Author response to "**Simulations of anthropogenic bromoform indicate high emissions at the coast of East Asia**"

Josefine Maas[1], Susann Tegtmeier[1,*], Yue Jia[1,*], Birgit Quack[1], Jonathan V. Durgadoo[1] and Arne Biastoch[1,2]

[1]GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany
[2]Kiel University, Kiel, Germany
*now at: Institute of Space and Atmospheric Studies, University of Saskatchewan, Saskatoon, Canada

We thank the reviewers for their valuable comments and suggestions, which have helped us to significantly improve the paper in revision. We appreciate the effort it took the referees to help with their many suggestions and hope we can satisfactorily reply to the comments. In the following, we repeat the comments of all three referees in black, followed by our responses in blue. The changes made in the manuscript are highlighted and attached to this document.

Referee 1

Maas et al. 2020 presents an estimate of near-coastal flux of by-product CHBr3 emissions from power plant discharges in Asia and its impact on atmospheric bromine loading. This analysis is based on some recent water sample measurements from power plant cooling water and surrounding waters, with the help of Lagrangian trajectory model calculation. This is an interesting study and provides some helpful information in terms of quantifying the anthropogenic contribution to the atmospheric bromine budget. However, I have several major concerns on the method, lack of adequate comparison for the most important region in this study (East Asia), and the major conclusion. These concerns should be addressed before the paper is considered for publication in ACP.

We thank the reviewer for his/her valuable comments which have helped us to improve the paper in revision. We have addressed the major comments by:

- Including a more detailed description of the FLEXPART model and validation studies
- Extending our one-year FLEXPART simulations to four years and including a discussion of interannual variability of VSLS transport from available literature
- Including a comparison of our results to measurements from the KORUS-AQ campaign
- Improving the discussion of bromoform transport in East and Southeast Asia
- Reformulating the conclusions

1. Section 2.3. The authors mention that the FLEXPART is run using the meteorological input stem from the ERA-Interim reanalysis . . . The FLEXPART simulations were performed for the boreal winter and summer seasons, for a total of three months with a one-month spin-up. Credible estimate of contribution of surface to UT/LS transport rely on the use of a model that can

properly represent this transport process. At minimum, in the case no transport evaluation is conducted for this study, you need to provide adequate peer-reviewed results showing FLEXPART-based analysis is suitable for this study; that it is adequate in representing the surface to UT/LS transport within the Asian tropical/subtropical deep convection and the Asian summer Monsoon over the continent.

> Thanks for the comment. We have included a more detailed description of the FLEXPART model and added the relevant citation of the convection validation paper from Forster et al. (2007). We have also added reference studies that have successfully used FLEXPART to simulate transport pathways over the Indian Ocean, Maritime Continent and West Pacific (e.g., Fiehn et al., 2017; 2018; Fuhlbruegge et al., 2016; Marandino et al., 2013; Tegtmeier et al., 2013; 2020). As these studies have included model validation based on comparisons to available aircraft measurements, we use them here as references justifying the choice of FLEXPART for our simulations.
>
> l. 226 ff.: "The FLEXPART model includes parameterisation for moist convection (Forster et al., 2007) and turbulence in the boundary layer and free troposphere (Stohl and Thomson, 1999). It has been used in previous studies with a similar model setup and shown robust VSLS profiles compared to observations (e.g. Fiehn et al., 2017; Fuhlbrügge et al., 2016; Tegtmeier et al., 2020a)."

2. Second, please state clearly the year of DJF & JJA months you are using to drive the FLEXPART simulation. I am also not convinced a single year (with only 2-seasons) simulation is statistically adequate to quantify the transport from surface to the UT/LS in Asia. The authors need to decide an appropriate length (number of years) to address such transport using FLEXPART and provide a discussion on the year-to-year variability of the above transport. My suggestion is that at minimum you need a 10- year simulation to cover a few full cycles of QBO and ENSO, which have significant impacts on the dynamical transport relevant to this study.

> We agree that one single year is not sufficient to capture all variations of atmospheric transport processes. Therefore, additional FLEXPART simulations were performed using the same setup as the existing runs. We now include FLEXPART simulations for four years (2015-2018) for the boreal winter (December–February, DJF) and summer (June–August, JJA) seasons, respectively. Each run is conducted with a two months spin-up phase.
> We found relatively small interannual variations in our results and therefore decided to not include a 10-year time period. A full discussion of the impact of different atmospheric modes such as ENSO and Indian Ocean dipole can be found in Tegtmeier et al. (2020), who simulated $CHBr_3$ entrainment for a 35-year long time period and found interannual variations of up to 15 % to be much smaller than seasonal variations of up to 50 %. A short discussion of the impact of interannual transport variations has been added to the manuscript.

3. This study is based extrapolating the information from a limited number of power plant effluents to the entire Asia power plants. As discussed in section 5, both the simulated oceanic and marine boundary layer concentrations of CHBr3 from this study, particularly those from the

HIGH scenario, are larger than most of the previous observations in general. The regions that where 90% of the largest simulated concentrations (see Figures 5, 6, 7) display extremely high level of bromoform levels compared to the original Ziska 2013 results. Yet, no comparison with previous measurements were presented in this work. NASA has recently conducted an aircraft field campaign KORUS-AQ (https://www-air.larc.nasa.gov/missions/korus-aq/index.html) in this region with extensive airborne measurements of CHBr3 (from the Whole Air Samplers, PI Donald Blake) from surface to mid/upper troposphere that is highly relevant to this study.
These measurements are publicly available at https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq#BLAKE.DONALD/. I strongly encourage the authors use the KORUS-AQ CHBr3 measurements to evaluate the simulated FLEXPART CHBr3 from the three scenarios for a proper assessment of the design of this experiment to see whether the extrapolation method used in this work is a reasonable approach.

Thanks for the suggestion. In addition to the already used observational data, we now include air measurements from the KORUS-AQ campaign over Korea in section 5.2. The comparison of the KORUS-AQ $CHBr_3$ measurements with the $CHBr_3$ obtained from FLEXPART simulations suggests very good agreement in this region for the MODERATE scenario. As existing bottom-up scenarios (Ziska et al., 2013) show significantly lower mixing ratios over South Korea and the Yellow Sea, the new comparison suggests that anthropogenic sources are required in order to explain observed $CHBr_3$ values. The comparison also confirms earlier conclusions that the HIGH scenario is unrealistic and results in too high abundances of atmospheric $CHBr_3$. We have revised the conclusion and discussion section taking the new information into account.

l. 445ff:" An extensive study of atmospheric measurements over South Korea and adjacent seas was performed in spring (May and June) 2016 from the Korea–United Sates Air Quality Study (KORUS-AQ; https://www-air.larc.nasa.gov/missions/korus-aq/). The aircraft measurements of various VSLSs including bromoform were repeatedly taken between 0 and 12 km in the region between 30° N-40° N and 120° E-145° E coinciding with our subtropical box discussed earlier (Figure S2). The data used here, is based on the 60 second merged dataset from all flight sections. In the campaign region around South Korea, an average bromoform atmospheric mixing ratio from all sections of 2.5±1.4 ppt was measured in the lower 100 m (Figure 8). In comparison, our simulations for the Ziska2013+MODERATE scenario show an average mixing ratio of 3.8±1.4 ppt in the lowest 100 m in the subtropical box during JJA. The simulations based on Ziska2013 give a bromoform mixing ratio of only 0.3±0.1 ppt for the same altitude range demonstrating that the additional anthropogenic bromoform sources results in a much better agreement with the observations in the marine boundary layer around South Korea.
Above the boundary layer, mixing ratios from KORUS-AQ rapidly decline to 0.5-0.7 ppt in the 3-9 km altitude range (**Fehler! Verweisquelle konnte nicht gefunden werden.**). Here, the Ziska2013+MODERATE simulation suggest seasonal mean mixing ratios between 0.4-0.7 ppt, which fit very well to the KORUS-AQ data. Simulations based on Ziska2013 suggest 0.2 ppt bromoform in this region clearly underestimating the observations (**Fehler! Verweisquelle konnte nicht gefunden werden.**). Between 9 and 12 km, the observed bromoform values drop sharply to values around 0.2±0.08 ppt suggesting that the airplane probed air masses above the convective

outflow. The smooth seasonal mean profiles from the two simulations do not show such sharp decrease of values and in consequence the lower Ziska2013 results agree better with the observations in the region 9-12 km. In general, the comparison with the KORUS-AQ data shows that simulations agree quite well the observations in the middle troposphere when anthropogenic emissions from cooling water treatment in East Asia are included based on the MODERATE scenario."

4. Section 4.2: the discussion on the vertical transport of bromoform in the troposphere. While tropical deep convection plays an important role in vertical lofting near the EQ, vertical lofting in subtropical Asia and East Asia is primarily driven by the Asian Summer Monsoon in the summer season. These transport processes were not discussed adequately in this work and past literature were not referenced either. Please add.

We have improved the discussion of the vertical transport of bromoform and how much of it is driven by tropical convection versus vertical lofting by the Asian Summer Monsoon. The impact of these processes on VSLS transport in the East and Southeast Asia region has been analysed and discussed by a number of recent studies (e.g., Fuhlbruegge et al., 2016; Hossaini et al., 2016; Fiehn et al., 2017) and we thus now include a summary of their most important findings in the introduction section. In addition, we have added past literature important for the overall discussion of tropospheric transport pathways in this region.

l. 80ff: "The Asian summer monsoon represents another important pathway to the lower stratosphere (e.g., Randel et al. 2010) entraining mostly Southeast Asian planetary boundary layer air. The monsoon also has the potential to include VSLSs emitted from the Indian Ocean and Bay of Bengal (Fiehn et al., 2017, 2018b). Model simulations suggest that the monsoon circulation transports the oceanic emissions towards India and the Bay of Bengal, from where they are convectively lifted and reach stratospheric levels in the south-eastern part of the Asian monsoon anticyclone. The stratospheric bromine injections from the tropical Indian Ocean and West Pacific depend critically on the seasonality and spatial distribution of the emissions (Fiehn et al., 2018a). Model studies based on bottom-up emission estimates indicate global bromoform maxima over India, the Bay of Bengal, and the Arabian Sea as well as over the Maritime Continent and West Pacific (Tegtmeier et al., 2020a). While aircraft measurements in the West Pacific have confirmed high concentrations of bromoform (Wales et al., 2018), the role of the Asian monsoon as an entrainment mechanism for VSLSs has not been confirmed yet due to the lack of observations in this region."

l. 409:" During the Asian summer monsoon, the region of main upward transport of VSLS lies at about 20°N over the Indian Ocean so that the main stratospheric injection region of VSLSs shifts to the Bay of Bengal and northern India (Fiehn et al., 2018b). However, most of the boundary layer bromoform from anthropogenic sources stays in the northern hemisphere around the coastline of China and over the West Pacific thus decoupled from the monsoon convection."

5. Figures 8 and 9 and related discussions. Using a climatological cold point altitude of 17km for discussion of vertical lofting and entrance to LS is not adequate, and this is particularly not suitable for the subtropical box (Figure 8). The tropopause in this region is likely very different

from the tropics and can be highly variable due to seasons or other dynamical processes. I would suggest the authors to use the tropopause height and potential temperature fields from ERA-Interim reanalysis. Only when the vertically lofted air mass cross the tropopause and enter beyond the 370-380 K potential temperature, the amount of the remaining $CHBr_3$ within the air mass would have a chance to survive the transport process, make to the stratosphere and have an impact on stratospheric bromine loading.

> We agree with this comment and have adapted our analyses. We now derive the $CHBr_3$ mixing ratios at the level of the ERA-Interim cold point tropopause taking into account temporal and spatial resolutions of this level. New versions of Figures 8, 9 and 10 show $CHBr_3$ at the cold point tropopause as derived from the ERA-Interim data (and not at 17 km as in the old version of the manuscript). As the cold point is the dehydration point of air masses on their way to the stratosphere, there will be very little impact of falling rain or ice on the $CHBr_3$ product gases above this level, which is therefore commonly used as the stratospheric injection level in VSLS studies. In the new version of the manuscript, we discuss the $CHBr_3$ contribution to the stratospheric bromine loading based on the mixing ratio at the cold point tropopause.
>
> l. 260f: "The UTLS region is calculated as the height of the cold point tropopause, which has been derived from ERA-Interim model level data at 6 hourly resolution (Tegtmeier et al., 2020b)."

6. Final major comment on the main conclusion of this work. With all the previous potential issues I have noted above, the authors concluded that these anthropogenic emissions only contribute 0.02-0.03 ppt to the stratospheric bromine budget. I find it not convincing, from the results presented in this work, to draw the conclusion that anthropogenic sources are important enough to be considered for future estimates of atmospheric bromine input. While local concentrations are high, due to the lack of efficient vertical delivering mechanism, these emissions have little chance reaching the stratosphere. This has been the conventional understanding on the vertical transport efficiency of very-short-lived bromine species and is seemingly confirmed again in this study.

> True enough, the amount of stratospheric halogen resulting from anthropogenic activities is rather small given that the majority of power plants is not located in the tropics. However, anthropogenic VSLS show high accumulations in the boundary layer and can change the tropospheric bromine budget and ozone chemistry. While we have not analysed this aspect in our current study, this should be investigated in follow-on projects. We have reformulated the conclusion to make it clear that we refer to the total bromine budget here and not to the impact of anthropogenic VSLS to the stratospheric bromine budget.

Minor comments:

1. Lines 60-62. These statements are missing proper references.

> We added the following references.

l. 62ff: “Top-down bromoform emission estimates, on the other hand, are based on global model simulations adjusted to match available aircraft observations (e.g. Butler et al., 2007; Liang et al., 2010; Ordóñez et al., 2012).”

2. Lines 149-152: Please list what are the non-volatile and volatile DBPs considered in this experiment

The non-volatile DBPs can be various. Thus, we mention bromoacetic acid as an example in paragraph 3 of section 2.2. The volatile DBP is explicitly given as bromoform in the text.

3. Figure 1. It would be helpful if you can add the locations of Table 1 results (the ones that in the region) on this plot, marked with a different symbol.

Only measurements from the South Korean power plant are situated in our study region. Therefore, we haven’t added the locations to the plot as suggested but have added this information to the text (paragraph 2 of section 2.1).
l. 139: “Only Yang (2001) provides DBP measurements in East Asia.”

Referee 2

This paper describes the estimation of sea surface concentrations of bromoform over East Asia resulting from the treatment of power station coolant water with chlorine-based disinfectants. The authors subsequently then estimate sea to air fluxes and test these within an atmospheric transport model to estimate the transport of bromoform in the atmosphere, in particular, via convection to the stratosphere. The authors estimate the sea surface concentrations using a bottom-up approach by first estimating bromoform within power station coolant waters, the discharge of this coolant water into the ocean, and then its subsequent transport in the ocean using oceanic transport model. Based on the bottom-up approach, the authors find a notable contribution to oceanic bromoform from this source that strongly affects oceanic bromoform concentrations close to the source region. Based on the sea-to-air fluxes and the atmospheric modelling, despite showing significant anthropogenic bromoform levels near the source regions and in the boundary layer, the authors find only a modest contribution of this source to stratospheric bromoform mixing ratios.

Bromoform has an important relevance to stratospheric ozone depletion. This paper therefore covers an important topic since current knowledge of bromoform sources is currently highly uncertain due to only limited monitoring of this gas. Attempts to improve our knowledge of its sources are therefore highly welcome. I therefore find that the paper sits well within the scope of the journal.

The subject matter and overall concept and methodology of the paper alone make it worthy for publication. On the whole, this is a good piece of work. Despite the manuscript’s strengths though, there are several weaknesses in the work. I therefore have a list of general and specific

comments that will need to be addressed to improve the manuscript to a sufficient level to merit final publication.

General Comments

1. The overall framing of the paper. I think it would help ease some concerns (see for instance reviewer #1's comments) if the paper's main findings regarding anthropogenic bromoform were to be framed as a set of predictions (that can be tested) based on independent knowledge and data. Your bottom-up method makes a set of predictions based on the data you have used. Then you have made efforts to validate those predictions using sea surface bromoform concentration and atmospheric measurements; these data provide somewhat limited but promising support for your predictions. As it is, the manuscript abstract and conclusions contains various statements that are rather definitive, e.g., "We find that bromoform..." (line 26 in the abstract) and, similarly, "We find that..." (line 388 conclusions). When in fact the observational support appears promising yet far from definitive, and would require more dedicated observational monitoring to really prove this hypothesis. I therefore propose the authors modify the manuscript so it clearly follows this chain of reasoning: prediction/hypothesis (emission atmospheric, oceanic modelling) into observational support, followed by evaluation, and then lastly clear statements on what is needed to provide stronger support for this hypothesis, i.e., more specific and targeted observations.

> Thanks for this suggestion. We agree that rephrasing parts of the manuscript in the suggested manner would benefit the overall message, highlight the remaining (large) uncertainties and provide clear motivations for follow-on studies. We have rephrased the introduction and in particular the two last paragraphs of the introduction to present our analyses in the hypothesis-evaluation-conclusion framework. We have also rephrased parts of section 5 (observational support) and section 6 (discussion and conclusions) in a consistent manner.

2. Treatment/explanations of the UTLS and cold point. I think that the UTLS and cold point definition is too simplistic. The use of UTLS throughout does not capture any of the essential details of this complex atmospheric region. Sticking to a single altitude of 17 km for the cold point is also not really realistic when looking at different latitudes and seasons. Furthermore, sticking to the cold point as a definition of the lower stratosphere alone is also not entirely suitable and the suggestion from reviewer #1 to simply use the 380-390 K potential temperature line also misses some of the subtle complexity. I recommend that the authors consult Corti et al. 2005 and 2006 (see below) that both provide clear explanations and observational support for more nuanced explanations of dynamical interactions in the UTLS. First, the level of zero radiative heating (LZRH) is also useful a measure for whether air masses will undergo slow radiatively driven ascent to above the 380-390 K levels, and it is usually at 15 km for clear sky conditions. Second, they show that in-cloud (cirrus) radiative heating can be responsible for lofting cloud containing air masses from as low as 11 km upwards to eventually reach the stratosphere. I would recommend that the authors try to calculate the LZRH using the ECMWF meteorological fields to try to diagnose this to help determine which air masses at altitudes below 17 km are heading up or down; this would really strengthen the paper and strongly aid the interpretation of the results,

which is quite difficult at this point. If this is not possible it would be very useful to see at least the 11 and 15 km levels, but this would be a much weaker alternative.

> We agree with the reviewer comment that our treatment of the cold point as the 17 km level was too simplistic. We have changed the manuscript and now use the ERA-Interim cold point tropopause instead, taking into account its spatial and temporal variability. We have changed our Figures 8, 9 and 10 and have updated the discussion in our text, so that the stratospheric contribution is now based on the $CHBr_3$ values at the cold point level.
> We also agree with the reviewer that the UTLS is a complex region with various levels that are of importance for the vertical transport. It would indeed be interesting to see, which fraction of air masses that reaches the LZRH will also reach the cold point. However, such analyses of vertical transport characteristics within the TTL region is beyond the scope of this manuscript. Furthermore, we believe that for the VSLS and their soluble product gases the most important level is the cold point. By using the cold point as entrainment level, we automatically include all air masses that have crossed the LZRH and have undergone radiatively driven ascent as well as all air masses resulting from high-reaching convective detrainment.
>
> l. 260f: "The UTLS region is calculated as the height of the cold point tropopause, which has been derived from ERA-Interim model level data at 6 hourly resolution (Tegtmeier et al., 2020b)."

3. Many missing details. There are several missing important details from various sections of the paper, e.g., the year that is studied – this is not mentioned at all. I have addressed each of my concerns in specific comments below.

> Thanks for pointing out the missing details. We have added the details as suggested below including information on the years, which are studied.

4. Clarity of the manuscript. At many points the information given is insufficient to understand precisely what is being said. I have made various specific remarks below to help address this concern.

> We have rephrased the sections that are pointed out below in order to improve the clarity of the manuscript.

5. Duration of FLEXPART simulations/transport times to the stratosphere. The duration of the FLEXPART runs is 3 months. As shown in Corti et al. 2005/2006, transport times from the boundary layer to the 390 K level of 50 days, and so even with a 1 month spin-up, we can expect a delay of ~20 days for air masses from the beginning of the spin up to reach this level. Indeed, this appears to be visible in Figs. 8b and 9c and d. This complicates the interpretation of the results both for the 5-day averages (i.e., when are they in the course of the simulations), and for the time series in Figs. 8 and 9. Similarly, the bromoform emitted in the last ~50 days of the 3 month simulations has no chance to reach these altitudes. Please discuss these issues.

We have improved our simulations by allowing now for a two-month spin-up phase. As the bromoform lifetime estimates a range from 16 days at the ocean surface to 29 days in the TTL (Hossaini et al., 2012), we can expect the simulated bromoform to have reached a 'steady state' after two months. Transport acting on time scales longer than two months will not impact the atmospheric bromoform distribution given the short lifetime of the compound and can thus be neglected in our simulations.
We have changed our analysis further, which is now based on seasonal mean (JJA and DJF) bromoform mixing ratios averaged over 4 years and have updated Figures 8, 9 and 10 of the manuscript accordingly. As the seasonal mean averages at the cold point tropopause cannot contain significant amounts of bromoform emitted more than two months before the start of the season, the model setup with a two-month spin-up is justified for our analyses.

6. Discussion of key results. Despite being an important component of the bromine lofted to the stratosphere resulting from bromoform, the authors make no mention of product gases (PGs). This is particularly important in light of comment #2 above. I do not expect the authors to simulate PG formation, chemistry, washout, and transport, but it should be clearly explained that we expect much of the bromoform to be chemically processed into PGs during the 50 days or so of vertical ascent to 390 K from the boundary layer. Further on this point, it would be worth having some discussion on CTM studies showing the partitioning of bromoform and PGs at different levels in the atmosphere.

Thanks for the comment. We agree that PG entrainment is an important component of the VSLS contribution to stratospheric bromine and have added this aspect to Section 6 of our manuscript. Based on recent measurement campaigns (that can estimate a total PG entrainment from VSLS), modelling studies (that can distinguish between PG from bromoform and other VSLS) and our own results, we have added a discussion on how much additional PG entrainment could potentially be expected from anthropogenic bromoform sources.

l. 540ff:" This study focuses on source gas entrainment into the stratosphere and does not take into account additional product gas entrainment resulting from anthropogenic bromoform sources. Most observational and modelling studies estimate the total stratospheric bromine contribution to be split half and half into source and product gas contributions (Engel and Rigby, 2018 and references therein). Therefore, we estimate the total stratospheric bromine contribution in form of both, source gas and product gases, from the East and Southeast Asia anthropogenic bromoform sources to be around 0.24–0.30 ppt Br. Compared to a total stratospheric bromine contribution from all VSLSs of about 3–7 ppt Br (Engel and Rigby, 2018), the anthropogenic input estimated in this study provides only a minor contribution."

7. Year of study. As mentioned, the year of study is not mentioned in the paper. While it could be interesting to do a multi-year analysis, if this is beyond the capabilities/time constraints of the authors, an alternative would be to provide some climatological context on the specific year of

study. The WMO annual climate reports usually give a good region by region analysis that would help to set the meteorological context.

> Thanks for the comment. We have chosen year 2006 for the oceanic transport and have shown in Maas et al. (2019), that the interannual variations in the oceanic $CHBr_3$ transport are small.
> For the atmospheric analysis, additional FLEXPART simulations were performed using the same setup as the existing runs. We now include FLEXPART simulations for four years (2015-2018) for the boreal winter (December–February, DJF) and summer (June–August, JJA) seasons, respectively. As we know from existing studies that the interannual variations of $CHBr_3$ reaching the TTL of around 15 % are much smaller than the corresponding seasonal variations of around 50 % (Tegtmeier et al., 2020), we have decided to not include a long-term time series analysis. A short discussion of the impact of interannual transport variations has been added to the manuscript.

8. I think it would really strengthen the paper if the authors included in the conclusions of the paper a comprehensive and thorough discussion of the uncertainties and limitations present in the work. As it is, it is very difficult for a reader to assess the different sources of error and uncertainty, and therefore to judge the authors claims and hypothesis. Following this, I think this would also allow a more precise identification of the required future work (this should be included as well) that needs to be undertaken to provide further proof/disproof of this hypothesis.

> Thanks for the comment. Largest sources of uncertainty are the highly variable bromoform amounts found in chemically treated cooling water. We aim to take these uncertainties into account by including three different scenarios, which result in highly uncertain atmospheric concentrations. Based on comparisons with observations we are able to narrow the uncertainty range to the two lower scenarios. We include a more detailed discussion of these uncertainties and how they compare to other error sources in Section 6.
>
> l. 551:" Highest uncertainties in the estimates presented here, arise from the highly variable bromoform amounts found in chemically treated cooling water. Since there are very few and no recent measurements from power plants in East and Southeast Asia available, the chosen scenarios aim to give a range of environmental concentrations of anthropogenic bromoform. Additional uncertainties can arise from oceanic and atmospheric transport simulations and the parameterisation of air-sea fluxes. Since bromoform is emitted into the atmosphere on very short timescales, uncertainties arising from oceanic transport simulations are small compared to scenario uncertainties. Similarly, given the high saturation of anthropogenic bromoform in surface water, the sensitivity of our results to the air-sea flux parameterisation can be expected to be small. Atmospheric modelling can introduce additional uncertainties, especially regarding the contribution of anthropogenic sources to stratospheric bromine. VSLS FLEXPART simulations have been evaluated in numerous previous studies and shown in most cases good agreement with upper air observations (e.g., Fuhlbruegge et al., 2016; Tegtmeier et al., 2020a). In summary, uncertainties of our results are dominated by uncertainties of the bromoform concentrations in

undiluted cooling water. We have successfully reduced these uncertainties by nearly a factor of two based on comparing our predictions to available observations."

References

Corti, T., B. P. Luo T. Peter H. Vömel Q. Fu., Mean radiative energy balance and vertical mass fluxes in the equatorial upper troposphere and lower stratosphere, Geophysical Research Letters, https://doi.org/10.1029/2004GL021889, 32 (6), 2005.

Corti, T., Luo, B. P., Fu, Q., Vömel, H., and Peter, T.: The impact of cirrus clouds on tropical troposphere- to-stratosphere transport, Atmos. Chem. Phys., 6, 2539-2547, https://doi.org/10.5194/acp-6-2539- 2006, 2006.

Specific Comments

I found the abstract to unclear and at time contradictory from line 20 onwards. I think this stems from the fact that the authors try to say a bit too much at the same time while also only partially introducing terms such as "bottom-up estimates". Here, this is a specific reference to the prior work Ziska et al. 2013, but when I initially read this it appears to be a reference to the method in the current work since one could also classify this as a bottom-up inventory set of sea-air fluxes. I found issue with the single number 0.03 pptv of bromoform in the stratosphere quoted in the abstract. Firstly, given that two scenarios are discussed (LOW and MODERATE), it seemed odd to only quote a single value. Further to this point, the authors look at two different seasons yet only quote one value – again, please resolve this issue. Second, if this is an average, it would make sense to quote the associated standard deviation. Third, there is no context or explanation given for this number: is it a temporal average, a spatial average, what is the duration of the average? These are all important details that would allow readers to understand the results.

Good point, we have rephrased parts of the abstract to clarify our reference related to Ziska et al. (2013). We also added more information on the estimates of stratospheric bromoform entrainment.

Line 43. It would make sense to show some of the chemical equations associated with bromoform formation in coolant water if they are known.

We have added the following information to the manuscript 'The generally proposed mechanism for generating DBPs is the reaction of oxidants such as chlorine and ozone with organic and inorganic substances, such as bromide (Br-) and iodide (I-), in the water via the formation of hypobromous (HOBr) and hypoiodous (HOI) acid.' In addition, we provide some references that discuss the complex formation mechanisms more in detail.

The ordering of the introduction was a bit disjointed in my opinion and to also contain some text that is not relevant to the work at hand. I would remove the sentences between lines 50 and 55.

We move parts of this section to the discussion.

In my opinion the text should be reordered such that the paragraph on lines 70-82 should be the second paragraph. The third paragraph should then be on lines 56-68. This would make a more logical flow in my opinion.

done

Line 117. It was not clear what you meant by the settlement of pathogens. Do you mean growth?

Changed to growth: "Colder water from mid- to high latitudes during winter requires less water treatment as the growth of pathogens takes longer compared to tropical or subtropical waters."

Line 137. I do not claim that this is important to their findings, but the authors should justify not including diffusion.

We rephrased the sentence. Ariane generally is a purely kinematic tool. Without a diffusivity parameterisation, the calculations are fast and can be done for large spatial scale over long time periods, and many particles, which make particle density calculations quite robust.
l. 168f: "The calculation of trajectories with Ariane is generally purely advective."

Line 140. Please mention the years you are looking at in this study and in Mass et al. 2019.

We have added the year (see above).

Line 149. I could not make sense of the following text. It was not clear how point 2 relates to the text that follows or where point 2 is discussed. It was unclear what "distinguish" meant in this context – this is too vague and a more precise explanation would be welcome. Are points 1 and 2 meant to describe separate simulations? Separate processes? And why are 1 and 2 being treated separately at all? Clearer explanations here would be very helpful to the clarity of the manuscript.

Thanks for the comment. We have rephrased the paragraph.

l. 182ff: "We conduct two different simulations allowing us to analyse the spread of long-lived DBPs in general and the spread of bromoform as specific case. First, we simulate the spread of a passive tracer, which does not have any environmental sinks and represents any long-lived non-volatile DBP. We consider the full history of simulated particle positions, which is equivalent to assuming no particles getting lost through sinks in the ocean or emission into the atmosphere. The resulting distribution shows locations where non-volatile DBPs such as bromoacetic acid are transported through the ocean currents within one year.
Second, we simulate the spread of bromoform as a major volatile DBP including the simulation of atmospheric fluxes and oceanic sinks. Each particle is assigned an initial mass of bromoform according to the amount of cooling water used by the respective power plant (**Fehler! Verweisquelle konnte nicht gefunden werden.**) and the bromoform concentration prescribed by

the three scenarios, MODERATE, HIGH and LOW. The particle density distribution is calculated at the sea surface down to 20 m on a 1°×1° grid. The distribution is given as particle density per grid box in percent for non-volatile DBPs and as concentration in pmol L^{-1} for bromoform."

Line 171. The authors should make it clearer how the values of Ceq are calculated from the outgassed bromoform; this is currently not explained.

We added the equation for C_{eq}.
l. 200: "$C_{eq} = C_{air} \cdot H_{CHBr3}^{-1}$ (2)"

Lines 167-173. In general, this section of text needs to be clearer. This could be improved by stating that the low Ceq values are driven by low atmospheric vmr. It would also be clearer if the authors stated how Ceq relates to vmr.

This was done by adding the equation for C_{eq}.

Line 178. "Mean concentrations are calculated...". In air, CW, or Ceq or atmospheric vmr?

See answer below.

Line 178-179. "...of bromoform, characterised by the highest local concentrations, accumulate." This is not very clear.

We have rephrased the paragraph and tried to clarify the statistical approach.
l. 218ff: "Mean sea surface concentrations C_w are calculated by averaging over the area where 90 % of all released bromoform accumulates. To this end, all grid cells are sorted according to descending bromoform concentrations and the average is calculated over the first grid cells that contain in total 90% of all bromoform. Maximum concentrations are calculated by averaging over the area where 10 % of the highest bromoform values accumulate."

Line 180. "Mean and maximum fluxes are calculated based on the same principle." What principle?

see answer above.

Line 181. "The annual mean atmospheric bromine input from industrial bromoform emissions". I think you mean resulting instead of "input".

Changed to: "The annual mean atmospheric bromine flux resulting from industrial bromoform emissions in East and Southeast Asia is derived from the air-sea flux maps of the whole domain."

Section2.3. We are missing a lot of details here. What resolution are the simulations carried out on? The same resolution as the meteorology? Are the emissions constant during a season? Are

Lagrangian particles emitted over the entire ocean and then the emission rate is proportional to the air-sea flux? What year are you looking at?

> Thanks for the comment. We added the resolution of the simulations and further information.
> l. 225: "Based on the seasonal mean emission maps, we obtain a source function of atmospheric bromoform. We simulate the atmospheric transport and distribution of bromoform for the three different emission strength scenarios with the Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005). Seasonal mean bromoform emissions derived from the three scenarios are used as input data at the air-sea interface over the East and Southeast Asia area defined as our study region. The meteorological input data (temperature, and winds) stem from the ERA-Interim reanalysis (Dee et al., 2011) and are given on a 1°×1° horizontal grid, at 61 vertical model levels and a 3-hourly temporal resolution. The chemical decay of bromoform in the atmosphere was accounted for by prescribing a half-life of 17 days during all runs (Montzka and Reimann, 2010). The FLEXPART simulations were performed for boreal winter (December–February, DJF) and summer (June–August, JJA) seasons, respectively, each with a two-month spin-up phase, for the years 2015-2018. A total of 1000 particles are randomly seeded inside each grid box at each time step according to the air-sea flux strength."

Line 195 onwards. We are told that there are three additional runs that are made. Then, over the course of four paragraphs with at times unclear descriptions we are told details about them, but they are only referred to as 'first run' and then 'two additional runs', and then 'first of two runs'. These descriptions are imprecise and confusing. Please can the authors define three names for the runs in line 195 first and then describe them in the following text as "Run A does this....Run B does that ... etc".

> We rephrased the paragraph clarifying the function of the different FLEXPART runs. We changed the names of the runs to make it clear which scenario they are based on and refer to each run by using the defined name throughout the rest of the manuscript.

> l. 243: "We perform three additional FLEXPART runs, Ziska2013-EastAsia, Ziska2013 and Ziska2013+MODERATE based on the updated Ziska2013 emission inventory with the same FLEXPART configuration as described above for both seasons, DJF and JJA. As the Ziska2013 inventory currently presents our best knowledge of bottom-up derived bromoform emissions, it is of interest to analyse how much of these emissions can be explained by industrial sources and how much stems from natural sources.
> The Ziska2013-EastAsia run uses only the Ziska2013 climatological emissions over the East and Southeast Asia area defined as our study region. Results from Ziska2013-EastAsia in the atmospheric boundary layer are used to compare the mixing ratios based on our anthropogenic emissions in the East and Southeast Asia region.
> For comparisons of mixing ratios in the free troposphere and upper troposphere/lower stratosphere (UTLS), air-sea fluxes from other parts of the tropics also need to be taken into account as the time scales for horizontal transport are often shorter than the ones for vertical transport. Therefore, we set up the runs, Ziska2013 and Ziska2013+MODERATE. Ziska2013 uses the air-sea flux of the

Ziska2013 climatology for the global tropics and subtropics between 45° S and 45° N. As the Ziska2013 climatology is taking into account only very few northern hemispheric coastal data points, it likely neglects anthropogenic fluxes in some regions. Therefore, the Ziska2013+MODERATE run uses the Ziska2013 fluxes between 45° S and 45° N, but replaces them with the anthropogenic MODERATE flux values in all grid boxes where the MODERATE fluxes are larger than the Ziska2013 fluxes. The two runs, Ziska2013+MODERATE and Ziska2013, are used to evaluate the additional anthropogenic bromoform based on the MODERATE scenario in the UTLS region. The UTLS region is calculated as the height of the cold point tropopause, which has been derived from ERA-Interim model level data at 6 hourly resolution (Tegtmeier et al., 2020b).“

Line 214. The authors refer to means of the whole domain, but what is the domain?

This refers to the study area (90° E–165° E, 10° S–45° N). We have added the information to the text (l. 263).

Line 214-215. I could not understand the descriptions as they are for “Mean mixing ratios from the whole domain in the marine boundary layer and in the UTLS are given as the average over the 90 % area characterised by the highest local values, and maximum mixing ratios as the average over the largest 10 % (see Section 2.2).” Also, how did the authors decide upon the 90% and 10% levels?

The explanation for the statistical approach is given in section 2.2. For the atmospheric mixing ratios, we use the same analysis as for the oceanic concentration and air-sea flux. For averaging, we chose the area given by the 90% highest mixing ratios, as it includes the majority of anthropogenic $CHBr_3$ in this region and at the same time ensures that empty boxes or negligible small concentrations are not considered in the calculation of the mixing ratios. For similar reasons, we chose the area given by the 10% highest mixing ratios to derive maximum abundances ensuring that these estimates do not only depend on single local peaks.
We have added more information to explain our approach in section 2.2.

Line 216. The authors say they identify two regions. I think they mean define.

Changed the wording l. 265: “In a second step, we define two regions in order to analyse the vertical transport of bromoform into the free troposphere and into the UTLS.”

Line 221. “...pattern in the research area of interest (Figure 3).” I think the authors mean region, and also which region? There are different areas being talked about. Please be precise for clarity.

Changed to l. 271: “The particle density distribution shows the annual mean DBP accumulation pattern in the region of interest in East and Southeast Asia (Figure 3).”

Line 231. Please can the authors show the Kuroshio current on the map?

We have added its approximate location to the text but decided against including one single current in our maps.

Lines 259-264. The section is unclear. The sentence on lines 262-264 is particularly unclear. Also, for clarity sake, please refer consistently to the Ziska et al. 2013 emissions as Ziska2013. These sentences are confusing because information is expressed imprecisely and there are references to prior statements that themselves unclear. Please try to arrange the information clearly, methodically, and logically.

Thanks for pointing this out. We have improved the clarity and message of this paragraph.

l. 314: "The annual bromine input from the ocean into the atmosphere in form of bromoform emissions in the East and Southeast Asia region is 118 Mmol Br according to the observation-based inventories from Ziska2013 (**Fehler! Verweisquelle konnte nicht gefunden werden.**). Our simulations suggest that the anthropogenic input alone amounts to 100, 300 and 500 Mmol Br a^{-1} (LOW, MODERATE, HIGH) for the same region, which corresponds to almost 99 % of the bromine produced during cooling water treatment in the power plant for each scenario. This implies that all bromoform from cooling water treatment is eventually outgassed from the ocean into the atmosphere. While average and maximum air-sea fluxes of anthropogenic bromoform are much higher and confined to small areas around the discharge locations, the Ziska2013 air-sea fluxes are distributed along all coastlines and the equator and result in similar total annual mean Br flux as the LOW emission scenario (**Fehler! Verweisquelle konnte nicht gefunden werden.**). 90 % of the annual mean atmospheric bromine input from anthropogenic bromoform in East Asia occurs north of 20° N where 89–447 Mmol Br are released over one year, compared to the tropical Southeast Asian regions south of 20° N where only 10–52 Mmol Br a^{-1} enter the atmosphere (from LOW to HIGH). In contrast, only 29 % of the total bromine from the Ziska2013 climatology in East Asia is released into the atmosphere north of 20° N, which suggests that the majority of the anthropogenic emissions from this region are missing in the Ziska2013 climatology."

Line 264. Is the implication of the results that most of the East Asian CHBr3 in Ziska2013 is anthropogenic in origin? I think the authors should state this more clearly if this is the prediction.

The results show, that a majority of the $CHBr_3$ that is released in East Asia is of anthropogenic origin, which however is largely missing in the Ziska2013 climatology. We rephrased the sentence to make this point clearer.

l. 324:"In contrast, only 29 % of the total bromine is released into the atmosphere north of 20° N from the Ziska2013 climatology, which suggests that the majority of the anthropogenic emissions from this region are missing in the Ziska2013 climatology."

Line 266. What is the 29% percentage relative to?

This refers to 29 % of the total bromine released into the atmosphere (see above).

Line 271. I found it odd that the authors make a 3 month long simulation and then only show a 5-day average in that entire simulation. Please can the authors explain or justify why such a short period of time is selected? Could the authors consider either monthly or 3-monthly averages as well? Also, which 5 days is this from within the 3 month simulation? All instances of this should be made clear and/or justified.

> We agree with this comment and have changed the configuration of the atmospheric simulations. The output is now presented as the seasonal average (section 2.3).

Lines 288-299. The authors discuss Figure 6 in relation to this text but do not mention the DJF results in Figure 7.

> We added the reference for Figure 7.
> "For both seasons, JJA and DJF, atmospheric bromoform based on industrial emissions is larger than atmospheric bromoform based on the Ziska2013 emissions (Figure 6d, Figure 7d)."

Lines 302-303. From the description given, it is not entirely clear what has been averaged. I assume it is a spatial average, but the authors should specify because the sentence implies it is spatial and temporal.

> We have added information on the averaging to the text.
> "In order to analyse atmospheric transport from the marine boundary layer into the free troposphere and UTLS, seasonal mean bromoform mixing rations are averaged over a subtropical box (30° N–40° N, 120° E–145° E, Figure 2) and a tropical box (10° S–20° N, 90° E–120° E, Figure 2**Fehler! Verweisquelle konnte nicht gefunden werden.**) […]."

Sentence on lines 321-324. I suggest placing this sentence prior to the sentence beginning "Thus, ..." on line 320.

> done

Line 333. Please explain when and where the 5-day snapshot is.

> We changed the 5-day snapshot to a seasonal mean over several years.

Line 340 and 343. Please state when and where the vmr values are calculated for.

> We have added detailed information on when and where the mixing ratios are calculated for.

Lines 363-369. I am concerned here at the averaging approach reduces the complexity and is masking effects of over sampling of the open ocean regions. Thus, I am not sure this shows a good comparison of the same thing. I think this highlights that more thorough statistical analysis

needs to be carried out, i.e., a simple x versus y spatial scatter plot. Including this would strengthen the conclusions of the paper.

> We agree that averaging can mask oceanic concentrations, especially at the coast. But we decided that it is not realistic to compare single point observational measurements with our large-scale modelling results. Especially, since the uncertainties in the modelling approach about the strength of the discharged $CHBr_3$ are very high. Therefore, we use the observations to assess, which of the scenarios chosen reproduces best the observational range of $CHBr_3$ in this region. We then conclude that from the three scenarios, the $CHBr_3$ emissions in the HIGH scenario are set too high and we expect industrial $CHBr_3$ emissions to be in the range of the LOW and MODERATE scenario.

Line 378. There is no mention of the year under comparison. Providing that there is overlap in the year, the KORUS-AQ data suggested by reviewer #1 could be useful here.

> We chose the year 2016 for the FLEXPART simulation, which is the same year of the KORUS-AQ campaign. We added the information in the manuscript.

Line 388. Recommend changing "find" to predict.

> done

Line 392. Make sure it is clear these are simulated vmrs.

> done

Line 392. What is a cloud of high bromoform? Perhaps use something more precise like "A diffuse area with high bromoform abundances".

> done

Line 395-396. Please be more specific as this sentence is unclear.

> We rephrased the sentence to clarify the discrepancy between point measurements that do not capture the whole distribution of bromoform at the surface, and our simulation that includes also the highest concentrations directly at the coast and discharge locations.

Line 403. Recommend stating that the assumptions are reasonable in the majority of case since the cited observations show larger ranges than those stated here.

> Good point, which we include in the discussion.

Line 406. Recommend stating that the HIGH results are only too high in the majority of cases.

> done

Line 408. Recommend being more specific. Instead of "results" state bottom-up emissions, modelling, and observations.

> done

Technical Comments

Recommendations. Please use a comma after uses of which in cases where it introduces a nonrestrictive phrase. When describing using a method from another publication use following instead of after.

done

Line 10. Modify to "...have increased rapidly exceeding mean global growth."

done

Line 36. Modify to "Discharge of DBPs within the cooling..."

done

Line 40. Modify to "...regularly involve the discharge large volumes of water into the marine environment."

Changed to: " …regularly involve the discharge of large water volumes into the marine environment."

Line 41. Modify to "...and its decreased density means it is at the sea surface. Chemicals such as DBPs contained in cooling water are likely to spread laterally...".

done

Line 83. Modify to "...contributions to VSLSs, in the form of..."

done

Line 84. Modify to "...50 % of the global coastal cooling..."

done

Line 87. Modify to "...we show oceanic distributions"

done

Section 2.1 title. Recommend changing to "Estimation of DBP production in cooling water from East Asian power plants".

done

Line 96. Modify to "...the ocean provides an unlimited water supply."

done

Line 136. Modify to "...discharged with the cooling water."

nothing changed here

Line 170. Modify to "...the impact that atmospheric bromoform abundances have upon on the flux calculations"

done

Line 185. Modify to "...bromoform for the three different emission strength scenarios with the Lagrangian..."

done

Line 187. "...(temperature, and winds)..."

done

Line 210. "...than the Ziska2013 emissions."

done

Line 218. "...and over another region from China..."

done

Line 219. "...we refer to this as the subtropical box..."

done

Line 221. “...in the region of interest...”

done

Line 222. “Non-volatile DBPs from cooling water usually accumulates...”

“accumulate” refers to the non-volatile DBPs. We kept the phrase as is.

Line 229. “...in the South China Sea suggests only small contributions...”

done

Line 234. “Figure 3, because the volatile DBPs...”

done

Line 235. “...for the three emissions scenarios LOW...”

Changed to: “…for the three cooling water discharge scenarios LOW…”

Line 236. “...smaller spread compared to the non-volatile DBPs.”

done

Line 263. “...the Ziska2013 biogenic emissions are spread out...”

Changed to: “…the Ziska2013 air-sea flux is spread out…”

Line 264. “...similar total emissions as in the LOW emission...”

Changed to: “…similar total fluxes as in the LOW emission scenario.”

Line 283. “...the three scenarios...”

nothing changed here

Line 292. “These differences are maximised...”

done

Line 319. “...in the tropical marine boundary layer where mixing ratios during DJF...”

done

Line 321. “...Ziska2013-Mixed that include...”

done

Line 323. “...the maritime continent, which increases tropical...”

done

Line 324. “...and even more so in the MODERATE run where...”

done

Line 327. “...that can lead to entrainment...”

done

Line 329. “...occur frequently in this region in both seasons...”

done

Line 352. “...and 17 pmol L-1...”

done

Line 405. “...concentrations to be between...”

done

Line 410. “...in the form of anthropogenic...”

done

Line 413. “...in this region and might explain some...”

done

Line 423. “...emissions with only slightly less bromoform (0.15–0.16 ppt) being transported into the UTLS...”

done

Line 436. “Desalination is mostly done in the Arabian Peninsula...”

done

Line 443. "...areas (Maas et al., 2019), respectively."

done

Anonymous Referee #3

The manuscript is an interesting manuscript that assess the amount of bromoform produced from power plant cooling water treatment in East and Southeast Asia. The spread of bromoform is simulated as passive particles that are adverted using the 3- dimensional velocity fields from the high-resolution ocean general circulation model. The manuscript is worth publication after minor revision.

Detailed comments

1. Include full name of FLEXPART in the abstract.

done

"Based on the emission estimates, atmospheric abundances of anthropogenic bromoform are derived from simulations with the Lagrangian particle dispersion model FLEXPART…"

2. What the author mean by "we expect" in their sentence "From comparison of our model results to observations, we expect initial bromoform concentrations between 20–60 µg L-1 used for the two lower scenarios, to be most realistic" in the abstract?. I think more proper word should be used.

done

"Comparing our model simulations with observations, the best agreement is achieved with initial bromoform concentrations in treated cooling water of 20-60 µg L^{-1} used for the lower two scenarios."

3. Introduction, Line 39-40: Include reference.

done

"Cooling water effluents regularly involve the discharge of large water volumes into the marine environment (Khalanski and Jenner, 2012)."

4. Line 77- 78: "Furthermore, new measurements of bromoform in disinfected cooling water have become available suggesting potentially higher concentrations of up to 500 nmol L-1 (Yang, 2001)". Is there any latest reference to represent "new measurements"?

We added additional references, all of which are newer than the studies by Jenner et al. 1997.
"Furthermore, new measurements of bromoform in disinfected cooling water have become available suggesting potentially higher concentrations of up to 500 nmol L^{-1} (Padhi et al., 2012; Rajamohan et al., 2007; Yang, 2001)."

5. Line 128: The DRAKKAR Group, 2007: Is this a reference? If it is a reference, please list it in the Reference list.

Thanks for notifying. We included the reference in the list.

References:

DRAKKAR Group: Eddy permitting ocean circulation hindcasts of past decades, CLIVAR Exchanges, 42, 8–10, 2007.

Hossaini, R., Chipperfield, M. P., Feng, W., Breider, T. J., Atlas, E., Montzka, S. A., Miller, B. R., Moore, F., and Elkins, J.: The contribution of natural and anthropogenic very short-lived species to stratospheric bromine, Atmos. Chem. Phys., 12, 371– 380, https://doi.org/10.5194/acp-12-371-2012, 2012

Marandino, C. A., Tegtmeier, S., Krüger, K., Zindler, C., Atlas, E. L., Moore, F. and Bange, H. W.: Dimethylsulphide (DMS) emissions from the western Pacific Ocean: A potential marine source for stratospheric sulphur?, Atmos. Chem. Phys., 13(16), 8427–8437, doi:10.5194/acp-13-8427-2013, 2013.

Tegtmeier, S., Atlas, E., Quack, B., Ziska, F. and Krüger, K.: Variability and past long-term changes of brominated very short-lived substances at the tropical tropopause, Atmos. Chem. Phys., 20(11), 7103–7123, doi:10.5194/acp-20-7103-2020, 2020.

Simulations of anthropogenic bromoform indicate high emissions at the coast of East Asia

Josefine Maas[1], Susann Tegtmeier[1,*], Yue Jia[1,*], Birgit Quack[1], Jonathan V. Durgadoo[1,2] and Arne Biastoch[1,2]

[1]GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany
[2]Kiel University, Kiel, Germany
*now at: Institute of Space and Atmospheric Studies, University of Saskatchewan, Saskatoon, Canada

Correspondence to: ~~Josefine Maas (jmaas@geomar.de)~~Susann Tegtmeier (susann.tegtmeier@usask.ca)

Abstract. Bromoform is the major by-product from chlorination of cooling water in coastal power plants. Power plants in East and Southeast Asian economies have increased rapidly exceeding mean global growth. Bottom-up estimates of bromoform emissions based on few measurements appear to under-represent the industrial sources of bromoform from East Asia. By means of Lagrangian analyses, we assess the amount of bromoform produced from power plant cooling water treatment in East and Southeast Asia. The spread of bromoform is simulated as passive particles that are advected using the 3-dimensional velocity fields from the high-resolution NEMO-ORCA0083 ocean general circulation model. Simulations are run for three scenarios with varying initial bromoform concentrations ~~given by~~based on the range of bromoform measurements ~~of bromoform~~ in cooling water discharge. ~~From comparison of our model results~~ Comparing the modelled anthropogenic bromoform to in-situ observations~~, we expect~~ in the surface ocean and atmosphere, the two lower scenarios show the best agreement suggesting initial bromoform concentrations ~~between~~in cooling water to be around 20 ~~–~~60 µg L^{-1} ~~used for the two lower scenarios, to be most realistic. From~~. Based on these two scenarios, ~~we find~~the model produces elevated bromoform along the coastlines of East Asia with average concentrations of 23 and 68 pmol L^{-1} and maximum values in the Yellow, Japan and East China Seas. The industrially~~-~~ produced bromoform is quickly emitted into the atmosphere with average air-sea flux of 3.1 and 9.1 nmol m^{-2} h^{-1}, respectively. ~~Based on the emission estimates, atmospheric~~

Atmospheric abundances of anthropogenic bromoform are derived from ~~FLEXPART~~ simulations ~~and compared to simulations based on climatological bottom-up emission estimates.~~with the Lagrangian particle dispersion model FLEXPART. In the marine boundary layer of East Asia, the FLEXPART simulations show mean anthropogenic bromoform ~~amounts up to~~mixing ratios of 0.~~5~~4–1.~~6~~3 ppt ~~during boreal summer and is thus~~, which are 2–~~7~~6 times larger compared to the ~~bottom-up estimates.~~climatological bromoform estimate. During boreal winter, the simulations show that some part of the anthropogenic bromoform is transported by the northeasterly winter monsoon towards the tropical regions, whereas during boreal summer anthropogenic bromoform is confined to the northern hemisphere subtropics. Convective events in the tropics entrain an additional 0.~~03~~04-0.05 ppt of anthropogenic bromoform into the ~~upper troposphere/lower~~ stratosphere~~.~~ averaged over tropical Southeast Asia. In our simulations, only about 10 % of anthropogenic bromoform is outgassed from power plants located in the tropics south of 20° N, so that only a small fraction of the anthropogenic bromoform reaches the stratosphere.

We ~~find~~conclude that bromoform from cooling water treatment in East Asia is a significant source of atmospheric bromine and might be responsible for annual emissions of 100–300 Mmol Br~~, which~~ in this region. These anthropogenic bromoform sources from industrial water treatment might be a missing factor in global flux estimates of organic bromine. ~~About 90 % of this anthropogenic bromoform is discharged north of 20° N, while in~~While the ~~tropics natural sources dominate and~~ industrial bromoform provides a significant contribution to regional tropospheric budgets, it provides only a ~~small fraction of~~minor contribution to the ~~anthropogenic bromoform reaches the stratosphere.~~stratospheric bromine budget of 0.24-0.30 ppt Br.

1 Introduction

Power plants require cooling water to regulate the temperature in the system. As their demand for cooling water is very high, power plants are often located at the coast to profit from an unlimited water supply. Seawater, however, needs to be disinfected to prevent biofouling and to control pathogens in effluents. The usual disinfection method, chlorination, is known to generate a broad suite of disinfection by-products (DBPs) including trihalomethanes, halogenated acetic acids and bromate (e.g. Helz et al., 1984; Jenner et al., 1997). ~~DBPs develop when hypochlorous acid and organic matter react with the bromide and chloride ions contained in sea water~~The generally proposed mechanism for generating DBPs is the reaction of oxidants such as chlorine and ozone with organic and inorganic substances, such as bromide (Br-) and iodide (I-), in the water via the formation of hypobromous (HOBr) and hypoiodous (HOI) acid ~~(Allonier et al., 1999). Discharge of DBPs with~~(Allonier et al., 1999; Khalanski and Jenner, 2012). Discharge of DBPs within the cooling water effluent can be harmful to the local ecosystem in combination with temperature and pressure gradients (Taylor, 2006). The composition and amount of generated DBPs depend on many factors including the type and concentration of the injected oxidant and the chemical characteristics of the treated water such as salinity, temperature and amount of dissolved organic matter (Liu et al., 2015). Cooling water effluents regularly involve the discharge of large water volumes ~~of water~~ into the marine environment~~.~~ (Khalanski and Jenner, 2012). This water is often warmer than the surrounding waters and ~~decreases~~its decreased density means it stays at the sea surface. Chemicals such as DBPs contained in cooling water are likely to spread ~~lateral~~laterally across the sea surface which facilitates air-sea gas exchange for volatile DBPs.

One of the major DBPs is bromoform ($CHBr_3$), a halogenated volatile organic compound. Bromoform is also naturally produced in the ocean by macroalgae and phytoplankton and is the largest source of organic bromine to the atmosphere (Quack and Wallace, 2003). ~~With an atmospheric lifetime of about 2–3 weeks, it~~Current estimates of bromoform emissions show large variations and ~~belongs to the so-called very short-lived substances (VSLSs) (Engel and Rigby, 2018). Once bromoform is photolysed in the atmosphere, it can deplete ozone by catalytic cycles (Saiz-Lopez and von Glasow, 2012) or change the oxidising capacity of the atmosphere by shifting HO_x ratios towards OH (Sherwen et al., 2016). In the tropics, VSLSs such as bromoform can be entrained into the stratosphere through deep convection (e.g. Aschmann et al., 2009; Tegtmeier et al., 2015) and contribute to stratospheric ozone depletion (Hossaini et al., 2015). While the atmospheric abundance of chlorine and bromine species has started to decline as a result of the~~

~~Montreal Protocol (Engel and Rigby, 2018), renewed productions and emissions of some long-lived ozone depleting substances (ODSs) have recently been discovered. The decline of CFC-11 has slowed unexpectedly, likely due to increasing emissions in eastern Asia (Montzka et al., 2018; Rigby et al., 2019). Atmospheric observations of carbon tetrachloride (CCl_4) also suggest ongoing anthropogenic emissions from feedstock and non-feedstock sources (Sherry et al., 2018). In contrast to the long-lived ODSs, emissions of halogenated VSLSs are not regulated by the Montreal Protocol, and their industrial contributions are not monitored.~~

~~Current estimates of bromoform emissions~~ suggest a global contribution to atmospheric bromine (Br) of 0.5–3.3 Gmol Br a^{-1} (Engel and Rigby, 2018). ~~A bottom-up approach by~~Bottom-up bromoform emission estimates based on statistical gap filling of observational surface data suggest in general smaller global fluxes when compared to other approaches. The bottom-up approach from Ziska et al. (2013) ~~estimates 1.5 Gmol Br a^{-1}. Their analysis is based on~~uses surface ocean and atmosphere measurement collected in the HalOcAt (Halocarbons in the Ocean and Atmosphere) database (https://halocat.geomar.de/) ~~which contains VSLSs data in surface ocean and atmosphere from measurement campaigns.~~to estimate bromoform emissions of 1.5 Gmol Br a^{-1}. Based on physical and biogeochemical characteristics of the ocean and atmosphere, the data are classified into 21 regions and extrapolated to a regular grid within each region. Top-down bromoform emission estimates, on the other hand, are based on global model simulations adjusted to match available aircraft observations~~.~~ (e.g. Butler et al., 2007; Liang et al., 2010; Ordóñez et al., 2012). They are in general, a factor of two larger than bottom-up emission estimates. Individual ship cruises, aircraft campaigns and modelling studies have demonstrated a large spatio-temporal variability of bromoform in surface water and air (e.g. Fiehn et al., 2017; Fuhlbrügge et al., 2016; Jia et al., 2019). These pronounced variations combined with the poor temporal and spatial data coverage is a major challenge ~~for~~when deriving reliable emission estimates and may explain the large deviations between bottom-up and top-down estimates. Geographical regions with poor data coverage might not be well~~-~~represented in the global emission scenarios. Furthermore, the anthropogenic input of bromoform might be under-estimated for large industrial regions (Boudjellaba et al., 2016).

With an atmospheric lifetime of about 2–3 weeks, bromoform belongs to the so-called very short-lived substances (VSLSs) (Engel and Rigby, 2018). Once bromoform is photolysed in the atmosphere, it can deplete ozone by catalytic cycles (Saiz-Lopez and von Glasow, 2012) or change the oxidising capacity of the atmosphere by shifting HO_x ratios towards OH (Sherwen et al., 2016). In the tropics, VSLSs such as bromoform can be entrained into the stratosphere (e.g. Aschmann et al., 2009; Liang et al., 2010; Tegtmeier et al., 2015) and contribute to stratospheric ozone depletion (Hossaini et al., 2015). Stratospheric entrainment of trace gases with very short lifetimes is most efficient in regions of strong, high reaching convective activity such as the West Pacific and Maritime Continent (e.g., Pisso et al., 2010; Marandino et al., 2013). The Asian summer monsoon represents another important pathway to the lower stratosphere (e.g., Randel et al. 2010) entraining mostly Southeast Asian planetary boundary layer air. The monsoon also has the potential to include VSLSs emitted from the Indian Ocean and Bay of Bengal (Fiehn et al., 2017, 2018b). Model simulations suggest that the monsoon circulation transports the oceanic emissions towards India and the Bay of Bengal, from where they are convectively lifted and reach stratospheric levels in the south-eastern part of the Asian monsoon anticyclone. The stratospheric bromine injections from the tropical Indian Ocean and West Pacific depend critically on

the seasonality and spatial distribution of the emissions (Fiehn et al., 2018a). Model studies based on bottom-up emission estimates indicate global bromoform maxima over India, the Bay of Bengal, and the Arabian Sea as well as over the Maritime Continent and West Pacific (Tegtmeier et al., 2020a). While aircraft measurements in the West Pacific have confirmed high concentrations of bromoform (Wales et al., 2018), the role of the Asian monsoon as an entrainment mechanism for VSLSs has not been confirmed yet due to the lack of observations in this region.

Quantifying the contribution of bromoform to tropospheric and stratospheric bromine budgets requires reliable emission estimates that include natural and anthropogenic sources. Industrially produced bromoform will spread in the marine environment once the treated water is released and will be emitted into the atmosphere together with naturally produced bromoform. Atmospheric and oceanic measurements cannot distinguish between naturally and industrially produced bromoform and all the top-down and bottom-up emission estimates discussed above automatically include the latter. A first comparison of natural and industrial bromoform sources from Quack and Wallace (2003) concluded a negligible global contribution of 3 % man-made bromoform. Their estimate was based on measurements of bromoform in disinfected water (80 nmol L^{-1}) from European power plants and cooling water use and projections of the global electricity production. In the meantime, the global electricity production has increased by almost 50 % from 16700 TWh in 2003 (IEA, 2005) to 25000 TWh in 2016 (IEA, 2018). Furthermore, new measurements of bromoform in disinfected cooling water have become available suggesting potentially higher concentrations of up to 500 nmol L^{-1} ~~(Yang, 2001). Especially emerging economies in East Asia, such as China~~(Padhi et al., 2012; Rajamohan et al., 2007; Yang, 2001). Especially emerging economies in East Asia, such as China and India have experienced a massive growth over the last years exceeding the global economic growth. As the existing estimate of industrially produced bromoform is outdated, updated estimates taking into account new measurements are required to assess the impact of anthropogenic activities on the production and release of brominated VSLSs as well as their contribution to stratospheric ozone depletion.

We ~~aim to quantify~~will derive a new bottom-up VSLS emission estimate for East and Southeast Asia by quantifying anthropogenic contributions to ~~VSLSs, in form of~~ bromoform ~~emitted from regional~~production. We will use available cooling water measurements to predict oceanic and atmospheric bromoform concentrations in regions of extensive industrial activities. Based on comparisons to available ocean surface and atmosphere measurements, we will evaluate our predictions and discuss implications for atmospheric bromine budgets as well as future research needs. As 50 % of the global coastal cooling water is produced in East and Southeast Asia, we define these areas as our study region. We identify locations of high industrial activity along the coast of East and Southeast Asia and derive estimates of released cooling water and therein contained bromoform (Section 2). Based on Lagrangian simulations in the ocean, we derive the general marine distribution of non-volatile DBPs released with cooling water. For the case study of bromoform, we show oceanic ~~distribution~~distributions of the volatile DBP by taking air-sea exchange into account (Section 3). Based on the oceanic emissions, the atmospheric distribution of bromoform generated in industrial cooling water is simulated with a Lagrangian particle dispersion model (Section 4). Results are compared to existing observational atmospheric and oceanic distributions (Section 5). Methods are described in Section 2, while discussion and summary are provided in Section 6.

2 Methods

2.1 Estimation of DBP production in cooling water from ~~global~~East Asian power plants

In this study, we investigate the oceanic distribution of DBPs produced in power plants that chlorinate seawater. We assume that all power plants located at the coast use seawater for cooling purposes. Most of the seawater is only used once in the system as the ocean provides an unlimited water supply. For the estimation of the cooling water volumes, we use the global power plant database Enipedia (enipedia.tudelft.nl, last access: 2017) where over 21,000 power plants are given together with location, electricity generation (in MWh) and sometimes fuel type. Based on the coordinates, we choose those power plants that are located less than 0.02 degrees (maximum 2 km at the equator) away from any coastline and refer to them as coastal. Based on this classification, 23 % of energy capacity from listed power plants in the database is generated by coastal power plants. The Key World Energy Statistics (IEA, 2018) give a total global electricity production of 24973 TWh in 2016. The average water use per MWh energy was given by Taylor (2006) to be 144 m^3 MWh^{-1}, which leads to a global cooling water discharge of about 800 billion m^3 a^{-1} along the coast in 2016. For the individual coastal power plants in East and Southeast Asia, annual cooling water volumes are shown in Figure 1.

To determine the amount of bromoform produced in the cooling water, there are only a few measurements available and the locations are limited (Table 1). Most data originate from several power plants in Europe (Allonier et al., 1999; Boudjellaba et al., 2016; Jenner et al., 1997) and some studies are based on measurements from single power plants in Asia (Padhi et al., 2012; Rajamohan et al., 2007; Yang, 2001). Only Yang (2001) provides DBP measurements in East Asia. Furthermore, the location where water is sampled is not consistent among the different studies. Some samples were taken in the coastal surface water at the power plant outlet (Fogelqvist and Krysell, 1991; Yang, 2001), while other studies sampled directly inside the power plant before dilution with the ocean (Jenner et al., 1997; Rajamohan et al., 2007). The measurements show a very large variability ranging from 8–290 µg L^{-1}. As there is no systematic difference between measurements inside the power plant and at the power plant outlet, both types of measurements are given in Table 1 together in the first column~~1~~.

In addition to the sampling location, differences in the concentrations can result from water temperature, salinity and dissolved organic carbon content, which are seasonally dependent. Colder water from mid~~-~~ to high latitudes during winter requires less water treatment as the ~~settlement~~growth of pathogens takes longer compared to warm tropical or subtropical waters. The chlorination dosage and frequency of treatment also play a distinct role for the resulting DBP concentrations (Joint Research Council, 2001).

Given that available measurements are sparse and depend on many factors, the uncertainties in initial bromoform concentrations in cooling water are relatively high. For our analyses we chose to scale the bromoform discharge according to three scenarios (LOW, MODERATE and HIGH), which reflect the range of values given in available literature (Table 1). For our simulations, we use initial bromoform concentrations of 20 µg L^{-1} (LOW), 60 µg L^{-1} (MODERATE) and 100 µg L^{-1} (HIGH) in undiluted cooling water.

2.2 Lagrangian simulations in the ocean

For the assessment of the long-term, large-scale effect of DBPs from power plant cooling water on the environment, we simulate the distribution of non-volatile DBPs and the concentration and emission of the volatile DBP bromoform in the ocean. The Lagrangian model runs are based on velocity output from the high-resolution, eddy-rich ocean general circulation model (OGCM) NEMO-ORCA version 3.6 (Madec, 2008). The ORCA0083 configuration (The DRAKKAR Group, 2007) has a horizontal resolution of 1/12 degrees at 75 vertical levels and output is given at a temporal resolution of five days for the time period 1963–2012. Atmospheric forcing comes from the DFS5.2 data set (Dussin et al., 2016). The experiment ORCA0083-N06 used in this study was run by the National Oceanography Centre, Southampton, UK. Further details can be found in Moat et al. (2016).

We simulate the spread of the DBPs from treated cooling water, by applying a Lagrangian trajectory integration scheme to the 3D velocity fields with the ~~ARIANE~~Ariane software (Blanke et al., 1999). We perform offline trajectory calculations by passively advecting virtual particles, which represent the DBP amount discharged with the cooling water. The calculation of trajectories with Ariane is generally purely advective ~~without diffusivity.~~ For each scenario we perform one simulation over the same time period from 2005-2006. In each simulation, particles are continuously released close to the power plant locations at 5-day time steps over two years. We allow for an accumulation period of 11 months and show the results of the seasonal and annual mean of the second year starting in December 2005. A detailed description of the applied method can be found in Maas et al. (2019), where it is also shown that interannual variability of surface velocity in the study region is small compared to seasonal variability.

Our study focusses on the region of East and Southeast Asia (90° E–165° E, 10° S–45° N), which comprises 50 % of the global coastal power plant capacity and cooling water discharge. The particle discharge locations have been chosen as close to the coastlines as possible (Figure 2). Particles are released approximately 8 to 40 km offshore, as the model-resolution does not allow to capture smaller-scale coastal structures such as harbours or estuaries nor does it simulate the near-costal exchange, e.g. through tides. Our approach ensures minimal influence of the land boundaries on the simulation in order to avoid numerically-related beaching of particles into the coastal boundary.

~~For~~We conduct two different simulations allowing us to analyse the ~~analysis of the experiments we distinguish 1) the passive~~ spread of long-lived DBPs ~~without~~in general and the spread of bromoform as specific case. First, we simulate the spread of a passive tracer, which does not have any environmental sinks~~, and 2) the spread of bromoform as a major volatile DBP accounting for atmospheric fluxes~~ and ~~oceanic sinks. For the passive spread of~~represents any long-lived non-volatile ~~DBPs, we~~DBP. We consider the full history of simulated particle positions, which is equivalent to assuming no particles getting lost through sinks in the ocean or emission into the atmosphere. The resulting distribution shows locations where non-volatile DBPs such as bromoacetic acid are transported through the ocean currents within one year.

~~For~~

Second, we simulate the spread of ~~anthropogenic~~ bromoform~~, each~~ as a major volatile DBP including the simulation of atmospheric fluxes and oceanic sinks. Each particle is assigned an initial mass of bromoform according to the amount of cooling water used by the respective power plant (Figure 1) and the bromoform concentration prescribed by the three scenarios, MODERATE, HIGH and LOW. The particle density distribution is calculated at the sea surface down to 20

m on a 1°×1° grid. The distribution is given as particle density per grid box in percent for non-volatile DBPs and as concentration in pmol L^{-1} for bromoform.

~~Sink~~For the second set of simulations, the sink processes of bromoform such as constant gas exchange at the air-sea interface or chemical loss rates are taken into account. The air-sea flux of bromoform is calculated ~~after~~following the general flux equation at the air-sea interface:

$$Flux = (C_w - C_{eq}) \cdot k \qquad (1)$$

Here Flux is positive when it is directed from the ocean to the atmosphere and is given in pmol m^{-2} h^{-1}. C_w is the actual concentration in the surface mixed layer in pmol L^{-1} and

$C_{eq} = C_{air} \cdot H_{CHBr3}^{-1}$ (2)

is the theoretical equilibrium concentration at the sea surface (in pmol L^{-1}) calculated from the atmospheric mixing ratio (in ppt~~), sea surface temperature and sea surface salinity (Quack and Wallace, 2003).~~) and the Henry constant H_{CHBr3} of bromoform. The gas transfer velocity k (in cm h^{-1}) mainly depends on the surface wind speed and temperature and is calculated ~~after~~following Nightingale et al., (2000). Wind velocities at 10 m height are taken from the NEMO-ORCA forcing data set DFS5.2 (Dussin et al., 2016), which is based on the ERA-~~interim~~Interim atmospheric data product.

As the oceanic and atmospheric terms in the air-sea flux parameterisation are of additive nature, it is possible to calculate the flux of anthropogenic and natural bromoform separately. For our simulations, we only consider bromoform from cooling water and apply the air-sea flux parameterisation to the anthropogenic portion of bromoform in water and air. We have conducted sensitivity tests (see section 2.3) to estimate the impact ~~of~~that atmospheric bromoform abundances ~~on~~have upon the flux calculations. The tests show that outgassed anthropogenic bromoform leads to atmospheric surface values C_{eq}, which are always below 8 % of the underlying sea surface concentration C_w (at a water temperature of 20°C). Such low equilibrium concentrations can be considered negligible for the flux calculation and therefore C_{eq} is set to zero in our study.

The sea surface concentration and air-sea flux from the three simulations are also compared to climatological maps of bromoform concentration and emissions from the updated Ziska et al. (2013) inventory (hereafter referred to as Ziska2013) (Fiehn et al., ~~2018~~2018a).

Mean sea surface concentrations C_w are calculated by averaging over the area where 90 % of all released bromoform~~, characterised by the highest local~~ accumulates. To this end, all grid cells are sorted according to descending bromoform concentrations~~, accumulate~~ and the average is calculated over the first grid cells that contain in total 90% of all bromoform. Maximum concentrations are calculated by averaging over the area where 10 % of the highest bromoform values accumulate. Mean and maximum air-sea fluxes are calculated ~~based on~~using the same averaging principle as for C_w. The annual mean atmospheric bromine ~~input~~flux resulting from industrial bromoform emissions in East and Southeast Asia is derived from the air-sea flux maps of the whole domain.

2.3 Lagrangian simulation in the atmosphere

Based on the seasonal mean emission maps, we obtain a source function of atmospheric bromoform. We simulate the atmospheric transport and distribution of bromoform for the three different emission strength scenarios with the

Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005). ~~Bromoform~~The FLEXPART model includes parameterisation for moist convection (Forster et al., 2007) and turbulence in the boundary layer and free troposphere (Stohl and Thomson, 1999). It has been used in previous studies with a similar model setup and shown robust VSLS profiles compared to observations (e.g. Fiehn et al., 2017; Fuhlbrügge et al., 2016; Tegtmeier et al., 2020a).

Seasonal mean bromoform emissions derived from the three scenarios are used as input data at the air-sea interface over the East and Southeast Asia area defined as our study region. The meteorological input data (temperature, ~~wind~~and winds) stem from the ERA-Interim reanalysis product (Dee et al., 2011) and are given on a 1°×1° horizontal grid, at 61 vertical model levels and a 3-hourly temporal resolution. The chemical decay of bromoform in the atmosphere was accounted for by prescribing a ~~half-life~~lifetime of 17 days during all runs (Montzka and Reimann, 2010).

The FLEXPART simulations were performed for boreal winter (December–February, DJF) and summer (June–August, JJA) seasons, respectively, each with a two-month spin-up phase. Since there are only weak dynamical variations between different years, we used an ensemble mean of four years (2015-2018) each. A total of 1000 particles are randomly seeded inside each grid box at each time step according to the air-sea flux strength. Output mixing ratios are given at the same horizontal resolution and 33 vertical levels from 50 to 20000 m. Detailed descriptions of model settings are described in Jia et al. (2019). ~~The FLEXPART simulations were performed for the boreal winter (December–February, DJF) and summer (June–August, JJA) seasons, respectively, for a total of three months with a one-month spin-up.~~

We perform three additional FLEXPART runs, Ziska2013-EastAsia, Ziska2013 and Ziska2013+MODERATE based on the updated Ziska2013 emission inventory with the same FLEXPART configuration as described above for both seasons, DJF and JJA. As the Ziska2013 inventory ~~–~~currently presents our best knowledge of bottom-up derived bromoform emissions, it is of interest to analyse how much of these emissions can be explained by industrial sources and how much stems from natural sources.

The ~~first~~ Ziska2013-EastAsia run uses only the Ziska2013 climatological emissions over the East and Southeast Asia area defined as our study region. ~~This run is named~~Results from Ziska2013-EastAsia ~~and is~~in the atmospheric boundary layer are used to compare the ~~resulting~~ mixing ratios ~~in the atmospheric boundary layer to results driven by~~based on our anthropogenic emissions in the East and Southeast Asia region.

For comparisons of mixing ratios in the free troposphere and upper troposphere/lower stratosphere (UTLS~~) approximately above 17 km, emissions~~), air-sea fluxes from other parts of the tropics also need to be taken into account as the time scales for horizontal transport are often shorter than the ones for vertical transport. Therefore, we set up ~~two additional runs using the Ziska2013 emissions for the global tropics and subtropics between 45° S and 45° N. This configuration is used as input for the first of the two runs, which is named Ziska2013-Tropics.~~the runs, Ziska2013 and Ziska2013+MODERATE. Ziska2013 uses the air-sea flux of the Ziska2013 climatology for the global tropics and subtropics between 45° S and 45° N. As the Ziska2013 climatology is taking into account only very few northern hemispheric coastal data points, it likely neglects anthropogenic fluxes in some regions. Therefore, the Ziska2013+MODERATE run uses the Ziska2013 fluxes between 45° S and 45° N, but replaces them with the anthropogenic MODERATE flux values in all grid boxes where the MODERATE fluxes are larger than the Ziska2013 fluxes. The two runs, Ziska2013+MODERATE and Ziska2013, are used to evaluate the additional anthropogenic bromoform based on the MODERATE scenario in the UTLS region. The UTLS region is calculated as the height of the

cold point tropopause, which has been derived from ERA-Interim model level data at 6 hourly resolution (Tegtmeier et al., 2020b).

~~As the Ziska2013 emissions are based on extrapolation of very few northern hemispheric coastal data, it likely neglects anthropogenic emissions in some regions. Therefore, the second run, Ziska2013 Mixed, uses the same Ziska2013 emissions between 45° S and 45° N, except for the East and Southeast Asia region. Here, the Ziska2013 emissions are replaced by the MODERATE emission values for every grid box where the MODERATE emissions are larger than Ziska2013. These two runs, Ziska2013 Mixed and Ziska2013 Tropics, are used to compare additional anthropogenic bromoform based on the MODERATE scenario to bromoform based on the Ziska2013 climatology for the UTLS region.~~

Mean mixing ratios from the whole domain (90° E–165° E, 10° S–45° N) in the marine boundary layer and in the UTLS are given as the average over the 90 % area characterised by the highest local values, and maximum mixing ratios as the average over the largest 10 % (see Section 2.2). In a second step, we ~~identify~~define two regions in order to analyse the vertical transport of bromoform into the free troposphere and into the UTLS. For the height profiles of the ~~Ziska-Tropics~~Ziska2013 and the ~~Ziska-Mixed~~Ziska2013+MODERATE runs, we average mixing ratios over a region above the ~~maritime continent~~Maritime Continent, which we refer to as the tropical box (10° S–20° N, 90° E–120° E), and over another region from China to Japan which we refer to this as the subtropical box (30° N–40° N, 120° E–145° E) (Figure 2).

3 Oceanic spread of DBPs and bromoform

The particle density distribution shows the annual mean DBP accumulation pattern in the ~~research area~~region of interest in East and Southeast Asia (Figure 3). Non-volatile DBPs from cooling water usually accumulate around the coast and in the marginal seas. There is a clear latitudinal gradient with only little DBP distribution south of 20° N, except for higher values in the Strait of Malacca. In contrast to the relatively low DBP density in the inner tropics, the subtropics show a very high accumulation of DPBs with a centre in the marginal seas between 25° N and 40° N. While power plants can be found along all coastlines (Figure 1), the power plant capacity and therefore the amount of treated cooling water is much higher along the subtropical coasts of China, Korea and Japan leading to the DBP distribution pattern shown in Figure 3. Hot spots are around the coast of Shanghai and Incheon with a DBP density of 1 %. A relatively high DBP density of 0.8 % can also be found in the East China Sea, the Yellow Sea, the southern Japan Sea, the Gulf of Tonkin and the Strait of Malacca. Medium to low DBP density in the South China Sea ~~suggest~~suggests only small contributions of cooling waters to this region. Since Japan and Korea have a large number of power plants with high volumes of cooling water discharge, a relatively large amount of DBPs is transported eastward with the Kuroshio Current east of Japan into the North Pacific.

The distribution of bromoform, as a volatile DBPs in the surface ocean differs from the DBP accumulation pattern shown in Figure 3, ~~as~~because the volatile DBPs are outgassed into the atmosphere. The annual mean sea surface concentration of bromoform from cooling water is shown in Figure 4 (panel a-c) for the three cooling water discharge scenarios LOW, MODERATE and HIGH and with a substantially smaller spread compared to the non-volatile DBPs. The area which contains the 90 % highest bromoform concentrations does not vary between the three scenarios, as the air-sea flux, which

determines how much bromoform remains in the water, is linearly proportional to the sea surface concentration. Higher surface concentrations result in higher fluxes into the atmosphere, which limits the spread of bromoform substantially compared to non-volatile DBPs. Bromoform concentrations are around 23, 68, and 113 pmol L^{-1} (LOW, MODERATE and HIGH) averaged over the region where the 90 % of bromoform with the highest concentrations accumulate (Table 2). This region is to a large degree limited to latitudes north of 20° N as a result of the power plant distribution. As in the case of the non-volatile DBPs, most of the bromoform is centred along the Chinese, Korean and Japanese coast line with a larger spread into the marginal seas for the latter two. One exception to this latitudinal gradient is the Strait of Malacca where local power plants result in average bromoform concentrations of 3.4, 10.3 and 16.7 pmol L^{-1} (LOW, MODERATE, and HIGH).

Observational based oceanic bromoform concentrations from Ziska2013 (Figure 4, panel d) are relatively evenly spread along the coastlines of the region and do not show the latitudinal gradient found for the anthropogenic concentrations. North of 20° N the anthropogenic bromoform is much higher than the oceanic distribution from Ziska2013, where the maximum lies around 21 pmol L^{-1}. Our simulations reach maximum values (averaged over the 10 % highest bromoform concentrations) of 112, 338 and up to 563 pmol L^{-1} (LOW, MODERATE and HIGH, Table 2) in the Japan Sea. These concentrations are all above 100 pmol L^{-1} and are very high compared to observational values from Ziska2013 (Figure 4, panel d).

~~Emissions~~Air-sea fluxes of anthropogenic bromoform show a similar distribution as the oceanic concentrations (Figure 5, panel a-c). Flux rates averaged over the region of the 90 % highest flux values are 3, 9 and 15 nmol m^{-2} h^{-1} (LOW, MODERATE and HIGH). Maximum flux rates (averaged over the highest 10 %) even reach 13, 41 and 68 nmol m^{-2} h^{-1} in the Japan Sea near the Korean and Japanese coast for the three scenarios (Table 2). In contrast, the existing observational based estimates from the Ziska2013 climatology peak with 1.1 nmol m^{-2} h^{-1} located in the South China Sea along the west coast of the Philippines (Figure 5, panel d).

The annual bromine input from ~~bromoform~~the ocean into the atmosphere in form of bromoform emissions in the East and Southeast Asia region is 118 Mmol Br according to the observation-based inventories from Ziska2013 (Table 2). Our simulations suggest that the anthropogenic input alone amounts to 100, 300 and 500 Mmol Br a^{-1} (LOW, MODERATE, HIGH) for the same region, which ~~is~~ corresponds to almost 99 % of the bromine produced ~~as bromoform~~ during cooling water treatment in the power plant~~.~~ for each scenario. This implies that all bromoform from cooling water treatment is eventually outgassed from the ocean into the atmosphere. While average and maximum ~~emissions are much higher for~~ air-sea fluxes of anthropogenic bromoform ~~as discussed above, the Ziska emissions spread out over a larger area thus resulting~~are much higher and confined to small areas around the discharge locations, the Ziska2013 air-sea fluxes are distributed along all coastlines and the equator and result in similar total ~~emissions~~annual mean Br flux as the LOW ~~scenario.~~ emission scenario (Table 2). 90 % of the annual mean atmospheric bromine input from anthropogenic bromoform in East Asia occurs north of 20° N where 89–447 Mmol Br are released over one year, compared to the tropical Southeast Asian regions south of 20° N where only 10–52 Mmol Br a^{-1} enter the atmosphere (from LOW to HIGH). In contrast, only 29 % of the total bromine from the Ziska2013 climatology in East Asia is released into the atmosphere north of 20° N ~~for~~, which suggests that the majority of the anthropogenic emissions from this region are missing in the Ziska2013 climatology.

4 Anthropogenic bromoform in the atmosphere

4.1 Mixing ratios in the marine boundary layer

Atmospheric mixing ratios of anthropogenic bromoform are derived from FLEXPART runs driven by the seasonal emission estimates discussed in section 3. Atmospheric bromoform from industrial emissions is shown for a ~~5-day~~seasonal average in the marine boundary layer at 50 m height for JJA for all three scenarios (Figure 6, panel a-c). Mean mixing ratios are 0.~~5~~4, 1.~~6~~3 and 2.~~4~~3 ppt (LOW, MODERATE, HIGH, Table 2). Overall, high atmospheric mixing ratios are found around the coastlines of Japan, South Korea and northern China. Although maximum emissions are located in the Japan Sea, maximum mixing ratios are mostly located south of Japan with values up to ~~4.6, 13.~~9.0, 27.1 and ~~23.3~~45.0 ppt (LOW, MODERATE, HIGH, Table 2). Here, the westerlies lead to bromoform transport from the Japan Sea into the Northwest Pacific. We also localise ~~hot spots~~hotspots of strong anthropogenic bromoform accumulations due to enhanced emissions over Shanghai, Singapore or the Pearl River Delta, respectively (Figure 6, panel a). During boreal summer, the West Pacific and Maritime Continent are influenced by southwesterly winds and the anthropogenic bromoform experiences northward transport, bringing some smaller portion of the subtropical emissions into the mid-latitudes (Figure 6, panel a, b and c).

During boreal winter (DJF, Figure 7, panel a-c), anthropogenic bromoform shows somewhat lower atmospheric mixing ratios with a mean of 0.3, 0.~~9~~8 and 1.~~5~~4 ppt and maximum values of ~~3.2, 9~~4.7, 13.5 and ~~15.9~~23.3 ppt for the three scenarios (Table 2). In contrast to boreal summer, the atmospheric transport is dominated by winds from the northeast and higher bromoform values are confined to tropical and subtropical regions (Figure 7). Thus, tropical mixing ratios show a clear seasonal variability and are on average over 3 times higher for DJF than for JJA without large shifts in the location of the bromoform emissions (Figure S1).

In order to compare the atmospheric impact of industrial emissions with existing results, we repeat our analysis for the bottom-up emissions scenario Ziska2013 for the same region, which has been frequently used in past studies (e.g. Hossaini et al., 2013, 2016). Atmospheric mixing ratios are derived from seasonal FLEXPART runs driven by Ziska2013-EastAsia and shown for a ~~5-day~~seasonal average at 50 m height for JJA (Figure 6d). For both seasons, JJA and DJF, atmospheric bromoform based on industrial emissions is larger than atmospheric bromoform based on the Ziska2013-EastAsia emissions (Figure 6d, Figure 7d). These differences ~~maximise~~are maximised in the subtropical regions, where anthropogenic bromoform dominates especially during JJA when anthropogenic mixing ratios are 2~~-7~~5 times larger ~~than from~~compared to climatological ~~emissions~~Ziska2013 bromoform (for LOW and MODERATE). In the tropical regions, the situation is more complicated. Atmospheric abundances driven by the industrial emissions reach higher peak values of up to 2 ppt especially in the Strait of Malacca (MODERATE, Figure 6b~~)~~), while mixing ratios driven by the observationally based emissions from Ziska2013-EastAsia are smaller only reaching peak values of up to 0.8 ppt, but are spread over a much wider area (Figure 6d). Given the comparison of the boundary layer values, it is not clear, which emission scenario will result in a larger contribution to stratospheric halogen budget.

4.2 ~~Vertical transport of bromoform~~Mixing ratios in the free troposphere and UTLS

In order to analyse atmospheric transport from the marine boundary layer into the free troposphere and UTLS, seasonal mean bromoform mixing rations are averaged over a subtropical box (30° N–40° N, 120° E–145° E, Figure 2) and a tropical box (10° S–20° N, 90° E–120° E, Figure 2) from the Ziska2013~~-Tropics~~ and Ziska2013~~-Mixed~~+MODERATE simulations for DJF and JJA. Both simulations are based on global climatological Ziska2013 ~~emissions~~bromoform air-sea fluxes between 45° S and 45° N, with Ziska2013~~-Mixed~~+MODERATE including additional anthropogenic bromoform ~~emissions~~fluxes in East and Southeast Asia.

In the subtropical box (Figure 8), there is a strong dominance of anthropogenic bromoform in the marine boundary layer during JJA several times higher compared to bromoform of climatological bottom-up emissions (Figure 8). Our simulations suggest that during convective events in JJA, anthropogenic bromoform from the subtropical marine boundary layer can be transported into the UTLS region, up to ~~17 km, the approximate~~ height of the cold point. In our ~~example~~simulation Ziska2013+MODERATE, convective events ~~occur~~ during the ~~second half of the~~ summer ~~bringing occasionally higher bromoform of~~bring on average over 0.3 ppt into the UTLS (Figure 8). During DJF (~~Figure S2~~not shown), there is only very little transport of bromoform out of the boundary layer, and entrainment of anthropogenic bromoform into the subtropical UTLS is confined to boreal summer when the intertropical convergence zone (ITCZ) is located north of 10° N (Waliser and Gautier, 1993).

In the tropical box (Figure 9), atmospheric bromoform mixing ratios in the marine boundary layer are generally weaker than in the subtropics ~~for the simulation based on Ziska2013-Mixed emissions (Figure 9, panel a and b). However, the vertical transport for the two simulations Ziska2013-Mixed and Ziska2013-Tropics are in the same range from 0.2–0.5 ppt (Figure 9) even though the spatial distribution of emissions between Ziska2013 and the MODERATE scenario differs strongly (Figure 5).~~(Figure 8). The seasonal difference between DJF and JJA is ~~very~~only pronounced in the tropical marine boundary layer for Ziska2013+MODERATE, where ~~tropical~~ mixing ratios during DJF exceed 0.5 ppt throughout the whole time period (Figure 9a~~). Thus, convective events during DJF bring more bromoform into the UTLS compared to~~) and are around 0.4 ppt during JJA (Figure 9b). The air-sea fluxes ~~in the tropics hardly change from DJF to JJA (Figure S1),~~show no strong seasonal variations, therefore this difference must be transport-driven. During DJF, the prevailing northeasterly winds ~~during DJF~~ advect the bromoform from ~~the~~regions of high anthropogenic emissions in East Asia towards the ~~maritime continent which increases~~ Maritime Continent, increasing the tropical ~~abundances~~bromoform abundance substantially. ~~This~~ Thus, tropical convection during DJF can ~~be seen for Ziska2013 and even stronger in the MODERATE run where the~~ transport more of the anthropogenic bromoform emitted in East ~~Asian emissions dominate over the Southeast Asian region (Figure 7, panel b and d).~~Asia into the UTLS compared to similar events during JJA (Figure 9). The difference between the Ziska2013+MODERATE and the Ziska2013 average mixing ratios in the UTLS is 0.05 ppt during DJF and 0.04 ppt during JJA. These values present the anthropogenic contribution to stratospheric bromine from East and Southeast Asian cooling water based on the MODERATE bromoform emission scenario.

~~4.3 Mixing ratios in the upper troposphere/lower stratosphere~~

Atmospheric processes over the ~~maritime continent~~Maritime Continent, which encloses the tropical box, are characterised by deep convective events ~~which~~, that can lead to entrainment of ~~VSLS~~VSLSs into the stratosphere (Aschmann and Sinnhuber, 2013; Tegtmeier et al., ~~2019~~2020a). For our case study, convective events reaching the UTLS occur ~~frequently~~ in both seasons ~~sometimes persisting over several days~~ (Figure 9). ~~There~~Moreover, here is a clear anthropogenic signal from Ziska2013+MODERATE compared to Ziska2013 in the free troposphere in this region in both seasons, which is more pronounced during DJF (Figure 9a) than during JJA (Figure 9b) in agreement with the elevated mixing ratios in the marine boundary layer.

In addition to the mixing ratios averaged over two boxes, we show the spatial distribution of seasonally averaged bromoform mixing ratios at ~~17 km~~the cold point tropopause for the whole domain ~~as a 5-day snapshot~~(90° E–165° E, 10° S–45° N) (Figure 10) based on the ~~bottom-up Ziska emissions only (~~Ziska2013 and Ziska2013~~ Tropics), and emissions estimates taking anthropogenic sources into account (Ziska2013 Mixed).~~+MODERATE emissions. During DJF (Figure 10~~, panel~~ a and c), there is a clear anthropogenic signal over the Bay of Bengal, across the equator towards Indonesia. Mixing ratios for the Ziska2013~~ Mixed~~+MODERATE run are 0.~~19~~22±0.07 ppt averaged over the area of 90 % highest mixing ratios and 0.~~16~~18±0.05 ppt for Ziska2013~~ Tropics, corresponding to 0.03~~, which implies that 0.04 ppt ~~being~~is of anthropogenic origin (Table S1). Again, the ~~stronger~~strong advective transport in the boundary layer during DJF bringing higher bromoform abundances from the subtropics into the tropics plays an important role here. ~~As a result more bromoform is picked up by convection and transported into the UTLS during DJF than during JJA. Bromoform mixing ratios are slightly smaller during JJA, with 0.17 ppt and 0.15 ppt based on the Ziska2013 Mixed and Ziska2013 Tropics emissions, respectively (Table S1). Here, more anthropogenic bromoform stays in the northern hemisphere and convection is confined to few areas in the Bay of Bengal and Thailand (Figure 10, panel b and d). Although over 90 % of anthropogenic bromoform is outgassed north of 20° N, we find that these emissions contribute 0.02–0.03 ppt to the stratospheric bromine budget which is an increase of 14–19 % in the MODERATE scenario compared to the Ziska2013 climatology.~~Some fraction of the advected bromoform is picked up by tropical deep convection and transported into the UTLS and up the cold point. As the latter represents the stratospheric injection level, the interaction of boundary layer advection and local convection over the Indian Ocean and Maritime Continent results in an efficient transport pathway for anthropogenic bromoform from industrial sources in East Asia to the stratosphere.

During JJA (Figure 10b and d), mean bromoform mixing ratios averaged over the area of 90 % highest mixing ratios are slightly smaller, with 0.20±0.06 ppt and 0.15±0.05 ppt based on the Ziska2013+MODERATE and Ziska2013 emissions, respectively (Table S1). During the Asian summer monsoon, the region of main upward transport of VSLS lies at about 20°N over the Indian Ocean so that the main stratospheric injection region of VSLSs shifts to the Bay of Bengal and northern India (Fiehn et al., 2018b). However, most of the boundary layer bromoform from anthropogenic sources stays in the northern hemisphere around the coastline of China and over the West Pacific thus decoupled from the monsoon convection.

While over 90 % of anthropogenic bromoform is outgassed north of 20° N, our simulations show that the additional anthropogenic emissions in the MODERATE scenario contribute on average 0.05 ppt $CHBr_3$ during JJA to 0.04 ppt $CHBr_3$ during DJF to the stratospheric bromine budget at the UTLS (Table S1). This is an increase of 22-32 % compared to the Ziska2013 mixing ratios of 0.15 ppt and 0.18 ppt $CHBr_3$ during JJA and DJF, respectively.

5 Comparison with observations

5.1 Bromoform measurements in the ocean

Observations of bromoform in the surface ocean and atmosphere from East and Southeast Asia can help to determine which scenario (LOW, MODERATE, HIGH) offers the best fit for simulating anthropogenic bromoform in this region. Recent measurement campaigns show elevated bromoform concentrations in the coastal waters of the East China and Yellow Seas (He et al., 2013a, 2013b; Yang et al., 2014, Yang et al., 2015). Average values of 6–13 pmol L^{-1} were measured in the Yellow and East China Seas during boreal spring and summer (Yang et al., 2014; Yang et al., 2015), and ~~of~~ 17 pmol L^{-1} were measured in boreal winter (He et al., 2013b). Particularly high concentrations were detected by He et al. (2013a) during spring in the East China Sea with a mean of ~~—~~134 pmol L^{-1}. Highest bromoform concentration over 34~~-~~ pmol~~-~~ L^{-1} (He et al., 2013b) and over 200 pmol L^{-1} (He et al. 2013a) were observed near the estuaries of the Yangtse River, which the authors attributed to anthropogenic activities including coastal water treatment in the Shanghai region. Our simulations also show mean surface concentrations around Shanghai of 14–71 pmol L^{-1} (LOW to HIGH), in the range of the observations by He et al. (2013a).

Measurements in the South China and Sulu Seas (Fuhlbrügge et al., 2016) show a high variability of bromoform in the surface seawater with average concentrations of 19.9 pmol L^{-1}. Highest values of up to 136.9 pmol L^{-1} are found close to the Malaysian Peninsula and especially in the Singapore Strait suggesting industrial contributions. Maximum anthropogenic bromoform from our simulations in the Singapore Strait ranges from 36–178 (LOW to HIGH), in good agreement with maximum values reported by Fuhlbrügge et al., (2016).

Average anthropogenic bromoform concentrations for the three scenarios are around 23–113 pmol L^{-1} (averaged over the region of the 90 % highest values, Table 2) and are larger than the observational average values. The larger model values might be due to the fact that the cooling water effluents do not distribute far into the marginal seas but stay near the coast as observed by Yang (2001) and confirmed by our simulations. Our simulated anthropogenic bromoform concentrations stay usually within 100 km of the coast, the averaged observational values, however, include also measurements that are up to 200 km away from the coastline and can therefore be expected to be lower. While observational mean values are slightly lower than ~~the~~our model results, maximum values found close to the coast line show very good agreement with the model results.

5.2 Bromoform measurements in the marine boundary layer

~~Atmospheric mixing ratios are 0.9 ppt and 0.3 ppt in the subtropical East China Sea~~An extensive study of atmospheric measurements over South Korea and adjacent seas was performed in spring (May and June) 2016 from the Korea–United Sates Air Quality Study (KORUS-AQ; https://www-air.larc.nasa.gov/missions/korus-aq/). The aircraft measurements of various VSLSs including bromoform were repeatedly taken between 0 and 12 km in the region between 30° N-40° N and 120° E-145° E coinciding with our subtropical box discussed earlier (Figure S2). The data used here, is based on the 60 second merged dataset from all flight sections. In the campaign region around South Korea, an average bromoform atmospheric mixing ratio from all sections of 2.5±1.4 ppt was measured in the lower 100 m (Figure 8). In comparison, our simulations for the Ziska2013+MODERATE scenario show an average mixing ratio of 3.8±1.4 ppt in the lowest 100 m in the subtropical box during JJA. The simulations based on Ziska2013 give a bromoform mixing ratio of only 0.3±0.1

ppt for the same altitude range demonstrating that the additional anthropogenic bromoform sources results in a much better agreement with the observations in the marine boundary layer around South Korea.

Above the boundary layer, mixing ratios from KORUS-AQ rapidly decline to 0.5-0.7 ppt in the 3-9 km altitude range (Figure 8). Here, the Ziska2013+MODERATE simulation suggest seasonal mean mixing ratios between 0.4-0.7 ppt, which fit very well to the KORUS-AQ data. Simulations based on Ziska2013 suggest 0.2 ppt bromoform in this region clearly underestimating the observations (Figure 8). Between 9 and 12 km, the observed bromoform values drop sharply to values around 0.2±0.08 ppt suggesting that the airplane probed air masses above the convective outflow. The smooth seasonal mean profiles from the two simulations do not show such sharp decrease of values and in consequence the lower Ziska2013 results agree better with the observations in the region 9-12 km. In general, the comparison with the KORUS-AQ data shows that simulations agree quite well the observations in the middle troposphere when anthropogenic emissions from cooling water treatment in East Asia are included based on the MODERATE scenario.

In the subtropical East China Sea, surface measurements are available and atmospheric mixing ratios of 0.9 ppt and 0.3 ppt were found during boreal winter and summer, respectively (Yokouchi et al., 2017). Our simulations in the East China Sea suggest anthropogenic bromoform contributions of 1.7–5.1 ppt near Shanghai, being on the upper side of the observations. Nadzir et al. (2014) observed relatively high values in the South China Sea (1.5 ppt) and the Strait of Malacca (3.7 ppt) during boreal summer. Our simulations show average mixing ratios of 0.5–1.8 ppt at the surface (LOW to MODERATE) near the Pearl River Delta in the South China Sea, in good agreement with Nadzir et al. (2014). In the Strait of Malacca, our simulations suggest 0.2–0.7 ppt (LOW to MODERATE), which is lower than the observations.

Further south in the South China and Sulu Seas, Fuhlbrügge et al. (2016) measured atmospheric bromoform mixing ratios of 2 ppt during November. Near Singapore, the authors reported 3.4 ppt consistent with the high oceanic concentrations observed in the same region. Our simulations result in peak bromoform mixing ratios around Singapore during DJF of up to 1.7 and 5.3 ppt for the LOW and MODERATE scenario, respectively, in good agreement with Fuhlbrügge et al. (2016). Especially the high atmospheric bromoform mixing ratios found near Singapore and the Pearl River Delta can be associated with anthropogenic activity.

The HIGH scenario shows average mixing ratios, which are in general too high for the whole domain. Thus, it is not likely that cooling water treatment produces anthropogenic bromoform with average concentrations of 100 µg L^{-1}. Nevertheless, such concentrations can occur at some locations and produce extremely high bromoform abundances near the coast of industrial regions, as confirmed by the observations presented here.

6 Discussion and conclusion

We ~~find~~predict that there is a strong anthropogenic source of bromoform along the coast of East Asia with particular large contributions north of 20° N from the East China, Yellow and Japan Seas. This anthropogenic source results from local cooling water treatment in power plants and leads to extremely high annual mean air-sea flux rates of 3.1–9.1 nmol m^{-2} h^{-1} in coastal waters in East Asia. ~~Atmospheric~~Simulations of atmospheric bromoform originating from industrial sources ~~accumulates~~show an accumulation in the marine boundary layer and result in mean bromoform mixing ratios of ~~up to 5–14~~0.4-1.3 ppt. ~~It shows~~ The simulations show a strong seasonal variability with ~~the 'cloud of~~ high

bromoform ~~abundances'~~abundances being transported into the mid-latitudes during boreal summer and ~~to~~into the tropics during boreal winter. In comparison, the bottom-up inventory by Ziska2013 shows much lower concentrations along the coast of East Asia, but higher mean sea surface concentrations in Southeast Asia. Our predictions are based on assuming initial bromoform concentrations in chemically treated cooling water from power plants. These concentrations depend on many different factors and observational studies provide a range of 8–290 µg $CHBr_3$ L^{-1}. We take the large range of possible bromoform concentrations into account by analysing three different scenarios that assume LOW, MODERATE and HIGH bromoform concentrations in undiluted cooling water.

~~In comparison,~~

We evaluate our predictions by comparing the ~~bottom-up inventory by Ziska2013 shows much lower values along~~ model results to available measurement data in the ~~coast of East Asia, but higher mean sea surface concentrations in Southeast Asia.~~ ocean and atmosphere.

Comparisons with some individual campaigns suggest that our averaged anthropogenic values ~~are higher than~~based on the MODERATE scenario agree very well with the observations. For other campaigns, the model results overestimate campaign-averaged ~~estimates~~bromoform concentrations in surface water and air. ~~This~~The latter discrepancy of the mean values is possibly related to the regional extent of the specific campaign data, given the very sharp bromoform gradients from the coast into the open ocean waters. Maximum values found in surface water and air during the campaigns, however, agree very well with our estimates based on industrial sources for the LOW and MODERATE scenarios. ~~Therefore, anthropogenic activities can be expected to cause extremely high bromoform concentrations and air-sea fluxes in locations relatively close to the source. Estimating the exact regional extent and distribution will require further targeted measurement campaigns.~~ in nearly all cases.

~~Concentrations of bromoform in chemically treated cooling water from power plants depend on many different factors and observational studies provide a range of 8–290 µg L^{-1}.~~ Based on the comparison of our model results to observations, we expect initial bromoform concentrations from cooling water effluents of coastal power plants to be between 20–60 µg L^{-1} given by the two scenarios LOW and MODERATE. In consequence, oceanic and atmospheric abundances based on the HIGH scenario are ~~most~~ likely too high in the majority of cases and only results based on the two lower scenarios are presented in this summary. As the LOW and MODERATE scenarios also suggest relatively high bromoform concentrations and air-sea fluxes when compared to existing climatologies, anthropogenic activities can be expected to significantly increase regional bromoform abundances. However, estimating the exact regional extent and distribution of additional anthropogenic bromine sources will require further targeted measurement campaigns, as demonstrated by the evaluations.

~~Our results indicate that cooling water from power plants provide a substantial and growing source of anthropogenic bromoform. Depending on the scenario, 100 to 300 Mmol bromine (Br) a^{-1} are released into the atmosphere from the coastal regions in Southeast and East Asia (LOW to MODERATE) in form of anthropogenic bromoform. The largest part, about 90 %, are emitted in coastal regions north of 20° N. In comparison, Ziska2013 estimates bromoform emissions of 34 Mmol Br a^{-1} for the same region north of 20° N. The high emissions of industrially produced bromoform in East Asia are most likely underrepresented in existing bottom-up estimates by Ziska et al. (2013) and Stemmler et al. (2015) and might explain some of their differences when compared to top-down estimates.~~

~~If bromoform is entrained into the stratosphere, it will contribute to ozone depletion driven by catalytic cycles. Atmospheric transport simulations show that during boreal winter strong northeasterly winds advect~~

Our predictions and their evaluation indicate that cooling water from power plants provide a substantial and growing source of anthropogenic bromoform. Depending on the scenario, 100 to 300 Mmol Br a^{-1} are released into the atmosphere from the coastal regions in Southeast and East Asia (LOW to MODERATE) in the form of anthropogenic bromoform. The largest part, about 90 %, are emitted in coastal regions north of 20° N. In comparison, the Ziska2013 climatology estimates bromoform emissions of 34 Mmol Br a^{-1} for the same region north of 20° N. The high emissions of industrially produced bromoform in East Asia are most likely underrepresented in existing bottom-up estimates by Ziska2013 and Stemmler et al. (2015) in these regions and might explain some of their differences when compared to top-down estimates.

If bromoform is entrained into the stratosphere, it will contribute to ozone depletion driven by catalytic cycles. Atmospheric transport simulations show that during boreal winter strong northeasterly winds transport the anthropogenic bromoform from the East China Sea towards the tropics. Here it can be taken up by deep convection and reach the ~~UTLS region.~~cold point tropopause thus being entrained into the stratosphere. On average 0.~~19~~22 ppt of bromoform are entrained above ~~17 km, the approximate altitude of~~ the cold point~~,~~ based on ~~climatological~~natural and additional anthropogenic emissions~~.~~ (from the MODERATE scenario). For the same configuration during boreal summer, the large amounts of anthropogenic bromoform emitted over the East China Sea do not reach the tropics, resulting in average mixing ratios of 0.~~17~~20 ppt at ~~17 km.~~the cold point level. In comparison, the mixing ratios based on the bottom-up Ziska2013 ~~emissions~~climatology are on average smaller~~, but spread out over a larger area thus resulting in similar total emissions, and only slightly less bromoform (~~ with values of 0.15–0.~~16~~18 ppt~~) is transported into the UTLS region during both seasons~~. In summary, the high anthropogenic bromoform emissions in the East China, Yellow and Japan Seas do not efficiently reach the stratosphere, ~~unless the anthropogenic bromoform~~except for some fraction that is advected with the Asian winter monsoon into the tropics, in which case it can lead to an increased entrainment of ~~14–19 % over this area.~~22-32 % over this area. Comparison with measurements up to 12 km in the subtropics show that the simulated bromoform agrees very well with the observations if additional anthropogenic sources from the MODERATE scenario are included. The good agreement suggests that anthropogenic bromoform as simulated in the MODERATE scenario can lead to an additional stratospheric entrainment of 0.04-0.05 ppt $CHBr_3$, which corresponds to a bromine input 0.12-0.15 ppt Br.

~~Ashfold et al., (2015) and Oram et al. (2017) showed for chlorine-based VSLSs that pollution from East Asia can be efficiently entrained into the upper troposphere during DJF. Chlorine-based VSLSs concentrations of 50–250 ppt were measured at 10–12 km height (Oram et al., 2017). While chlorine-based species are still the largest contributor to ODSs, an increase in anthropogenic emission of brominated VSLSs is nevertheless of concern since bromine is about 60 times more effective in destroying ozone than chlorine (Sinnhuber et al., 2009). In particular during the northeasterly winter monsoon, many anthropogenic VSLSs from industrial emissions in East Asia can be entrained into the UTLS above the tropics.~~

This study focuses on source gas entrainment into the stratosphere and does not take into account additional product gas entrainment resulting from anthropogenic bromoform sources. Most observational and modelling studies estimate the total stratospheric bromine contribution to be split half and half into source and product gas contributions (Engel and Rigby, 2018 and references therein). Therefore, we estimate the total stratospheric bromine contribution in form of both, source gas and product gases, from the East and Southeast Asia anthropogenic bromoform sources to be around 0.24–0.30 ppt Br. Compared to a total stratospheric bromine contribution from all VSLSs of about 3–7 ppt Br (Engel and Rigby, 2018), the anthropogenic input estimated in this study provides only a minor contribution.

Our analyses suggests that anthropogenic bromoform accumulates in the boundary layer increasing the bromine budget in East and Southeast Asia by 85-254 % compared to the Ziska2013 climatology. This input can be expected to impact tropospheric bromine budgets and ozone chemistry. While we have not analysed these aspect in our study, it should be investigated in follow-on projects. Highest uncertainties in the estimates presented here, arise from the highly variable bromoform amounts found in chemically treated cooling water. Since there are very few and no recent measurements from power plants in East and Southeast Asia available, the chosen scenarios aim to give a range of environmental concentrations of anthropogenic bromoform. Additional uncertainties can arise from oceanic and atmospheric transport simulations and the parameterisation of air-sea fluxes. Since bromoform is emitted into the atmosphere on very short timescales, uncertainties arising from oceanic transport simulations are small compared to scenario uncertainties. Similarly, given the high saturation of anthropogenic bromoform in surface water, the sensitivity of our results to the air-sea flux parameterisation can be expected to be small. Atmospheric modelling can introduce additional uncertainties, especially regarding the contribution of anthropogenic sources to stratospheric bromine. VSLS FLEXPART simulations have been evaluated in numerous previous studies and shown in most cases good agreement with upper air observations (e.g., Fuhlbruegge et al., 2016; Tegtmeier et al., 2020a). In summary, uncertainties of our results are dominated by uncertainties of the bromoform concentrations in undiluted cooling water. We have successfully reduced these uncertainties by nearly a factor of two based on comparing our predictions to available observations.

Our study suggests that current bottom-up bromoform climatologies miss the large anthropogenic sources. Further measurement campaigns in coastal, shelf and open ocean regions are required to estimate the regional extent and distribution of anthropogenic bromine sources. Detailed information about the water volumes used for each power plant, as well as the disinfection technique can also help to better localise regions of high DBP discharge.

While this study exclusively looks at the DBPs from cooling water treatment in power plants, other anthropogenic sources also contribute to local and global emissions of organic bromine, like desalination plants or ballast water from commercial ships, which produce DBPs in chemically treated water. Desalination is mostly done ~~at~~in the Arabian Peninsula ~~(Jones et al., 2019)~~(Jones et al., 2019), and ballast water volumes with 3–5 billion m^3 a^{-1} (Tamelander et al., 2010) are globally negligible compared to cooling water volumes from coastal power plants but can locally increase DBP discharge (Maas et al., 2019). ~~For~~However, for assessing the total impact of anthropogenic VSLSs on a local industrial area, such as Singapore or the Pearl River Delta region, all sources of chemical water treatment need to be taken into account. Comparison of these two regions show that the bromoform from cooling water dominates above ballast water, leading to emissions of around 990 pmol m^{-2} h^{-1} in Singapore and 6430 pmol m^{-2} h^{-1} in the Pearl River Delta

(MODERATE, Figure 5b), while bromoform from ballast water is expected to cause 900 and 2000 pmol m^{-2} h^{-1} for these two areas (Maas et al., 2019)~~.~~, respectively. Direct outgassing during treatment of circulating water through the cooling towers into the atmosphere can also occur, which has not been quantified yet and is therefore not considered here. Overall, cooling water from power plants can be assumed to be the largest global source of anthropogenic bromoform as it has by far the largest water volumes and is present in all regions and climate zones. The contribution of bromoform from anthropogenic sources should be considered as relevant next to natural sources for future estimates of the ~~atmospheric~~global bromine ~~input~~fluxes.

Acknowledgements

The OGCM model data used for this study were kindly provided through collaboration within the DRAKKAR framework by the National Oceanographic Centre, Southampton, UK. We especially thank Andrew C. Coward, Adrian L. New and colleagues for making the data available. The OGCM and trajectory simulations were performed in the High-Performance Computing Centre at the Christian-Albrechts-Universität zu Kiel. Furthermore, we wish to thank Bruno Blanke and Nicolas Grima for realising and providing the Lagrangian software ARIANE; and Siren Rühs for helping with the set-up of the ARIANE environment. And many thanks to Donald Blake for providing the KORUS-AQ bromoform measurements. This study was carried out within the Emmy-Noether group AVeSH (A new threat to the stratospheric ozone layer from Anthropogenic Very Short-lived Halocarbons) funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – TE 1134/1. JVD acknowledges the Helmholtz-Gemeinschaft and the GEOMAR Helmholtz Centre for Ocean Research Kiel (grant IV014/GH018).

Author contribution

JM wrote the manuscript, performed the Lagrangian ocean simulations and created the output. YJ performed the Lagrangian simulations in the atmosphere. ST developed the research question and guided the research process. BQ developed the research question and gave input on the observational data. AB and JVD provided the NEMO-ORCA model data and gave input on the ocean simulations. All authors took part in the process of the manuscript preparation.

The authors declare that they have no conflict of interest.

Data availability

Data from the ARIANE and FLEXPART simulations are available upon request from the corresponding author. The KORUS-AQ data are available from https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq?MERGE=1.

References

Allonier, A.-S., Khalanski, M., Camel, V. and Bermond, A.: Characterization of Chlorination By-products in Cooling Effluents of Coastal Nuclear Power Stations, Mar. Pollut. Bull., 38(12), 1232–1241, doi:10.1016/S0025-326X(99)00168-X, 1999.

Aschmann, J. and Sinnhuber, B.-M.: Contribution of very short-lived substances to stratospheric bromine loading: uncertainties and constraints, Atmos. Chem. Phys., 13(3), 1203–1219, doi:10.5194/acp-13-1203-2013, 2013.

Aschmann, J., Sinnhuber, B.-M., Atlas, E. L. and Schauffler, S. M.: Modeling the transport of very short-lived substances into the tropical upper troposphere and lower stratosphere, Atmos. Chem. Phys., 9(23), 9237–9247, doi:10.5194/acp-9-9237-2009, 2009.

Ashfold, M. J., Pyle, J. A., Robinson, A. D., Meneguz, E., Nadzir, M. S. M., Phang, S. M., Samah, A. A., Ung, H. E., Peng, L. K., Yong, S. E. and Harris, N. R. P.: Rapid transport of East Asian pollution to the deep tropics, Atmos. Chem. Phys., 15, 3565–3573, doi:10.5194/acp-15-3565-2015, 2015.

Blanke, B., Arhan, M., Madec, G. and Roche, S.: Warm Water Paths in the Equatorial Atlantic as Diagnosed with a General Circulation Model, J. Phys. Oceanogr., 29(11), 2753–2768, doi:10.1175/1520-0485(1999)029<2753:WWPITE>2.0.CO;2, 1999.

Boudjellaba, D., Dron, J., Revenko, G., Démelas, C. and Boudenne, J.-L.: Chlorination by-product concentration levels in seawater and fish of an industrialised bay (Gulf of Fos, France) exposed to multiple chlorinated effluents, Sci. Total Environ., 541, 391–399, doi:10.1016/j.scitotenv.2015.09.046, 2016.

Butler, J. H., King, D. B., Lobert, J. M., Montzka, S. A., Yvon-Lewis, S. A., Hall, B. D., Warwick, N. J., Mondeel, D. J., Aydin, M. and Elkins, J. W.: Oceanic distributions and emissions of short-lived halocarbons, Global Biogeochem. Cycles, 21(1), GB1023, doi:10.1029/2006GB002732, 2007.

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N. and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Q. J. R. Meteorol. Soc., 137(656), 553–597, doi:10.1002/qj.828, 2011.

Dussin, R., Barnier, B., Brodeau, L. and Molines, J. M.: The Making Of the DRAKKAR FORCING SET DFS5, DRAKKAR/MyOcean Rep. 01-04-16, 2016(April), 1–34, 2016.

Engel, A., Rigby, M. (Lead A., Burkholder, J. B., Fernandez, R. P., Froidevaux, L., Hall, B. D., Hossaini, R., Saito, T., Vollmer, M. K. and Yao, B.: Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1, in Scientific Assessment of Ozone Depletion: 2018, Global Ozone Research and Monitoring Project – Report No. 58., 2018.

Fiehn, A., Quack, B., Hepach, H., Fuhlbrügge, S., Tegtmeier, S., Toohey, M., Atlas, E. and Krüger, K.: Delivery of halogenated very short-lived substances from the west Indian Ocean to the stratosphere during the Asian summer monsoon, Atmos. Chem. Phys., 17(11), 6723–6741, doi:10.5194/acp-17-6723-2017, 2017.

Fiehn, A., Quack, B., Stemmler, I., Ziska, F. and Krüger, K.: Importance of seasonally resolved oceanic emissions for bromoform delivery from the tropical Indian Ocean and west Pacific to the stratosphere, Atmos. Chem. Phys., 18(16), 11973–11990, doi:10.5194/acp-18-11973-2018, ~~2018~~2018a.

Fiehn, A., Quack, B., Marandino, C. A. and Krüger, K.: Transport Variability of Very Short Lived Substances From the West Indian Ocean to the Stratosphere, J. Geophys. Res. Atmos., 123(10), 5720–5738, doi:10.1029/2017JD027563, 2018b.

Fogelqvist, E. and Krysell, M.: Naturally and anthropogenically produced bromoform in the Kattegatt, a semi-enclosed oceanic basin, J. Atmos. Chem., 13(4), 315–324, doi:10.1007/BF00057749, 1991.

Forster, C., Stohl, A. and Seibert, P.: Parameterization of convective transport in a Lagrangian particle dispersion model and its

evaluation, J. Appl. Meteorol. Climatol., 46(4), 403–422, doi:10.1175/JAM2470.1, 2007.

Fuhlbrügge, S., Quack, B., Tegtmeier, S., Atlas, E., Hepach, H., Shi, Q., Raimund, S. and Krüger, K.: The contribution of oceanic halocarbons to marine and free tropospheric air over the tropical West Pacific, Atmos. Chem. Phys., 16(12), 7569–7585, doi:10.5194/acp-16-7569-2016, 2016.

He, Z., Yang, G.-P., Lu, X.-L. and Zhang, H.-H.: Distributions and sea-to-air fluxes of chloroform, trichloroethylene, tetrachloroethylene, chlorodibromomethane and bromoform in the Yellow Sea and the East China Sea during spring, Environ. Pollut., 177, 28–37, doi:10.1016/j.envpol.2013.02.008, 2013a.

He, Z., Yang, G.-P. and Lu, X.-L.: Distributions and sea-to-air fluxes of volatile halocarbons in the East China Sea in early winter, Chemosphere, 90(2), 747–757, doi:10.1016/j.chemosphere.2012.09.067, 2013b.

Helz, G. R., Sugam, R. and Sigleo, A. C.: Chemical modifications of estuarine water by a power plant using continuous chlorination, Environ. Sci. Technol., 18(3), 192–199, doi:10.1021/es00121a011, 1984.

Hossaini, R., Mantle, H., Chipperfield, M. P., Montzka, S. A., Hamer, P., Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., Sala, S., Engel, A., Bönisch, H., Keber, T., Oram, D., Mills, G., Ordóñez, C., Saiz-Lopez, A., Warwick, N., Liang, Q., Feng, W., Moore, F., Miller, B. R., Marécal, V., Richards, N. A. D., Dorf, M. and Pfeilsticker, K.: Evaluating global emission inventories of biogenic bromocarbons, Atmos. Chem. Phys., 13(23), 11819–11838, doi:10.5194/acp-13-11819-2013, 2013.

Hossaini, R., Chipperfield, M. P., Montzka, S. A., Rap, A., Dhomse, S. and Feng, W.: Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone, Nat. Geosci., 8(3), 186–190, doi:10.1038/ngeo2363, 2015.

Hossaini, R., Patra, P. K., Leeson, A. A., Krysztofiak, G., Abraham, N. L., Andrews, S. J., Archibald, A. T., Aschmann, J., Atlas, E. L., Belikov, D. A., Bönisch, H., Carpenter, L. J., Dhomse, S., Dorf, M., Engel, A., Feng, W., Fuhlbrügge, S., Griffiths, P. T., Harris, N. R. P., Hommel, R., Keber, T., Krüger, K., Lennartz, S. T., Maksyutov, S., Mantle, H., Mills, G. P., Miller, B., Montzka, S. A., Moore, F., Navarro, M. A., Oram, D. E., Pfeilsticker, K., Pyle, J. A., Quack, B., Robinson, A. D., Saikawa, E., Saiz-Lopez, A., Sala, S., Sinnhuber, B. M., Taguchi, S., Tegtmeier, S., Lidster, R. T., Wilson, C. and Ziska, F.: A multi-model intercomparison of halogenated very short-lived substances (TransCom-VSLS): Linking oceanic emissions and tropospheric transport for a reconciled estimate of the stratospheric source gas injection of bromine, Atmos. Chem. Phys., 16(14), 9163–9187, doi:10.5194/acp-16-9163-2016, 2016.

IEA: Key world energy statistics 2005, Int. Energy Agency, 2005.

IEA: Key world energy statistics 2018, Int. Energy Agency, 2018.

Jenner, H. A., Taylor, C. J. L., van Donk, M. and Khalanski, M.: Chlorination by-products in chlorinated cooling water of some European coastal power stations, Mar. Environ. Res., 43(4), 279–293, doi:10.1016/S0141-1136(96)00091-8, 1997.

Jia, Y., Tegtmeier, S., Atlas, E. and Quack, B.: How marine emissions of bromoform impact the remote atmosphere, Atmos. Chem. Phys., 19(17), 11089–11103, doi:10.5194/acp-19-11089-2019, 2019.

Joint Research Council: Integrated Pollution Prevention and Control (IPPC) Reference Document on the application of Best Available Techniques to Industrial Cooling Systems, Eur. Comm., (December), 335, 2001.

Jones, E., Qadir, M., van Vliet, M. T. H. Van,, Smakhtin, V. and Kang, S.: Science of the Total Environment The state of desalination and brine production:, A global outlook, Sci. Total Environ., 657, 1343–1356, doi:10.1016/j.scitotenv.2018.12.076., 2019.

Khalanski, M. and Jenner, H. A.: Chlorination Chemistry and Ecotoxicology of the Marine Cooling Water Systems in: Operational and Environmental Consequences of Large Industrial Cooling Water Systems, Ch. 9, Springer, 2012.

Liang, Q., Stolarski, R. S., Kawa, S. R., Nielsen, J. E., Douglass, A. R., Rodriguez, J. M., Blake, D. R., Atlas, E. L. and Ott, L. E.: Finding the missing stratospheric Br y : a global modeling study of CHBr 3 and CH 2 Br 2, Atmos. Chem. Phys., 10(5), 2269–2286, doi:10.5194/acp-10-2269-2010, 2010.

Liu, Z., Wang, X., Luo, Z., Huo, M., Wu, J., Huo, H. and Yang, W.: Removing of Disinfection By-Product Precursors from Surface Water by Using Magnetic Graphene Oxide, edited by Y. K. Mishra, PLoS One, 10(12), e0143819, doi:10.1371/journal.pone.0143819, 2015.

Maas, J., Tegtmeier, S., Quack, B., Biastoch, A., Durgadoo, J. V., Rühs, S., Gollasch, S. and David, M.: Simulating the spread of disinfection by-products and anthropogenic bromoform emissions from ballast water discharge in Southeast Asia, Ocean Sci., 15(4), 891–904, doi:10.5194/os-15-891-2019, 2019.

Madec, G. and the N. T.: NEMO ocean engine, Note du Pôle modélisation l'Institut Pierre-Simon Laplace No 27, (27), 2008.

Marandino, C. A., Tegtmeier, S., Krüger, K., Zindler, C., Atlas, E. L., Moore, F., and Bange, H. W.: Dimethylsulphide (DMS) emissions from the western Pacific Ocean: a potential marine source for stratospheric sulphur?, Atmos. Chem. Phys., 13, 8427–8437, https://doi.org/10.5194/acp-13-8427-2013, 2013.

Moat, B. I., Josey, S. A., Sinha, B., Blaker, A. T., Smeed, D. A., McCarthy, G. D., Johns, W. E., Hirschi, J. J. M., Frajka-Williams, E., Rayner, D., Duchez, A. and Coward, A. C.: Major variations in subtropical North Atlantic heat transport at short (5 day) timescales and their causes, J. Geophys. Res. Ocean., doi:10.1002/2016JC011660, 2016.

Montzka, S. a. and Reimann, S.: Ozone-Depleting Substances (ODSs) and Related Chemicals, Sci. Assess. Ozone Deplet. 2010, Chapter 1, 1–108, 2010.

~~Montzka, S. A., Dutton, G. S., Yu, P., Ray, E., Portmann, R. W., Daniel, J. S., Kuijpers, L., Hall, B. D., Mondeel, D., Siso, C., Nance, J. D., Rigby, M., Manning, A. J., Hu, L., Moore, F., Miller, B. R. and Elkins, J. W.: An unexpected and persistent increase in global emissions of ozone-depleting CFC-11, Nature, doi:10.1038/s41586-018-0106-2, 2018.~~

Nadzir, M. S. M., Phang, S. M., Abas, M. R., Abdul Rahman, N., Abu Samah, A., Sturges, W. T., Oram, D. E., Mills, G. P., Leedham, E. C., Pyle, J. A., Harris, N. R. P., Robinson, A. D., Ashfold, M. J., Mead, M. I., Latif, M. T., Khan, M. F., Amiruddin, A. M., Banan, N. and Hanafiah, M. M.: Bromocarbons in the tropical coastal and open ocean atmosphere during the 2009 Prime Expedition Scientific Cruise (PESC-09), Atmos. Chem. Phys., 14(15), 8137–8148, doi:10.5194/acp-14-8137-2014, 2014.

Nightingale, D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J. and Upstill-Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, Global Biogeochem. Cycles, 14(1), 373–387, 2000.

Oram, D. E., Ashfold, M. J., Laube, J. C., Gooch, L. J., Humphrey, S., Sturges, W. T., Leedham-Elvidge, E., Forster, G. L., Harris, N. R. P., Iqbal Mead, M., Samah, A. A., Phang, S. M., Ou-Yang, C. F., Lin, N. H., Wang, J. L., Baker, A. K., Brenninkmeijer, C. A. M. and Sherry, D.: A growing threat to the ozone layer from short-lived anthropogenic chlorocarbons, Atmos. Chem. Phys., 17(19), 11929–11941, doi:10.5194/acp-17-11929-2017, 2017.

Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Sousa Santos, G., Brasseur, G. and Saiz-Lopez, A.: Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources, Atmos. Chem. Phys., 12(3), 1423–1447, doi:10.5194/acp-12-1423-2012, 2012.

Padhi, R. K., Subramanian, S., Mohanty, A. K., Bramha, S. N., Prasad, M. V. R. R. and Satpathy, K. K.: Trihalomethanes in the Cooling Discharge of a Power Plant on Chlorination of Intake Seawater, Environ. Eng. Res., 17(S1), 57–62, doi:10.4491/eer.2012.17.S1.S57, 2012.

Quack, B. and Wallace, D. W. R.: Air-sea flux of bromoform: Controls, rates, and implications, Global Biogeochem. Cycles, 17(1), 1023, doi:10.1029/2002GB001890, 2003.

Rajamohan, R., Vinnitha, E., Venugopalan, V. P. and Narasimhan, S. V: Chlorination by-products and their discharge from the cooling water system of a coastal electric plant, Curr. Sci., 93(11), 1608–1612, 2007.

~~Rigby, M., Park, S., Saito, T., Western, L. M., Redington, A. L., Fang, X., Henne, S., Manning, A. J., Prinn, R. G., Dutton, G. S., Fraser, P. J., Ganesan, A. L., Hall, B. D., Harth, C. M., Kim, J., Kim, K. R., Krummel, P. B., Lee, T., Li, S., Liang, Q., Lunt, M. F.,~~

~~Montzka, S. A., Mühle, J., O'Doherty, S., Park, M. K., Reimann, S., Salameh, P. K., Simmonds, P., Tunnicliffe, R. L., Weiss, R. F., Yokouchi, Y. and Young, D.: Increase in CFC-11 emissions from eastern China based on atmospheric observations, Nature, 569(7757), 546–550, doi:10.1038/s41586-019-1193-4, 2019.~~

Saiz-Lopez, A. and von Glasow, R.: Reactive halogen chemistry in the troposphere, Chem. Soc. Rev., 41(19), 6448, doi:10.1039/c2cs35208g, 2012.

~~Sherry, D., McCulloch, A., Liang, Q., Reimann, S. and Newman, P. A.: Current sources of carbon tetrachloride (CCl 4) in our atmosphere, Environ. Res. Lett., 13(2), 024004, doi:10.1088/1748-9326/aa9c87, 2018.~~

Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., Jacob, D. J., Dix, B., Koenig, T. K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A. S. and Ordóñez, C.: Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem, Atmos. Chem. Phys., 16(18), 12239–12271, doi:10.5194/acp-16-12239-2016, 2016.

Sinnhuber, B.-M., Sheode, N., Sinnhuber, M., Chipperfield, M. P. and Feng, W.: The contribution of anthropogenic bromine emissions to past stratospheric ozone trends: a modelling study, Atmos. Chem. Phys., 9(8), 2863–2871, doi:10.5194/acp-9-2863-2009, 2009.

Stemmler, I., Hense, I. and Quack, B.: Marine sources of bromoform in the global open ocean – global patterns and emissions, Biogeosciences, 12(6), 1967–1981, doi:10.5194/bg-12-1967-2015, 2015.

Stohl, A. and Thomson, D. J.: A density correction for Lagrangian particle dispersion models, Boundary-Layer Meteorol., doi:10.1023/A:1001741110696, 1999.

Stohl, A., Forster, C., Frank, A., Seibert, P. and Wotawa, G.: Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, Atmos. Chem. Phys., 5(9), 2461–2474, doi:10.5194/acp-5-2461-2005, 2005.

Tamelander, J., Riddering, L., Haag, F. and Matheickal, J.: Guidelines for development of a national ballast water management strategy, GEF-UNDP-IMO Glob. London, UK IUCN, Gland. Switz., GloBallast(No. 18) [online] Available from: http://globallast.imo.org/wp-content/uploads/2014/11/Mono18_English.pdf, 2010.

Taylor, C. J. L.: The effects of biological fouling control at coastal and estuarine power stations, Mar. Pollut. Bull., 53(1–4), 30–48, doi:10.1016/j.marpolbul.2006.01.004, 2006.

Tegtmeier, S., Ziska, F., Pisso, I., Quack, B., Velders, G. J. M., Yang, X. and Krüger, K.: Oceanic bromoform emissions weighted by their ozone depletion potential, Atmos. Chem. Phys., 15(23), 13647–13663, doi:10.5194/acp-15-13647-2015, 2015.

Tegtmeier, S., Atlas, E., Quack, B., Ziska, F. and Krüger, K.: Variability and past long-term changes of brominated ~~VSLS~~very short-lived substances at the tropical tropopause, Atmos. Chem. Phys~~. Discuss., 1–44~~., 20(11), 7103–7123, doi:10.5194/acp-~~2019-490, 2019~~20-7103-2020, 2020a.

Tegtmeier, S., Anstey, J., Davis, S., Dragani, R., Harada, Y., Ivanciu, I., Pilch Kedzierski, R., Krüger, K., Legras, B., Long, C., Wang, J. S., Wargan, K., and Wright, J. S.: Temperature and tropopause characteristics from reanalyses data in the tropical tropopause layer, Atmos. Chem. Phys., 20, 753–770, https://doi.org/10.5194/acp-20-753-2020, 2020b.

The DRAKKAR Group: Eddy permitting ocean circulation hindcasts of past decades, CLIVAR Exch., 42, 8–10, 2007.

Waliser, D. E. and Gautier, C.: A satellite-derived climatology of the ITCZ, J. Clim., 6(11), 2162–2174, doi:10.1175/1520-0442(1993)006<2162:ASDCOT>2.0.CO;2, 1993.

Yang, B., Yang, G.-P., Lu, X.-L., Li, L. and He, Z.: Distributions and sources of volatile chlorocarbons and bromocarbons in the Yellow Sea and East China Sea, Mar. Pollut. Bull., 95(1), 491–502, doi:10.1016/j.marpolbul.2015.03.009, 2015.

Yang, G.-P., Yang, B., Lu, X.-L., Ding, H.-B. and He, Z.: Spatio-temporal variations of sea surface halocarbon concentrations and fluxes from southern Yellow Sea, Biogeochemistry, 121(2), 369–388, doi:10.1007/s10533-014-0007-x, 2014.

Yang, J. S.: Bromoform in the effluents of a nuclear power plant: A potential tracer of coastal water masses, Hydrobiologia, 464, 99–105, doi:10.1023/A:1013922731434, 2001.

Yokouchi, Y., Saito, T., Zeng, J., Mukai, H. and Montzka, S.: Seasonal variation of bromocarbons at Hateruma Island, Japan: implications for global sources, J. Atmos. Chem., 74(2), 171–185, doi:10.1007/s10874-016-9333-9, 2017.

Ziska, F., Quack, B., Abrahamsson, K., Archer, S. D., Atlas, E., Bell, T., Butler, J. H., Carpenter, L. J., Jones, C. E., Harris, N. R. P. P., Hepach, H., Heumann, K. G., Hughes, C., Kuss, J., Krüger, K., Liss, P., Moore, R. M., Orlikowska, A., Raimund, S., Reeves, C. E., Reifenhäuser, W., Robinson, A. D., Schall, C., Tanhua, T., Tegtmeier, S., Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S. and Yokouchi, Y.: Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide, Atmos. Chem. Phys., 13(17), 8915–8934, doi:10.5194/acp-13-8915-2013, 2013.

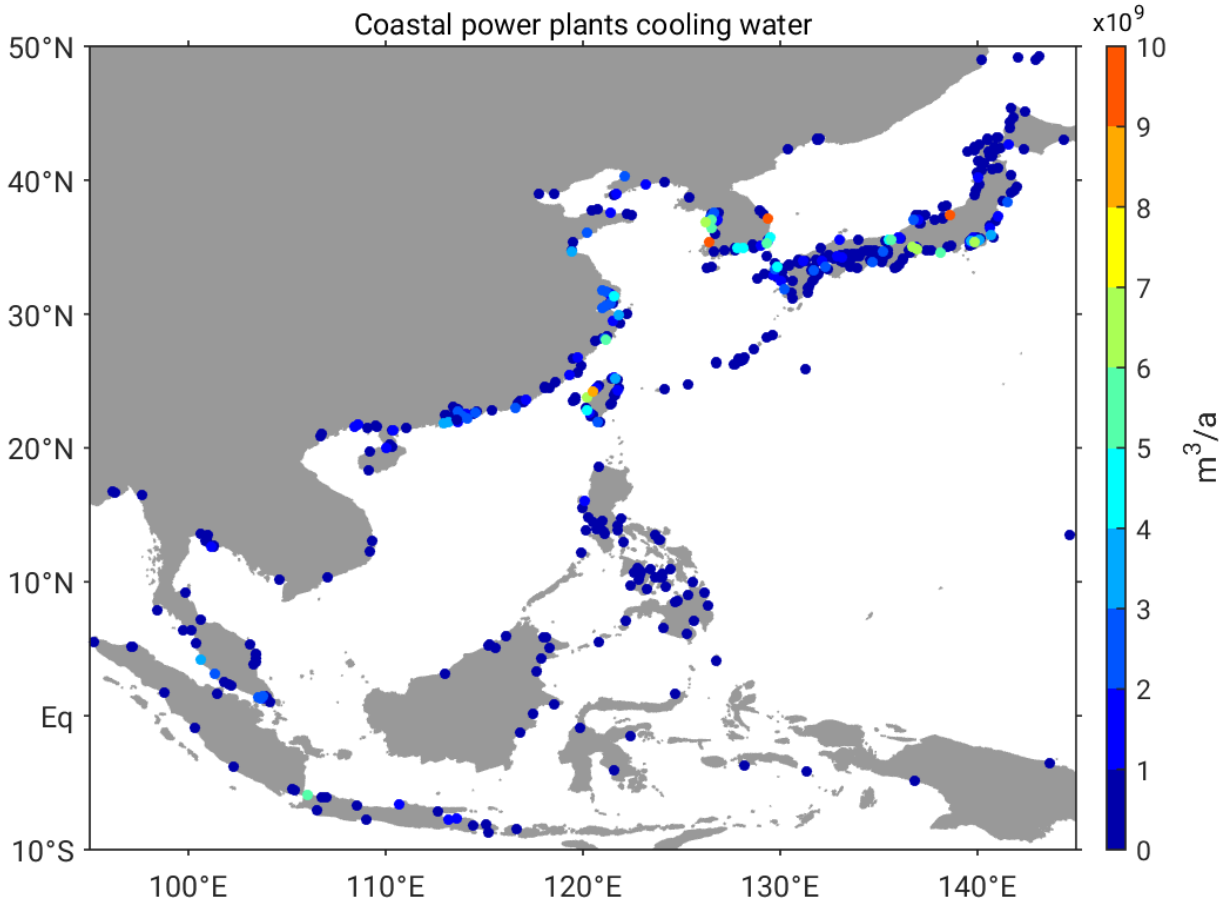


Figure 1: Location and annual cooling water volume [billion m^3 a^{-1}] of coastal power plants in East and Southeast Asia extracted from the enipedia-database and color-coded by the cooling water discharge.

Table 1: Bromoform concentrations measured in water samples from power plant cooling water and surrounding waters. Measurements in the power plant effluent can refer to both, samples of the undiluted water stream or sea water samples at the outlet.

Power plant effluent/ near outlet		Surroundings		Location	Reference
µg L^{-1}	nmol L^{-1}	µg L^{-1}	nmol L^{-1}		
90-100	356-396	1-20	4-79	Gothenburg, Sweden, Kattegatt	Fogelqvist, 1991
9-17	35-67	0.1-5	0.4-20	North Sea	Jenner, 1997
8-27	32-107	n/a	n/a	English Channel	Allonier, 1999
124	495	1-50	4-200	Youngkwang, South Korea, Yellow Sea	Yang, 2001
20-290	79-1147	0-54	0-214	Kalpakkam, India, Bay of Bengal	Rajamohan, 2007
12-41	47-162	n/a	n/a	Kalpakkam, India, Bay of Bengal	Padhi, 2012
19	75	0.5-2.2	2-9	Gulf of Fos, France, Mediterranean	Boudjellaba, 2016

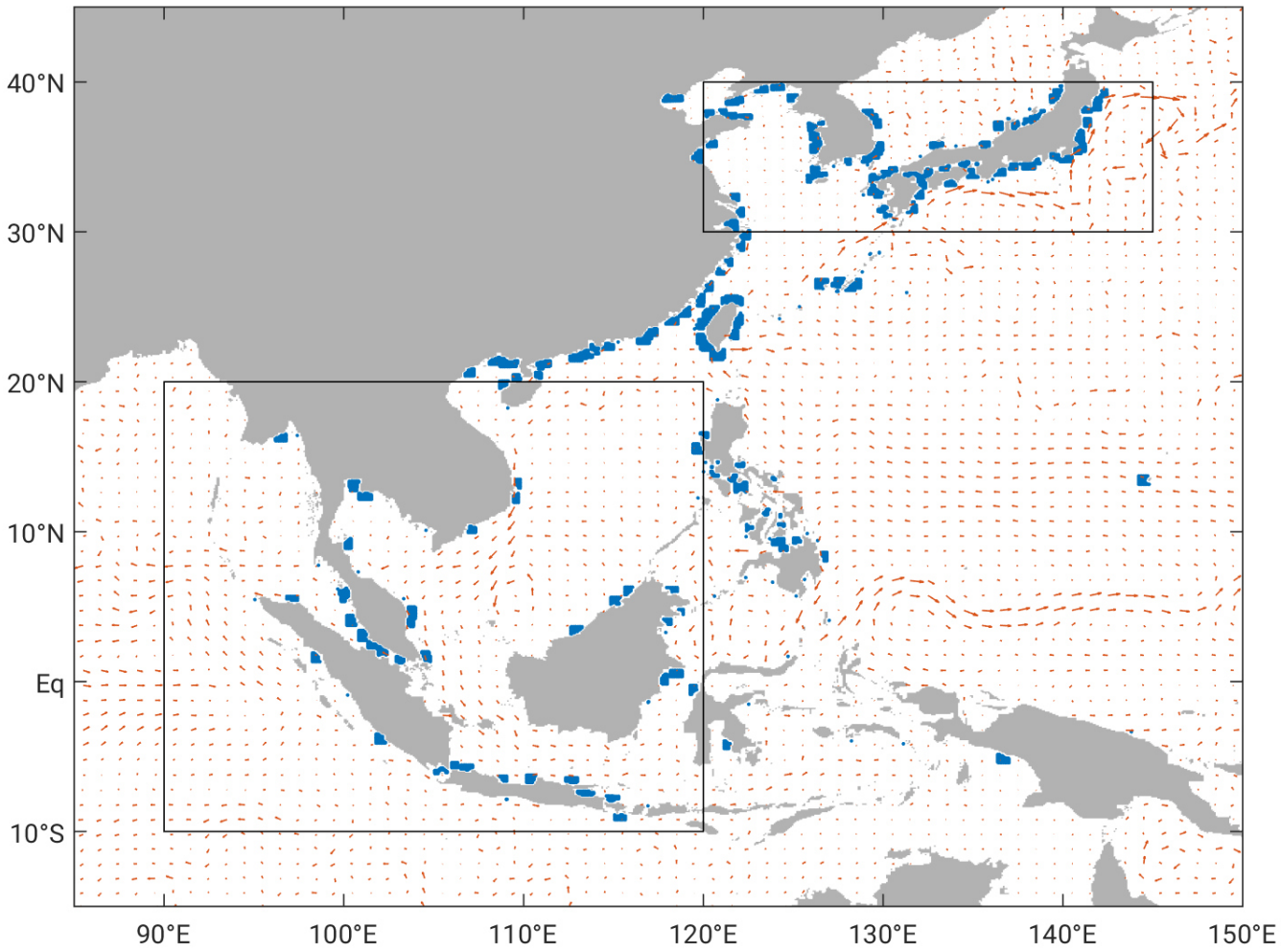


Figure 2: Initial position of particles in East and Southeast Asia (blue dots). NEMO-ORCA12 ocean currents from the initialisation time in January 2005 (red arrows); and the two boxes, which mark the region referred to as tropics and subtropics as described in section 2.3.

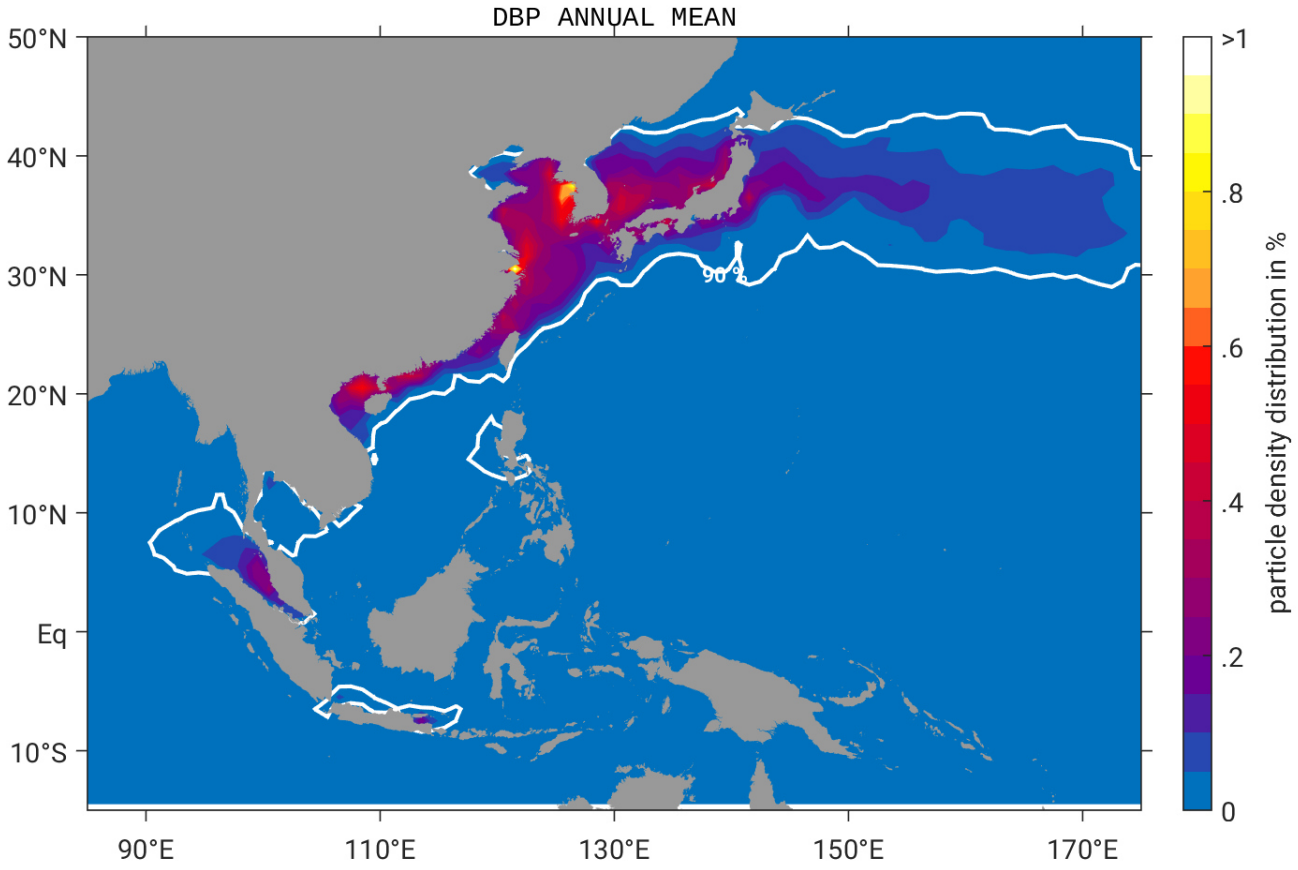


Figure 3: Annual mean particle density distribution in % of DBPs from cooling water treatment in coastal power plants in East and Southeast Asia. The white contour line shows the patches where 90 % of the largest particle density are located.

Table 2: Average valuesMean and maximum bromoform concentration [pmol L^{-1}] for the three ~~scenarios~~Ariane runs LOW, MODERATE, HIGH, as well as the climatological values from the Ziska2013 bottom-up estimate in East and Southeast Asia. ~~Sea surface concentrations [pmol L^{-1}],~~ Mean and maximum air-sea flux [pmol m^{-2} h^{-1}] ~~and atmospheric mixing ratios~~ from ~~Ziska-EastAsia in~~ the ~~marine boundary layer [ppt] are given as the mean~~three scenarios and the ~~standard deviation over the largest 90 % (referred to as mean values)~~Ziska2013 air-sea flux in East and ~~over the largest 10 % (referred to as maximum values).~~Southeast Asia. The annual mean bromine flux [Mmol Br a^{-1}] is derived from the air-sea flux of the total domain in East and Southeast Asia. Mean and maximum atmospheric bromoform mixing ratios in the marine boundary layer [ppt] from the four FLEXPART runs. Values are given as the mean and the standard deviation averaged over the largest 90 % (referred to as mean values) and over the largest 10 % (referred to as maximum values).

Scenario	Sea surface concentration [pmol L^{-1}]		Air-sea flux [pmol m^{-2} h^{-1}]		Bromine flux [Mmol Br a^{-1}]	Atmospheric mixing ratio [ppt]			
						JJA		DJF	
	Mean	Max	Mean	Max	Total	Mean	Max	Mean	Max
LOW	23 ± 24	112.1 ± 6.3	3.1 ± 3.4	13.7 ± 0.9	100	0.~~5~~4 ± 0.~~6~~9	~~4.6~~9.0 ± 1.~~2~~3	0.3 ± 0.4~~5~~	~~3.~~4.7 ± 2~~ ± 1.5~~.6
MODERATE	68 ± 74	338.3 ± 16.6	9.1 ± 10.2	41.1 ± 2.9	300	1.~~6~~3 ± 2.~~0~~7	~~13.9~~27.1 ± 3.4~~5~~	0.~~9~~8 ± 1.~~3~~4	~~9~~13.5 ± ~~4.6~~7.7
HIGH	113 ± 122	563.6 ± 28.8	15.1 ± 16.9	68.5 ± 4.7	500	2.2 ± 4~~ ± 3.3~~.4	~~23~~45.0 ± 6.3~~ ± 5.5~~	1.~~5~~4 ± 2.~~2~~4	~~15~~23.3 ± 12.9~~ ± 8.3~~
~~Ziska~~Ziska2013-EastAsia	7 ± 6	21.3 ± 1.3	0.4 ± 0.2	1.1 ± 0.2	118	0.2 ± 0.~~2~~1	0.8 ± 0.~~1~~2	0.2 ± 0.1	0.5 ± 0.1

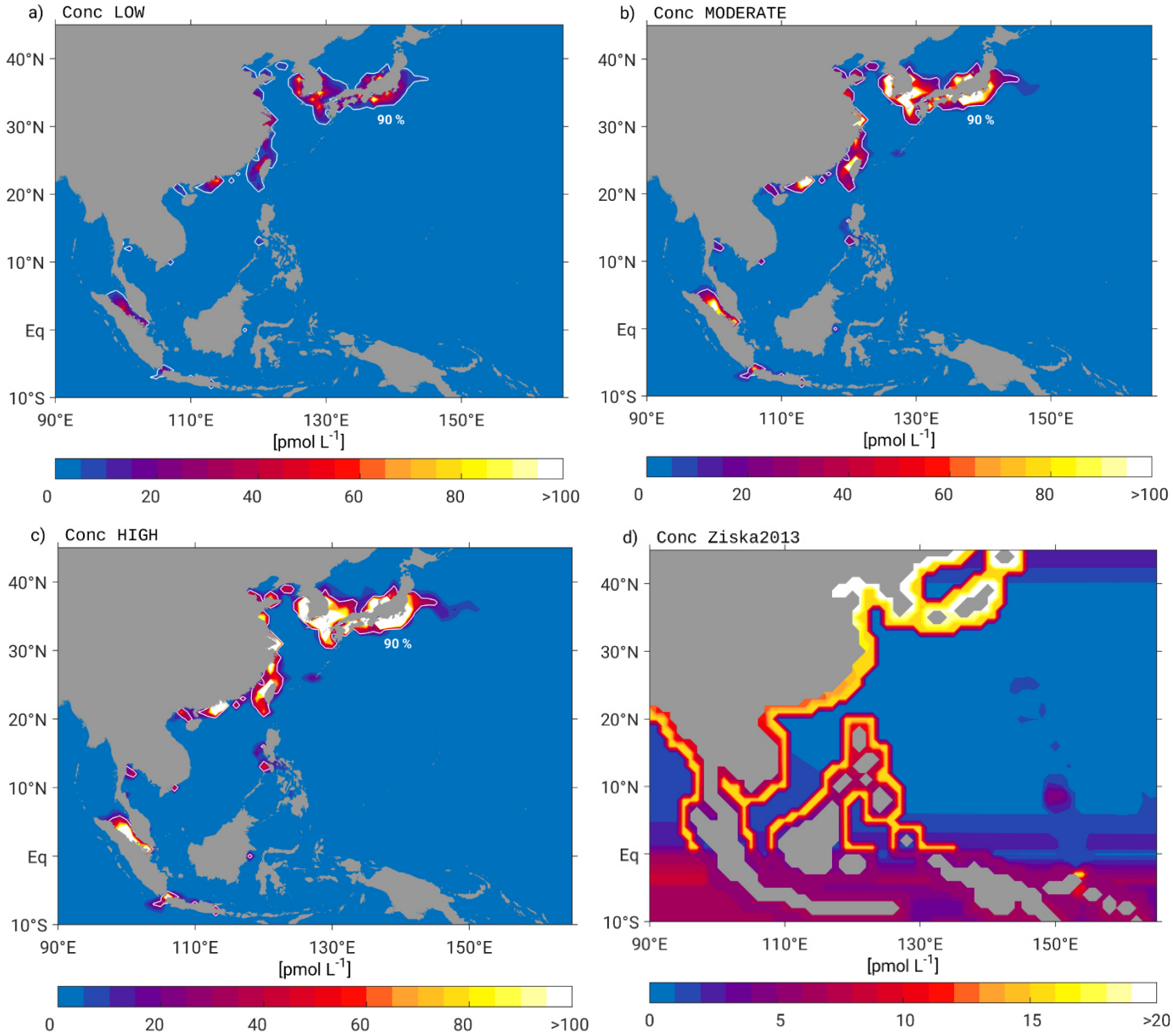


Figure 4: Annual mean surface bromoform concentration in pmol L^{-1} for the three scenarios a) LOW, b) MODERATE and c) HIGH as well as d) the bromoform surface map updated from Ziska2013. Note, that the ~~colorbar~~colourbar limits for d) varies from the limits in a)-c). The white contour line in panel a)-c) shows the patches where 90 % of the largest concentrations are located.

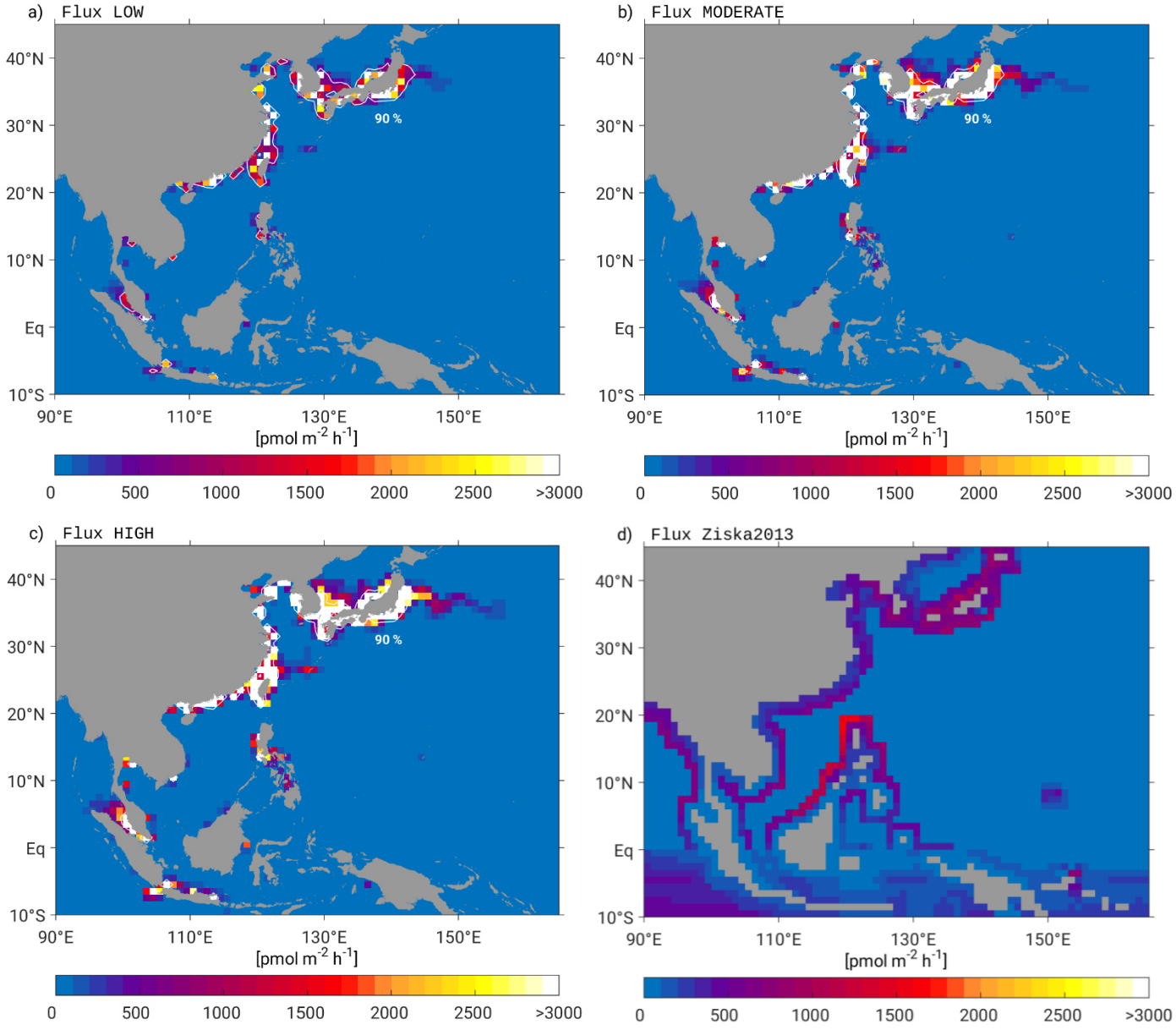
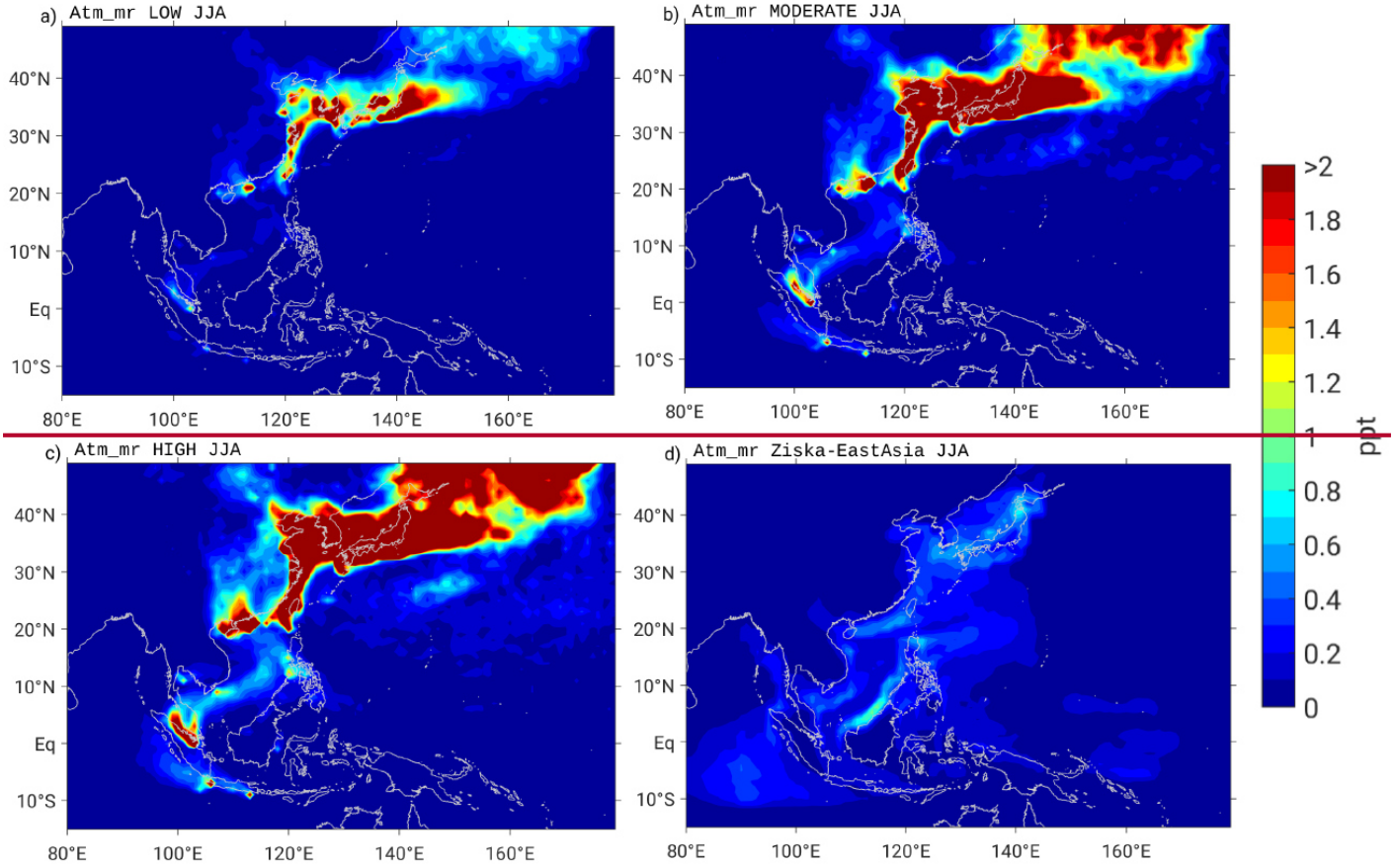


Figure 5: Annual mean air-sea flux of bromoform in pmol m^{-2} h^{-1} for the three scenarios a) LOW, b) MODERATE, c) HIGH, as well as d) the air-sea flux calculated from updated ocean and atmospheric maps ~~after~~following Ziska2013. The white contour line in panel a)-c) shows the patches where 90 % of the largest emissions are located.


a) Atm_mr LOW JJA
b) Atm_mr MODERATE JJA
c) Atm_mr HIGH JJA
d) Atm_mr Ziska-EastAsia JJA
40°N
30°N
20°N
10°N
Eq
10°S
80°E
100°E
120°E
140°E
160°E
>2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
ppt

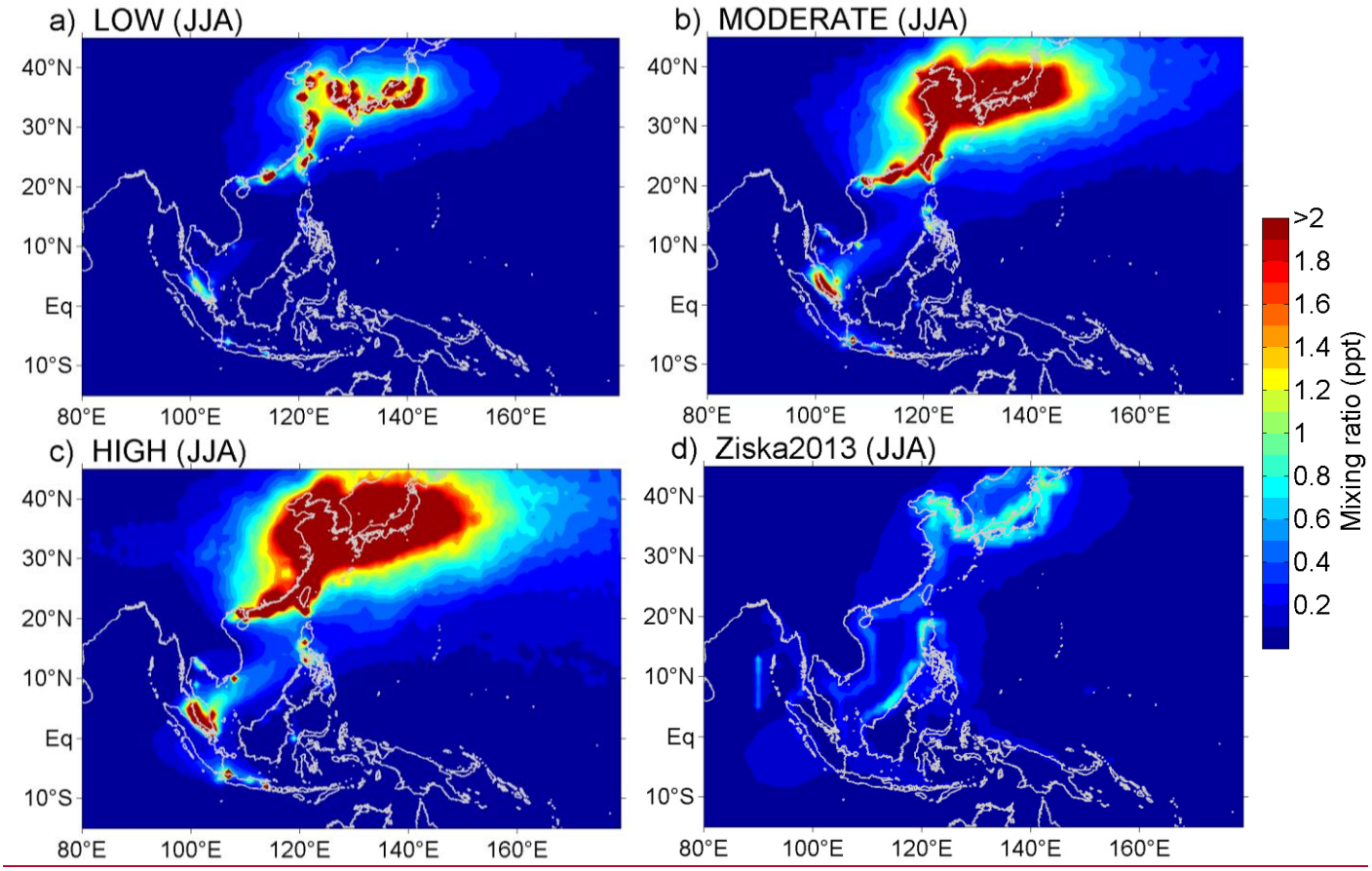
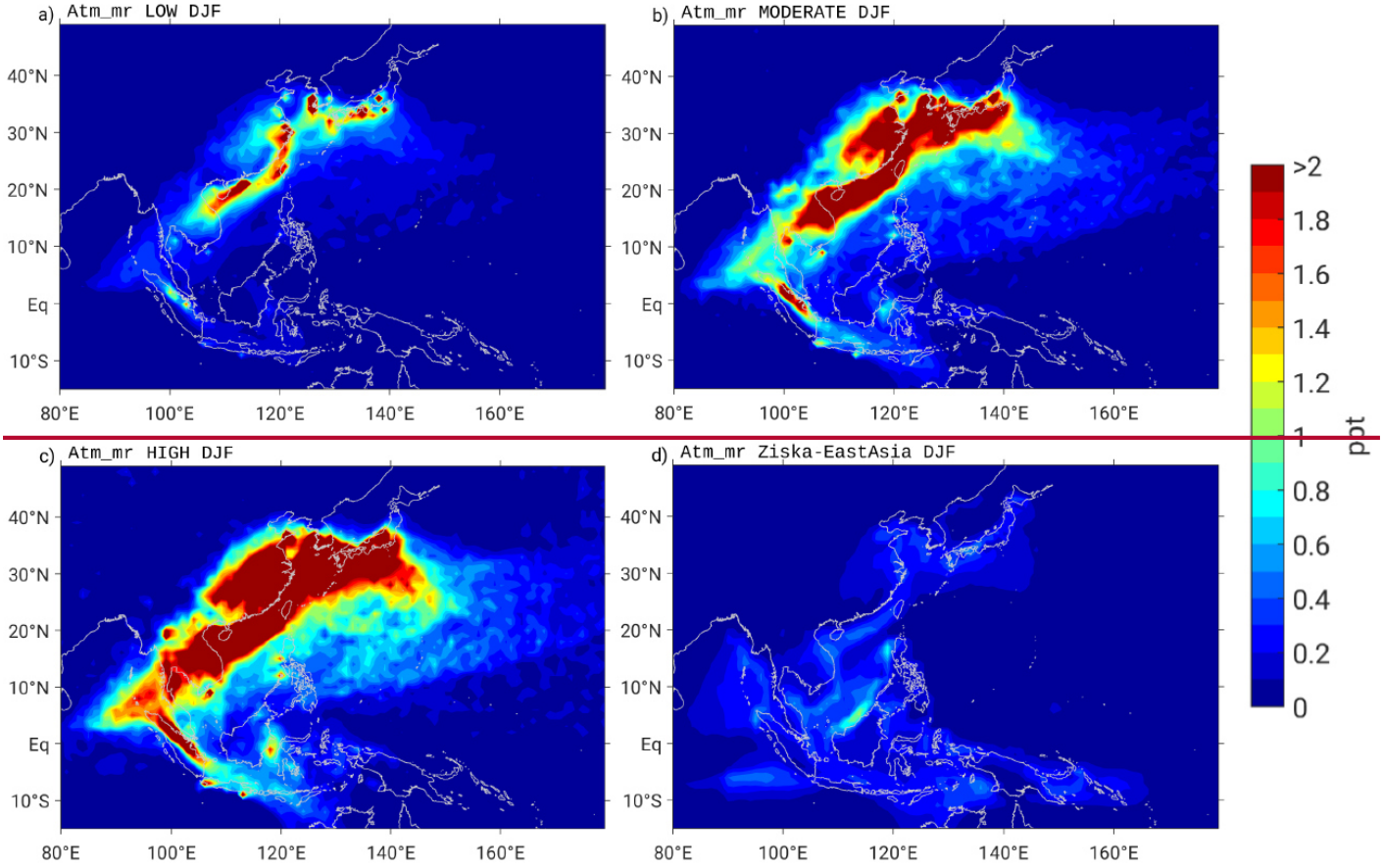


Figure 6: ~~5 day~~Seasonal mean bromoform mixing ratios [ppt] in 50 m height during JJA derived from FLEXPART runs driven by the three scenarios a) LOW, b) MODERATE, c) HIGH, and d) Ziska2013-EastAsia.


a) Atm_mr LOW DJF
b) Atm_mr MODERATE DJF
c) Atm_mr HIGH DJF
d) Atm_mr Ziska-EastAsia DJF
40°N
30°N
20°N
10°N
Eq
10°S
80°E
100°E
120°E
140°E
160°E
>2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
ppt

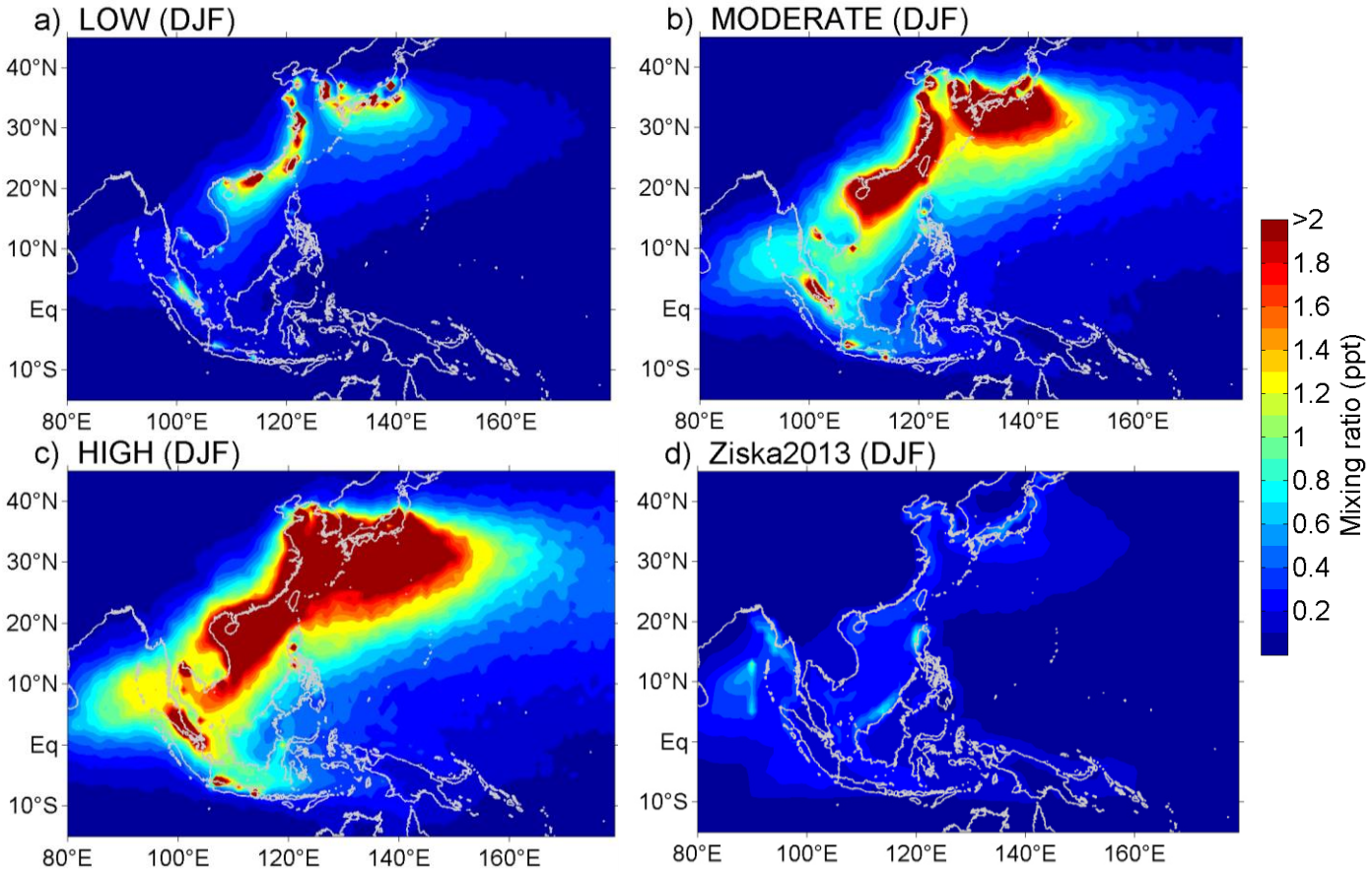
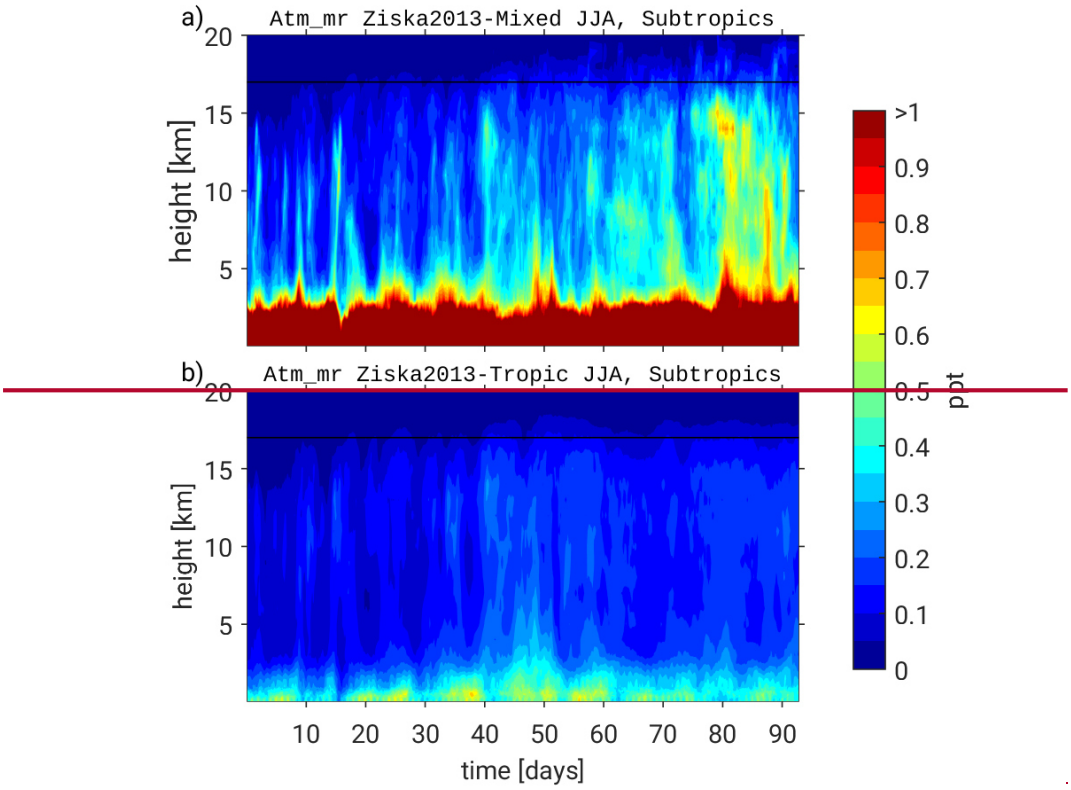


Figure 7: Same as Figure 6 only during DJF.


a)
Atm_mr Ziska2013-Mixed JJA, Subtropics
height [km]
20
15
10
5
b)
Atm_mr Ziska2013-Tropic JJA, Subtropics
height [km]
20
15
10
5
10
20
30
40
50
60
70
80
90
time [days]
>1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
ppt

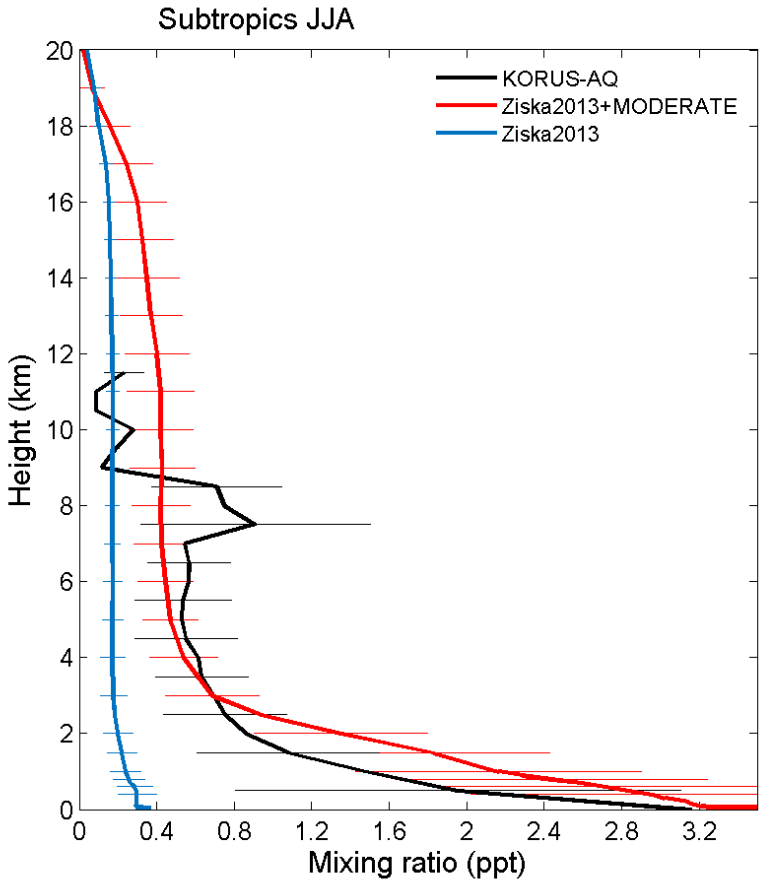
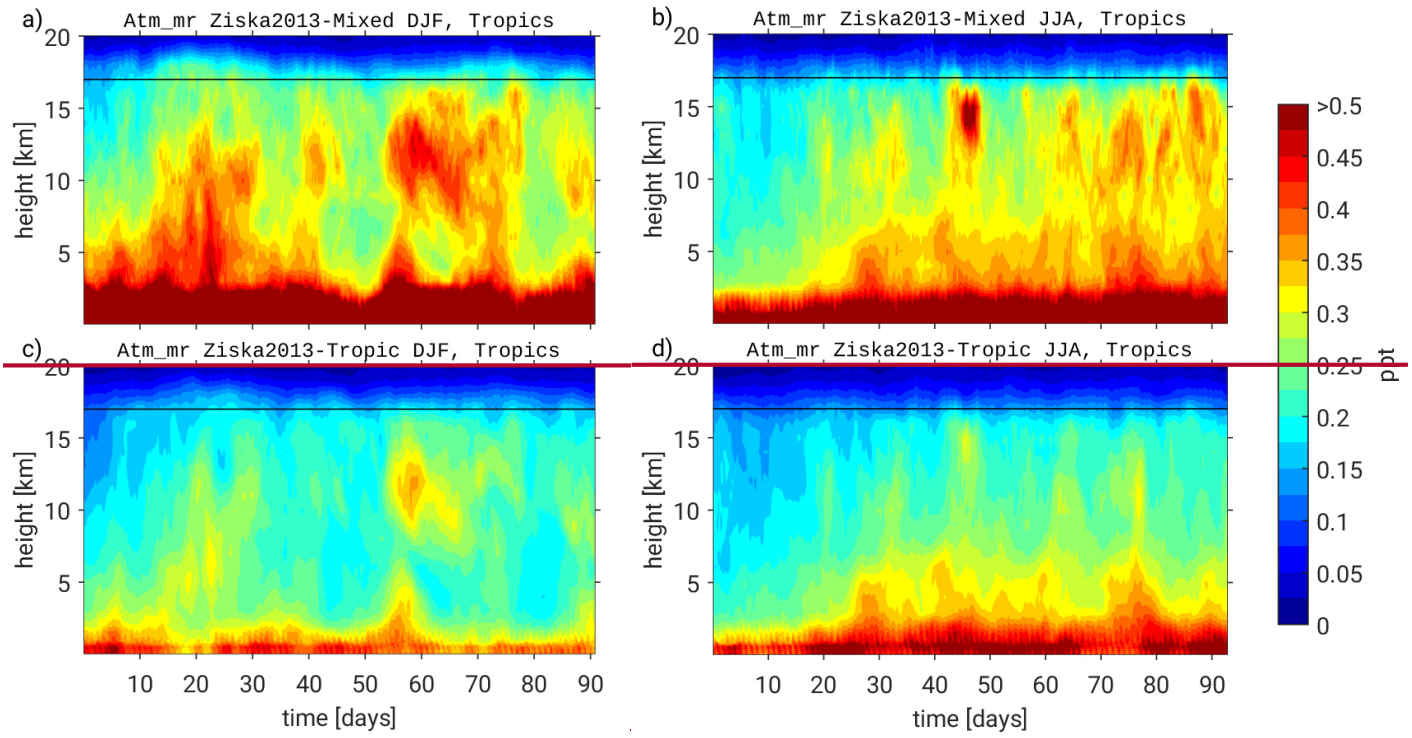


Figure 8: ~~Time series of~~Height profile of seasonal mean bromoform mixing ratio [ppt] in the subtropics (30° N–40° N, 120° E–145° E) during JJA for ~~a)~~ the Ziska2013~~ Mixed~~+MODERATE run (red) and ~~b)~~ the Ziska2013~~ Tropics~~ run~~. The black line marks~~ (blue). Additionally shown is the ~~approximate location of the cold point tropopause at 17 km~~averaged profile of bromoform measurements from the KORUS-AQ campaign over South Korea and the Yellow Sea (black). Horizontal lines show the standard deviation for specific heights.


a)
Atm_mr Ziska2013-Mixed DJF, Tropics
b)
Atm_mr Ziska2013-Mixed JJA, Tropics
c)
Atm_mr Ziska2013-Tropic DJF, Tropics
d)
Atm_mr Ziska2013-Tropic JJA, Tropics
height [km]
time [days]
ppt
>0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0

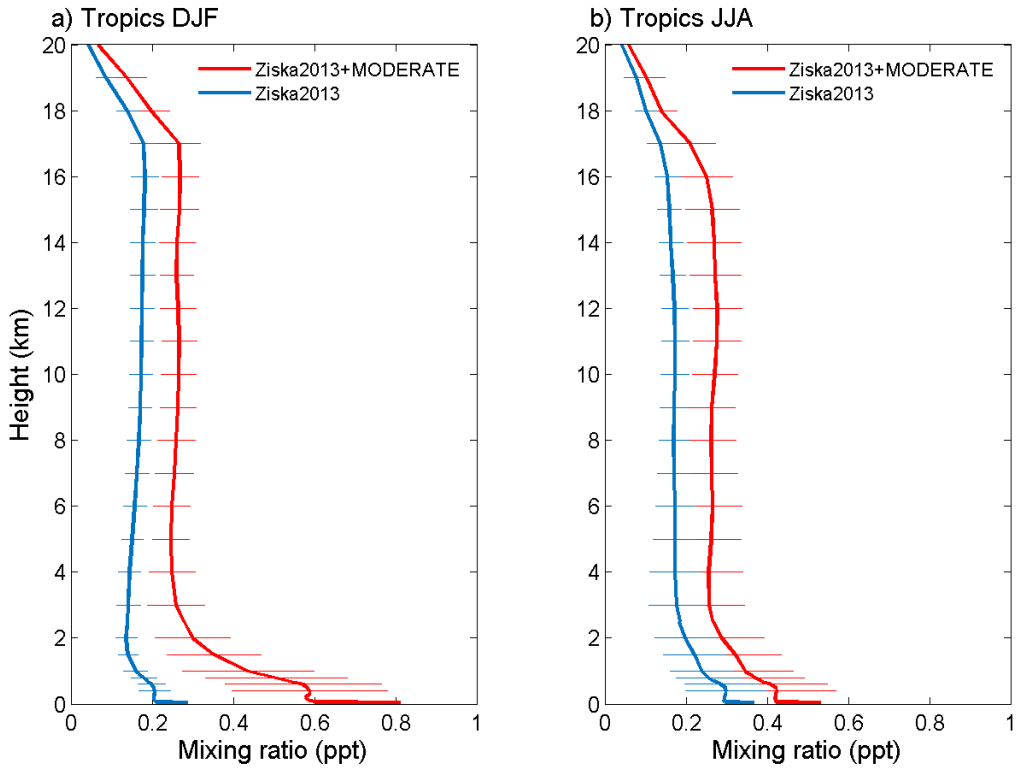
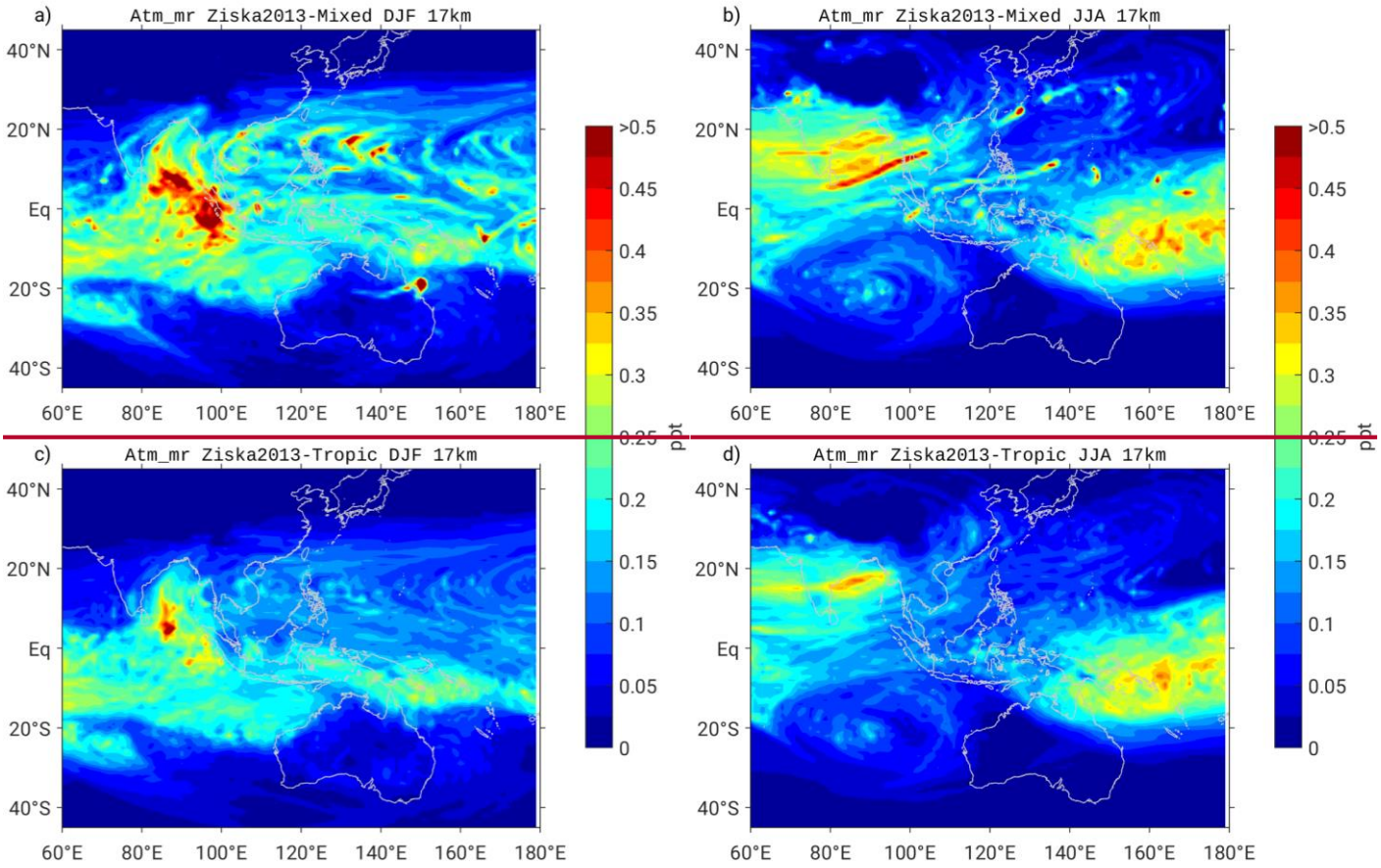


Figure 9: ~~Time series~~Height profile of seasonal mean bromoform mixing ratio [ppt] in the tropics (10° S–20° N, 90° E–120° E) for ~~a) and b)~~ the Ziska2013~~ Mixed~~+MODERATE run (red) and ~~c) and d)~~ Ziska2013~~ Tropics~~ run (blue) for both a) DJF ~~(left)~~ and b) JJA ~~(right). The black line marks the approximate location of the cold point tropopause at 17 km~~. Horizontal lines show the standard deviation for specific heights.


a)
Atm_mr Ziska2013-Mixed DJF 17km
b)
Atm_mr Ziska2013-Mixed JJA 17km
c)
Atm_mr Ziska2013-Tropic DJF 17km
d)
Atm_mr Ziska2013-Tropic JJA 17km
40°N
20°N
Eq
20°S
40°S
60°E
80°E
100°E
120°E
140°E
160°E
180°E
>0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
ppt

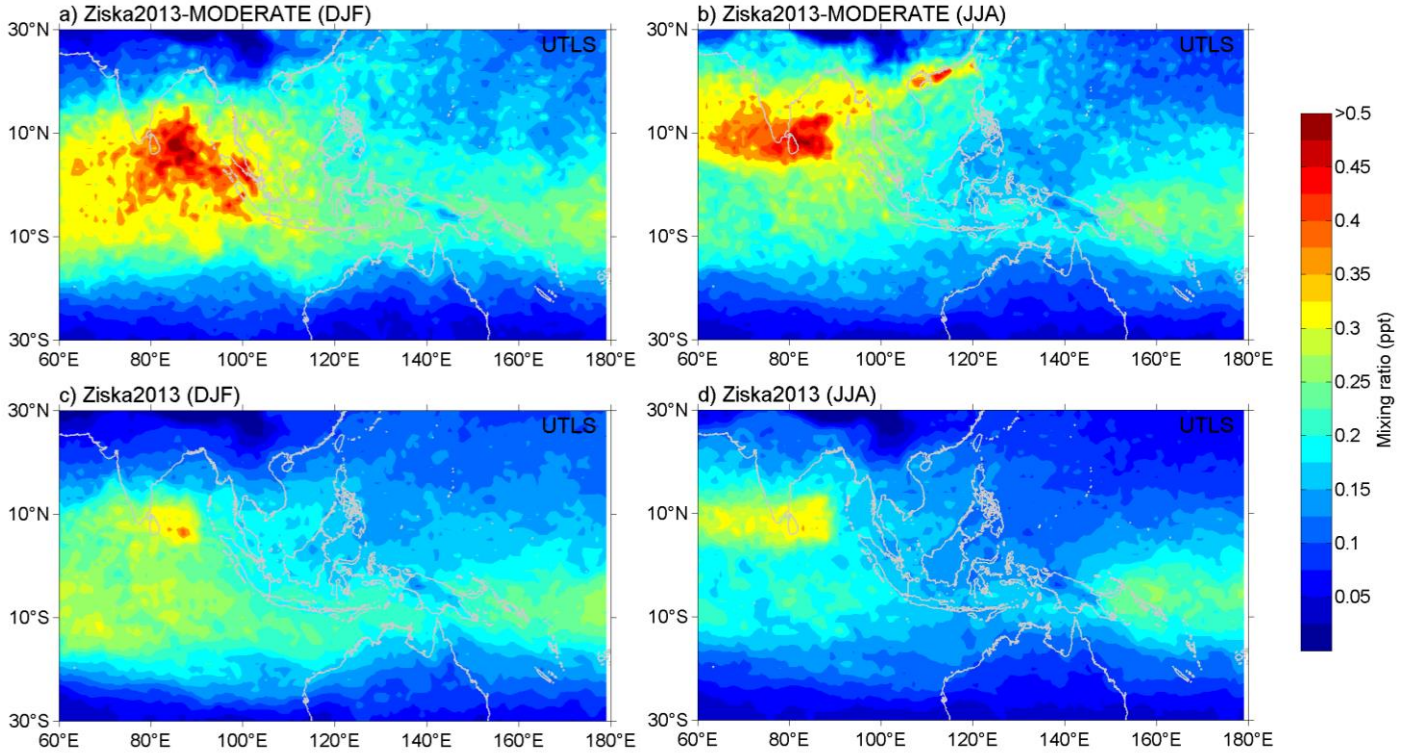


Figure 10: ~~5 day~~Seasonal mean atmospheric mixing ratios [ppt] for a) and b) the Ziska2013~~+ Mixed~~MODERATE and c) and d) Ziska2013~~ Tropics~~ simulation at ~~17 km~~ the cold-point tropopause height for DJF (left) and JJA (right).