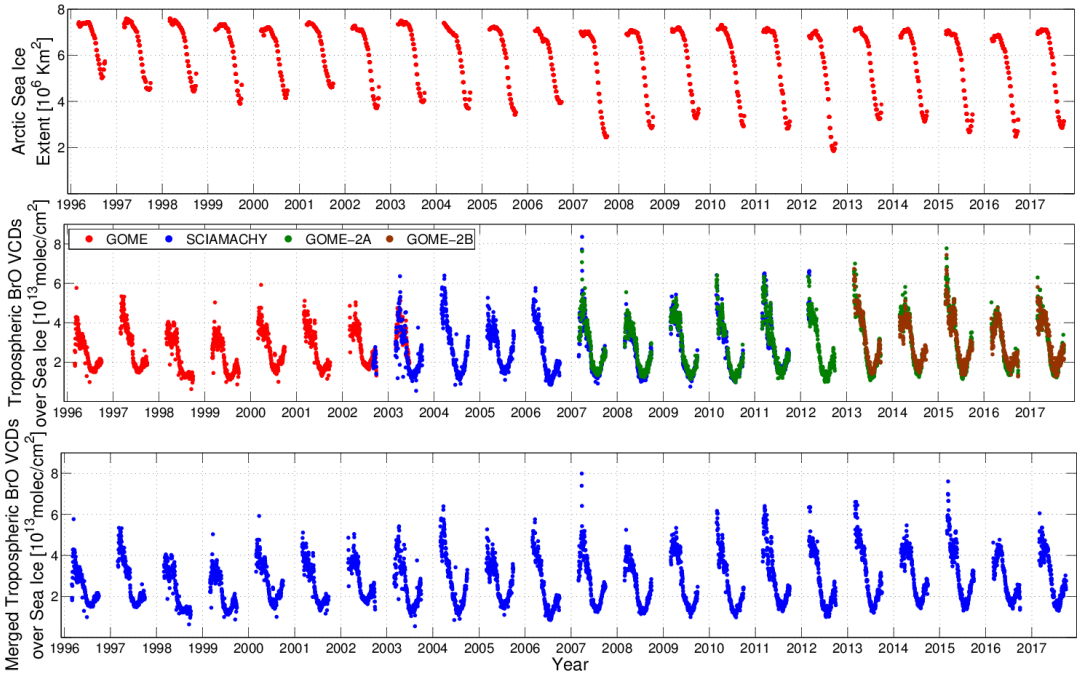
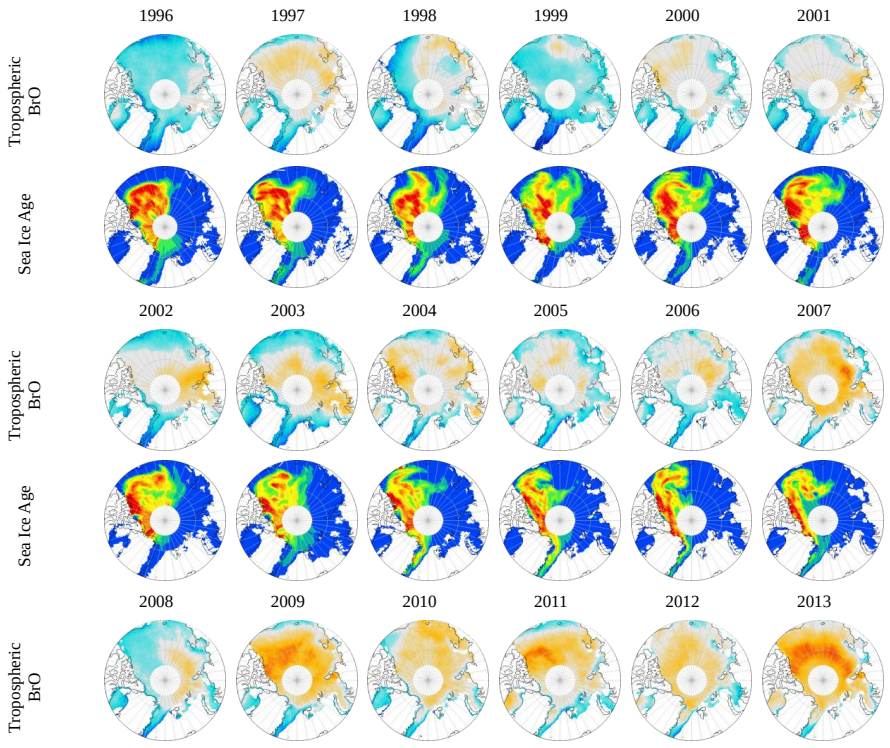


Figure 8: a) Arctic sea ice extent, from March till September from Tschudi et al. (2019), b) tropospheric BrO VCDs above sea ice in the Arctic. (GOME data is shown in red, SCIAMACHY in blue, GOME-2A in green and GOME-2B in brown), c) the sensor merged tropospheric BrO VCDs above sea ice in the Arctic.

By comparing Figures 8b and 3c, it is found that ~~BrO~~bromine explosion events are becoming more evident (for example in years 2007 and 2015) if we apply the sea ice flagging (i.e. keeping only scenes with sea ice coverage).

In order to investigate the spatial evolution of tropospheric BrO in time and its relationship to sea ice age, polar spring (March to May) average maps of tropospheric BrO and corresponding sea ice age maps are displayed in Figure 9 for each year between 1996 and 2017.



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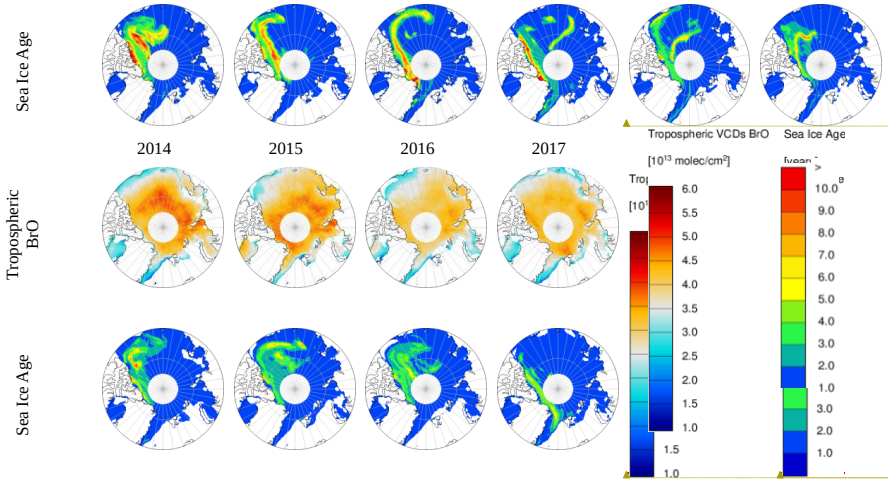

~~We find~~ In the past two decades, the area covered by multiyear ice has decreased and that by first year ice increased. The elevated levels of BrO are predominantly found over first year ice. The magnitude of the elevated BrO plumes ~~have intensified over the latest~~ has generally increased, with the maximum occurring in the years ~~(especially during~~ 2013~~-~~ to 2015~~).~~. In addition, the ~~regions~~area in which ~~BrO~~bromine explosion events occur ~~have~~in the March to May period has changed over the years. For example, ~~over the last years (i.e.~~from 2010 and onwards~~),~~. BrO is formed at the eastern coastline of Greenland comparatively at lower latitudes and inside the Arctic Ocean ~~(~~at higher latitudes (larger than 80.~~0~~°0°N), something not evident in the early years (i.e. 1996 to 2001). ~~Also, in the early years (i.e.~~ In addition, from 2001 ~~-~~to 2003~~),~~ most of the BrO is found in the region of the Barents and Kara Sea (to the north of Scandinavia and Russia). However, ~~over the last years (~~from 2009 ~~and~~ onwards~~),~~. BrO plumes "have spread" over the Arctic region~~, even appearing at comparatively lower latitudes, to the eastside of Greenland.~~ .

First year ice has become more dominant over the Arctic region in recent years (i.e. 2009 onwards). 2009 was the first year for which large tropospheric BrO VCDs were evident over the Canadian archipelago and the Beaufort Sea. In 2009, the area of multi-year ice decreased significantly in these regions. Similarly, the appearance of BrO plumes over the north-west coast of Greenland in 2015 is in agreement with the appearance of first year ice during this year. The relationship between first year ice and BrO ~~plumes~~VCD is not straightforward or linear ~~and~~but apparent in all years. ~~This can be explained by transport of BrO and of~~ We attribute the behaviour to BrO sources ~~(such as~~, conditions at the surface of potential frost flowers, blowing snow and cold brine~~),~~, and the transport of air masses in which bromine explosions are occurring. In 2004 for example, the highest BrO VCDs are found over a multi-year ice area, ~~while~~whereas in 2002 BrO is mainly seen over first year ice. The increase of magnitude of BrO plumes is not simply related to the development of first year ice as identified in

Figure 9: Polar ~~Spring (~~spring (March, April and May, MAM) averages of tropospheric BrO VCDs [10^{13} molec/cm^2] over sea ice, compared to sea ice age in the Arctic. Columns refer to years, odd rows to tropospheric BrO VCDs and even rows to sea ice age.

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the maps above. In summary, the increase of the areas where tropospheric ~~BrO~~bromine explosions ~~occurs~~occur is related in a ~~complex~~non-linear way to the increase of first year ice covered Arctic regions.

Figure 10 shows yearly anomaly polar spring maps of tropospheric BrO VCDs with respect to the 22-~~-~~year mean. The 22-~~-~~year average is shown in the last row of the Figure:

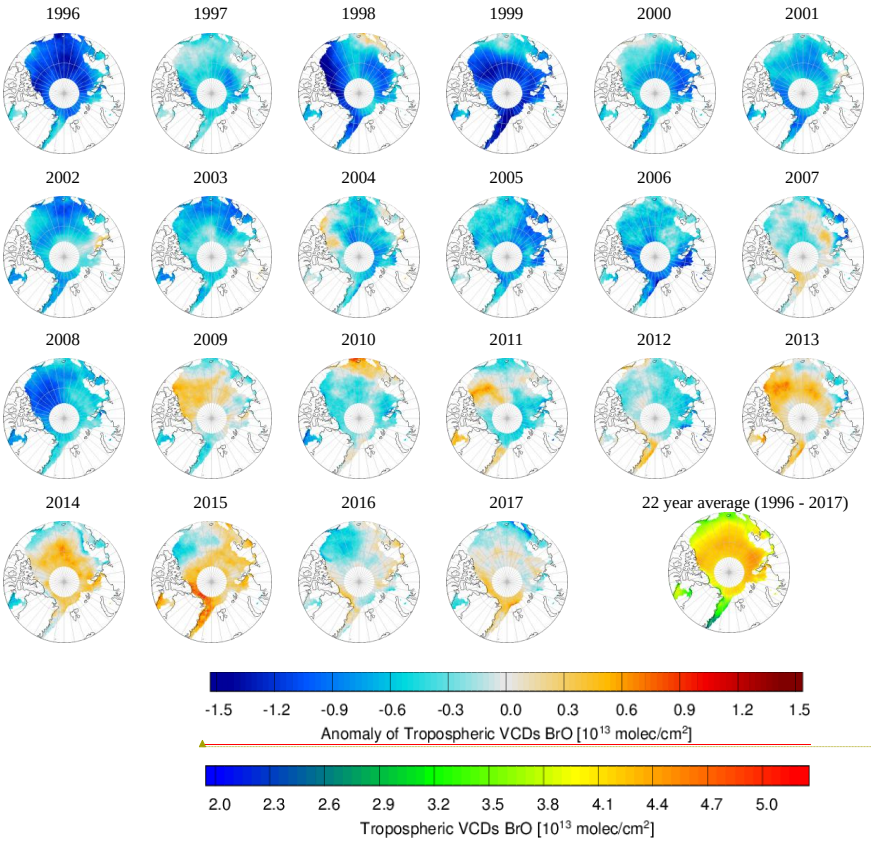

Figure 10: Anomaly maps of polar spring (MAM) tropospheric BrO VCD [10^{13} molec/cm^2] over sea ice. From every MAM average, the 22 year average (1996 to 2017, shown at the bottom right of row four) of tropospheric BrO VCDs was subtracted.

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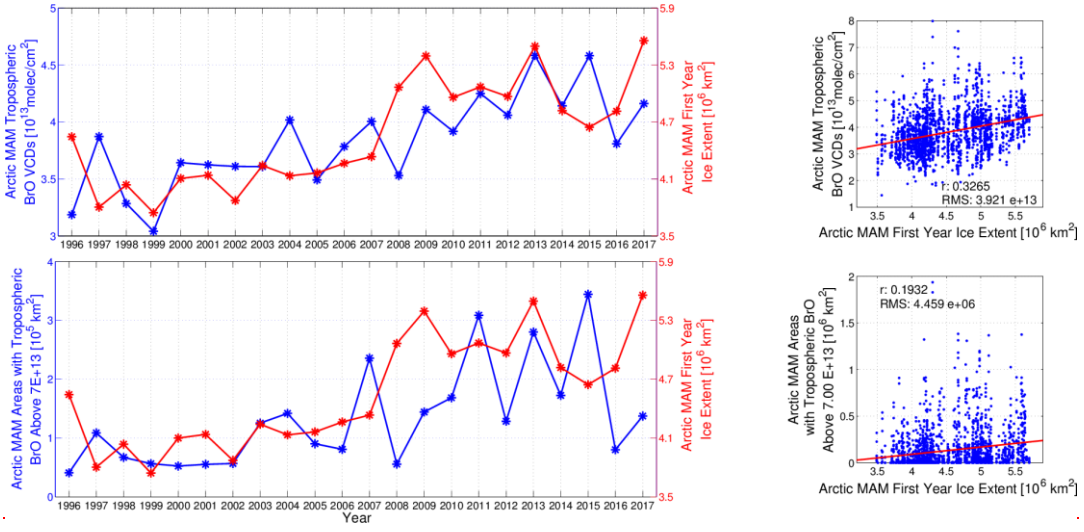
During the first years of the time-series, BrO VCDs are lower than on average in most regions of the Arctic. The first large positive anomaly compared to the mean occurs in 2009, and in areas where first year ice appeared for the first time.

~~Over the last years (~~From 2011 onwards~~), positive differences appear to~~, BrO VCDs grow in the north and to the east of Greenland. ~~Overall, and when~~When comparing the last with the first five years~~, we see that the increase~~ of ~~BrO plumes is apparent over the last years of Arctic Amplification~~the time-series, BrO VCDs have increased.

Figure 11 shows plots ~~which~~that probe the relationship between tropospheric BrO and first year ice extent. More specifically, Figure 11a shows a plot of the polar spring tropospheric BrO ~~over sea~~VCD above first year ice and first year ice extent, Figure11b shows the area ~~extent~~of ice where the tropospheric BrO VCD exceeds ~~the~~a threshold of $7x10^{13}$ molecules per cm^2. This threshold value was chosen empirically, as in previous studies (Hollwedel et al., 2003; Choi et al., 2018). First year ice extent~~,~~ and corresponding scatter plots are also given. For the time-series of this figure, all the polar spring values north of 70° N for each year were averaged, thereby deriving one value per year.



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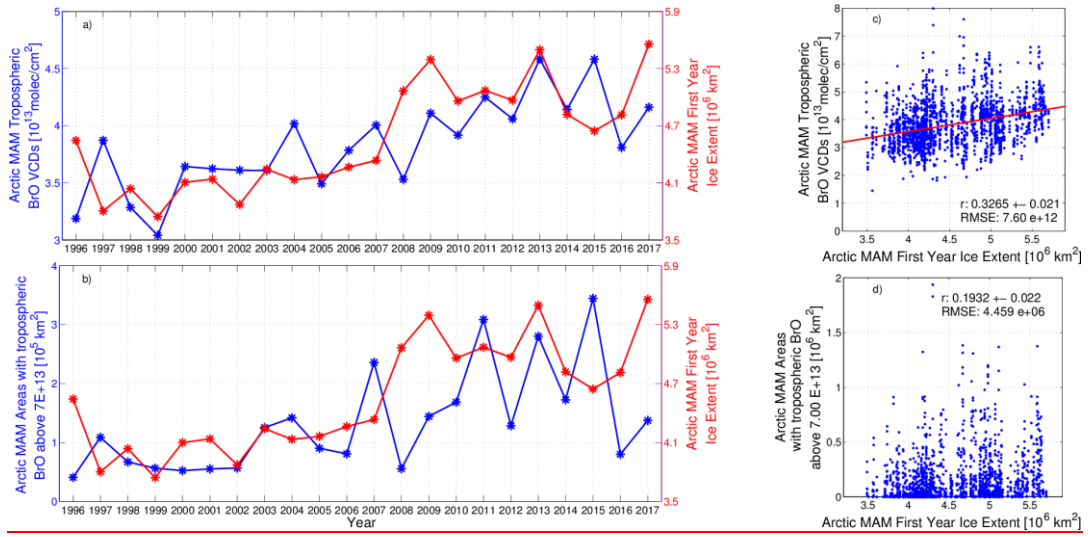

Figure 11: a) Polar spring (MAM) mean time series of tropospheric BrO VCDs over sea ice and first year sea ice extent over the Arctic, b) Polar spring (MAM) mean time series of areas with BrO VCDs above the threshold of 7x10^{13} molec/cm^2 and first year sea ice extent over the Arctic, c) scatter plots showing polar spring averages of tropospheric BrO VCDs against first year ice extent and d) ~~polar~~Polar spring averages of areas with tropospheric BrO VCDs exceeding the threshold of 7x10^{13} molec/cm^2 against first year ice extent in the Arctic. The linear regression ~~line is~~lines in 11c) and 11d) are shown in red in each scatter plot.~~.~~ The Pearson correlation coefficient (r), its error and the root mean square errors (RMSE) between the regression line and plotted quantities are shown in each scatter plot.

The total Arctic sea ice extent has decreased over the last years, but the area covered by first year sea ice has increased. The type of ice encountered at the surface is ~~hence~~ changing. Due to the increasing temperatures in the Arctic, more sea ice now melts every year, and more ~~fresh~~first or young sea ice is formed each winter period. Figure 11a shows that 2008 was the first year that first year ice extent exceeded the threshold of 5x10^6 km^2, which is also the case for almost all of the following years. ~~During~~The first year ice extent in spring (i.e. the area of first year ice in the months March till May) for the decade ~~from~~ 2007 to 2017~~, first year ice extent was~~ is larger ~~polar springs~~ than that from 1996 to 2006. Although tropospheric BrO ~~VCDs seem to~~VCDs have also increased in magnitude approximately from 2007 onwards, ~~the yearly evolution between the two does~~BrO VCD and sea ice area do not correlate strongly. ~~For example, for~~ In the years 2008 and 2016, a decrease of tropospheric BrO VCDs, when compared to ~~the previous year~~2007 and 2015 respectively is found, while first year ice extent increased. In 2015, the highest tropospheric BrO VCDs polar spring averages are found. In the same year, the polar spring first year sea ice extent average has its lowest value after 2008. Similar conclusions can be drawn from ~~the top right scatter plot (~~Figure 11c~~):~~. Although most days of average BrO above 7x10^{13} molec/cm^2 are occurring with first year ice extent above 4.5x10^6 km^2, we can see such days also below this threshold. The positive correlation coefficient between polar spring tropospheric BrO VCDs and first year sea ice extent for the same period is 0.32 with an error of 0.021. The significance of

the correlation was verified by performing a significance test, based on the p values. The null hypothesis (there is no correlation between the two quantities) was rejected, as the p value was < 0.05. Therefore the significance test was successful, meaning there is a correlation between tropospheric BrO and sea ice age (although, based on the actual value of the correlation coefficient, it is moderate). The correlation between areas of enhanced tropospheric BrO VCDs and first year ice extent is ~~even~~ lower, approximately 0.2 with an error of 0.022. This is evident from both the time-series (Figure 11b) and their scatter plot (Figure 11d, bottom right). In this case, the significance test was not successful, i.e. there is not a correlation between areas of BrO VCDs > $7x10^{13}$ molec/cm^2 and first year ice extent. We have also calculated correlation coefficients for the annual time-series (Figures 11a and 11b). In this case, the correlation coefficient between tropospheric BrO VCDs and sea ice extent is 0.62 and for the area of BrO VCDs > $7x10^{13}$ molec/cm^2 and first year ice extent 0.46. However, since these calculations are based on only 22 values, they are statistically less important than the correlation coefficients calculated based on the daily time-series. It seems that in both cases, the largest number of days with high tropospheric BrO VCDs or largest areas of ~~BrO~~bromine explosion events are occurring when first year ice extent is between 4.5 and $5x10^6$ km^2, and not when it reaches its peak. The magnitude of tropospheric BrO ~~VDs~~VCDs is positively, significantly, but not ~~closely~~strongly related to first year ice extent. This ~~agrees~~conclusion is consistent with ~~the findings~~a strongly nonlinear bromine explosion mechanism dependent on more than one key parameters. This finding is in contrast to the results by Choi et al. (2018), where ~~a similar~~an analysis ~~is provided based on~~ of BrO VCD retrieved from OMI ~~data~~was performed. They found a correlation coefficient of -0.32 between first year ice extent and tropospheric ~~BrO~~bromine explosion frequency. The negative sign ~~may be~~is attributed to ~~the~~a decrease of tropospheric BrO VCDs over the ~~latest~~latter years~~, which arguably is linked to~~ of the trend analysis. The differences to Choi et al. (2018) may be explained by a degradation of the OMI instrument (Kroon et al., 2011).

4.3 Trend analysis

~~Finally,~~A trend analysis of the tropospheric BrO VCDs time-series is performed, in order to investigate the statistical significance of the observed temporal and spatial changes in tropospheric BrO VCDs ~~described above in relation to~~associated with the Arctic warming. The tropospheric BrO VCDs time-series shows a seasonality, with a maximum every polar spring (March in most cases) and a minimum every summer. Consequently, a model, which combines a linear trend and seasonal ~~components~~variations is selected, ~~as~~similar to that used in ~~other~~previous studies (Hendrick et al., 2008; Georgoulias et al., 2018~~), to calculate the~~). We calculated trends ~~appearing in our time-series, expressed by the following formula:~~using Eq. (7):

$$d(t) = At + B + \sum_{i=1}^{3} \left\{ C_i cos\left(\frac{2\pi}{M}(t)\right) + D_i sin\left(\frac{2\pi}{M}(t)\right) \right\} \quad \text{Eq. (7}$$

~~)~~, where A is the slope, B the intercept, d(t) is the modelled value of BrO VCD on a given day, t is the day of the dataset (expressed in fractional years) and M is the ~~time period. It should also be stated, that the~~period in years. The number of

harmonic functions was chosen based on the minimization of the residuals between the model and the dataset. ~~Furthermore, the~~The error of each trend was calculated~~, based on the formula:~~ using Eq. (8) (Weatherhead et al., 1998):

$$\sigma_B = \left[\frac{\sigma_M}{M^{3/2}}\sqrt{\frac{1+\varphi}{1-\varphi}}\right] \quad \text{Eq. (8)}$$

~~)~~.

where, σ_M is the standard deviation of the residuals between the model and the time-series, M is the period in years, and φ is the autocorrelation of the residuals~~.~~ (0.2). Finally, a trend is considered significant if the ratio between it and its error is greater than 2 (Weatherhead et al., 1998).

Table 4 shows the trends of tropospheric BrO over sea ice north of 70° N over the whole period (see Figure 8c), for individual months and for ~~BrO explosion extent~~the area of the BrO VCD associated with bromine explosions (Figure 11b). For the trends of the individual months, we did not use the trend model with harmonics in Eq. (7) and used Eq. (9) instead:

$$d(t) = At + B \quad \text{Eq. (9)}$$

Table 4: Trends of tropospheric BrO VCD (over the whole period and for individual months) and for ~~BrO explosion extent~~the area of plumes from bromine explosions between 1996 and 2017, together with their errors and significance of each trend. The unit for all quantities is molec/cm^2, except the Area of BrO plumes (km^2).

Quantiny	Trend [units/year]	Error in trend [units/year]	Trend percentage (%/year)	Significant
Merged BrO VCD [molec/cm^2] (Figure 8c)	+ 2.4x10^{11}	1.1x10^{11}	+ 0.99	Yes
March BrO VCD [molec/cm^2] (Figure 8c)	+ 5.2x10^{11}	8.5x10^{10}	+ 1.50	Yes
April BrO VCD [molec/cm^2] (Figure 8c)	+ 4.9x10^{11}	5.0x10^{10}	+ 1.60	Yes
May BrO VCD [molec/cm^2] (Figure 8c)	+ 3.9x10^{11}	5.0x10^{10}	+ 1.30	Yes
June BrO VCD [molec/cm^2] (Figure 8c)	+ 1.5x10^{11}	4.3x10^{10}	+ 0.74	Yes
July BrO VCD [molec/cm^2] (Figure 8c)	+ 2.9x10^{10}	2.2x10^{10}	+ 0.18	No
August BrO VCD [molec/cm^2] (Figure 8c)	+ 4.5x10^{10}	3.1x10^{10}	+ 0.26	No
September BrO VCD [molec/cm^2] (Figure 8c)	+ 2.8x10^{11}	4.3x10^{10}	+1.43	Yes
Area of BrO ~~Explosion extent~~plumes [km^2] (Figure 11b)	+ 896	2280	+ 0.06	No

~~As can be seen from Table 4, almost all~~The monthly trends ~~(~~in Table 4 with the exception of the trends of the summer months July and August and for the trend of BrO ~~explosion extent)~~plumes are statistically significant. The linear trend of the annual tropospheric BrO VCD over the Arctic shows an approximately ~~a~~ 1% increase per year over the last 22 years. ~~However, during~~ During individual polar spring months the increase of BrO VCD is stronger, reaching a value of 1.5% per year~~, while~~. The trends of BrO VCD during ~~polar~~ summer ~~(which can be regarded as background BrO in contrast to polar spring when BrO explosion events occur) shows only~~months are smaller and those in July and August are statistically insignificant ~~change~~.

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Figure 12 shows the trends appearing in the tropospheric BrO time-series, based on different time periods, i.e. different starting and ending years. ~~In contrast to the values derived in Table 4, simple linear trends were calculated (as time periods over multiples of one year are regarded).~~Eq. (9) was used to calculate the trends, starting from and to the same date for both the starting and the ending years (i.e. end of March).

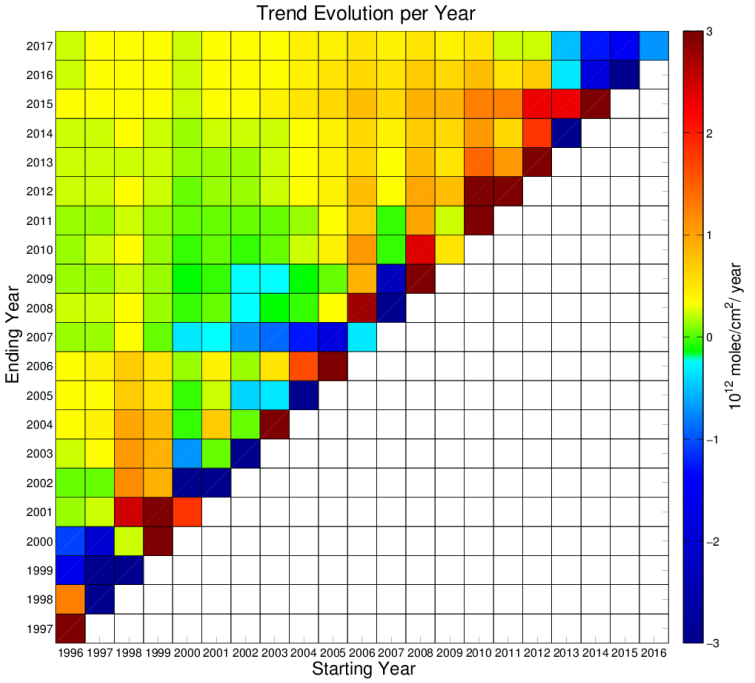

Figure 12: Trend [10^{12} molecules/cm^2/year] evolution of the merged tropospheric BrO dataset (i.e. slope of the linear regression line) over sea ice. The x-~~ ~~axis shows the starting year, the y-~~ ~~axis shows the ending year of the ~~time~~ period over which the trend was calculated.

~~Trends~~Linear trends calculated by starting in one year and ending in the next one (e.g. from 1996 to 1997) are in agreement with the BrO VCD shown in Figure 8c (for example, the strong positive ~~trend~~change from 2014 to 2015, or the decrease from 1997 to 1998). Trends over short periods are dominated by inter-annual variability. ~~Mainly~~The positive linear trends are ~~found, especially for trends covering~~largest when the ~~latest~~later years ~~as finishing years~~are included. We see that that the strongest long-term positive trends occur when we choose as starting point the years 2006 – 2008, and as ending point the year 2017.

In Figure 13, the trend for each individual grid box during polar spring months is displayed, for tropospheric BrO, sea ice age and first year ice frequency occurrence. All three maps are gridded in 0.125°x0.125° resolution. The trend for every grid box is calculated ~~based on the method described above, i.e. in Equation 7.~~using Eq (9).

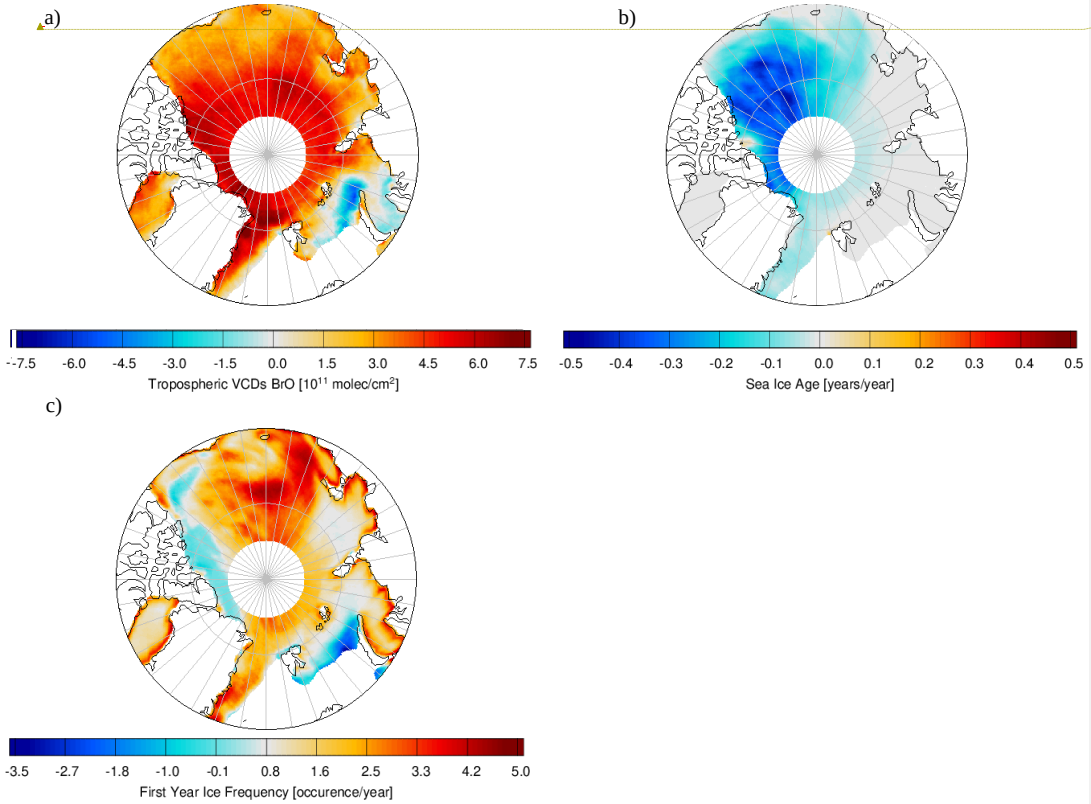

Figure 13: ~~Maps~~Polar projection of the trend ~~for~~in each grid box (0.125°x0.125°) during polar spring ~~(~~months (March, April, May, MAM) for a) tropospheric BrO VCD over sea ice [10^{11} molecules /cm^2 /year], b) sea ice age [years /year] and c) first year ice frequency [occurrence/year]. The trends calculated over a 22 year period (1996 to 2017).

~~As shown in Figure 13, tropospheric~~Tropospheric BrO VCDs values increase inside the region of the Arctic Ocean~~,~~ and also to the north and east of Greenland, where sea ice age shows ~~a~~ negative ~~trend. From~~ trends. We learned from Figure 9, ~~we see~~ that ~~from~~after 2008 ~~and afterwards~~, first year ice appears in the same area. This can be verified also by Figure 13c, as in the same area we see a positive increase of first year ice occurrence of about 2.5 to 3 grid boxes per year. However, the trends of tropospheric BrO VCD and sea ice age do not match everywhere. The strongest negative trends in the sea ice map occur in

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areas where multiyear ice was dominant in the past, and first year ice ~~is forming in the latest~~has formed in the recent years (Beaufort Sea and Canadian archipelago). However, in the same area, we do not see the most pronounced increase in the trend map of tropospheric BrO VCDs (the increase is smaller than in other areas). The strongest increase in tropospheric BrO VCDs occurs to the northeast of Greenland close to the Fram Strait, to the north of Greenland and close to Ellesmere Island. Although first year ice seems to be appearing more frequently in the east of Greenland, we do not see the same evolution on the north side of Greenland. On the contrary, we see a decrease of first year ice occurrences over the latest years. Therefore, we can conclude that, although first year ice has a relation to the increased tropospheric BrO plumes observed over the recent years, it is not the only parameter affecting the formation of enhanced BrO.

5 Summary and conclusions

~~Arctic Amplification, the rapid and intense increase of air temperature over high latitudes is expected to have drastic impacts on all constituents of the Arctic ecosystem. Bromine release from young sea ice, frost flowers, blowing snow and liquid brine was first discovered about 30 years ago. This is of great significance in the Arctic atmosphere, as, through a set of autocatalytic reactions, bromine depletes tropospheric ozone very efficiently, potentially altering the oxidizing capacity of the troposphere.~~ In this study, ~~the first consistent and long term~~a merged dataset of tropospheric BrO VCD over the Arctic~~,~~ north of 70° N retrieved from the measurements of four similar UV-VIS remote sensing satellite instruments, over a 22-year time period is presented. ~~The results demonstrate a~~A high level of consistency of the retrieved BrO VCDs was found between the retrievals from the different sensors.

Time-series of tropospheric BrO VCDs over the Arctic north of 70° N and corresponding trends indicate that the magnitude of tropospheric BrO ~~explosion events~~ VCDs has increased, especially ~~over~~in the ~~last years~~decade from 2007 to 2017, when we observe a 1.23 times stronger increase than from the period 1996 - 2017. This increase is pronounced in polar spring, when ~~BrO~~ the majority of bromine explosion events occur. Additionally, ~~by studying~~from the spatial patterns of tropospheric BrO~~, it can be seen~~ VCD, we infer that the size of the areas ~~where BrO~~ of elevated BrO VCD (i.e. impacted by bromine explosions ~~occur~~) has increased about 896 km^2 per year.

~~In order to investigate the mechanisms behind these trends,~~The correlation between tropospheric BrO VCD and sea ice age time-series and spatial trends ~~were evaluated~~was investigated. The overall increase in tropospheric BrO ~~is, in theory, in agreement with~~VCD is taking place at the same time as the increase in first year ice coverage. Dependent on the meteorological conditions, the presence of first year ice, which ~~favours~~has a higher salinity than multiyear ice, facilitates the release of ~~BrO~~bromine and ~~is widely believed to be a main driver of the BrO explosion~~thus the production of BrO. However, our analysis shows that there are areas where tropospheric BrO ~~can be linked directly to locations of~~correlates well with first year sea ice, while in other regions ~~no~~this was not clear ~~relationship was found~~. Tropospheric BrO ~~is not~~VCD is moderately (correlation coefficient of 0.32 for daily time-series and 0.62 for the annual), but significantly correlated with first year sea ice extent, ~~neither~~both temporally ~~nor~~and spatially~~, suggesting~~. We suggest that the transport of BrO plumes away from their

source regions complicates the analysis~~. Our comparisons hence suggest~~, and that the temperature dependence of the bromine explosions induces variability. We infer that the increase in magnitude of BrO VCD and in the extent of the areas where BrO plumes appear ~~is~~are linked ~~in a complex way~~ to the retreat of multi-year ice and the ~~appearance~~increase of first year ice in the Arctic region due to the Arctic warming. Although an overall increase of tropospheric BrO VCDs is found, there is also large inter-annual variability. While the time-series shows a positive trend ~~on the order~~ of approximately 1.5% per year during polar springs~~,~~ for a period of 22 years (1996 to 2017), tropospheric BrO decreased in during the last two years of the time-series. It remains to be seen ~~if~~, whether the positive trend in tropospheric BrO VCDs will continue and develop to be more pronounced in future years~~.~~ or decrease as the area of first year ice eventually decreases as the Arctic warms.

Yang et al. (2010) investigated ozone loss using numerical modelling and found that blowing snow~~–~~sourced bromine reduces tropospheric ozone amounts by up to 8% in polar spring in the Arctic. ~~Based on~~ The positive trend and inter-annual variability of tropospheric BrO VCDs reported in the present study ~~future ones need to elaborate more deeply on the impact of~~would imply increasing ~~amounts of tropospheric BrO on ozone~~but highly variable losses of O_3 and deposition of Hg over the Arctic region, which would also impact on the oxidizing capacity of the Arctic atmosphere. The datasets discussed here can be used as a basis to validate BrO simulations of chemical transport models, in order to quantify this O_3 loss, ~~mercury~~and potential OH changes. As Arctic warming will continue, tropospheric BrO abundances will also continue to change. Therefore, the assessment of the impact on O_3 depletion ~~and alteration of the oxidizing capacity of the atmosphere.~~ is essential.

~~We note that the air temperature was reported to be the highest on record over the Arctic in 2016 (Overland et al., 2016).~~ In addition to sea ice conditions, the appearance of plumes of tropospheric BrO ~~VCDs~~VCD and their intensity~~,~~ are ~~known to be~~ influenced by several meteorological drivers (air temperature, sea level pressure, wind speeds and cyclones) and the amounts of blowing snow (Blechschmidt et al., 2016; Seo et al., 2019b). Further ~~investigation is~~investigations are required ~~in order~~ to ~~link~~understand the evolution of tropospheric BrO ~~to~~and its dependence on these drivers of tropospheric BrO release~~, in order to better understand the relationship between them and the effect~~. This is required to accurately project changes in tropospheric O_3, Hg deposition and oxidizing capacity of ~~Arctic Amplification on bromine concentrations in~~ the Arctic region in a warming Arctic using numerical models.

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Acknowledgements

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Data availability

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Author contributions

~~Ilias~~I. Bougoudis ~~performed~~undertook the retrieval of BrO from the different satellite instruments, collected and processed the sea ice age data, performed the analysis and ~~wrote~~prepared the paper. ~~Anne Marlene~~ This study was initiated by J.P. Burrows and A.-M. Blechschmidt~~ performed~~. The research presented was supervised by A.-M. Blechschmidt, A. Richter and J.P. Burrows. A.-M. Blechschmidt and N. Theys provided the stratospheric separation. ~~Anne Marlene~~A.-M. Blechschmidt, ~~Andreas~~A. Richter, ~~Sora~~S. Seo, N. Theys and ~~John Philip~~J.P. Burrows provided ~~insights and knowledge on the study. Andreas~~input with respect to BrO issues of relevance. A. Richter developed software which was used for processing and ~~analyzing~~analysing the BrO data. ~~Nicolas Theys developed the stratospheric separation method~~A. Rinke provided input on sea ice and trend analyses. All authors contributed to the writing of the paper.

Competing interests

On behalf of my co-authors, I declare that I have no significant competing financial, professional or personal interests that might have influenced the performance or presentation of the work described in this manuscript.

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