We would firstly like to thank the reviewer for their helpful comments. We have taken the reviewers comments into consideration and revised the manuscript accordingly. All the changes have been highlighted in the revised manuscript and are detailed as follows.

Reviewer's comments for the paper (acp-2017-244), entitled: "Atmospheric bromoform at Cape Point, South Africa, a first time series on the African continent" by Kuyper et al., submitted to ACP.
Recommendation: Major revision

General comments

> *Comment on Kuyper et al., Atmospheric Bromoform at Cape Point, South Africa.... This manuscript discusses measurements of bromoform at a Global Atmospheric Watch station on the coast of South Africa. Coastal zones have been identified as potentially large sources of bromoform to the global atmosphere, but measurements in these regions are limited. Thus, the month long set of measurements of bromoform along the African coast is interesting and should eventually be published. However, I find myself in full agreement with the points offered by Referee #1 that the data are either over-interpreted or misinterpreted. As the authors recognize to some degree, the correlation between anthropogenic tracers (such as CO) and bromoform in certain air masses does not necessarily indicate a common source, but more likely that the sampled air masses have been exposed to multiple and independent sources. The authors suggest that potential anthropogenic sources include water treatment plants, but this source might be readily identified by looking at the location of any nearby plant relative to Cape Point. Further, examination of the chromatograms might also reveal a different proportion of bromocarbons (e.g., dibromochloromethane/ bromoform ratio) in anthropogenically influenced air vs. biogenic and kelp emissions. Without further information, I would suggest separating (or removing) the discussion of source attribution, and focus on the statistics of the bromoform measurements, including relationships to the standard GAW measurements of CO, CO2, CH4, Rn, etc. As noted by Reviewer #1, a more complete description of factors such as local and regional kelp/seaweed distributions, ocean color, tidal/diurnal factors, boundary layer height (a significant factor for surface emissions!) would be useful in the data interpretation and discussion.*

Response: The comments and recommendations from the reviewer will greatly improve the quality and substance of this paper. The reviewer raises some concerns over possible over-interpretation of data and highlights that the discussion surrounding source attribution is too speculative. In the vast majority of cases we agree with the reviewer and have taken on board the criticisms, elsewhere we have clarified any ambiguities. As a result of the reviewer's comments, the calibration method was extensively examined and an error identified. This has had a material impact on the data and this is reflected in the revised manuscript. The error resulted in a systematic overestimation of the observed bromoform mixing ratios by a factor of two. We believe that the revised data is much more inline with previously published measurements.

Finally, we accept and have followed the reviewer's comment about focusing rather on relationships to the GAW measurements. This has been done, especially, in light of the calibration error. It is hoped that through this response we can alleviate the reviewer's concerns. The revised manuscript the discussion is simplified throughout, with updated results and analysis.

Major comments

1. *Regarding the title: I don't know that I would advertise a one-month campaign as a "time-series". This is especially the case, since there are large gaps in the month long*

data set. The measurements are sufficiently novel as "first-time" data. Also, I would not refer to the other trace gas data from the month long campaign as a "climatology".

Response: We thank the author for these comments.

Remedial action: The title and terminology in the text have been revised as follows:

" Atmospheric bromoform at Cape Point, South Africa: An initial fixed point dataset on the African continent. "

Terminology: 'Climatology' has been replaced with '*local conditions'* or '*meteorological conditions*' depending on the situation.

2. *Not to be too picky, but the authors suggest a great advantage for single location time series over measurements from cruises or airborne surveys. All measurements contribute to understanding the various sources and transport of trace gases. One could argue that the Cape Point site is less useful for bromoform, since it appears to be dominated by local sources. Further, though I don't argue interest in the measurements, the impact of bromoform emissions near Cape Point on stratospheric bromine is likely minimal.*

Response: We do not dispute that any measurements in any region are beneficial. The argument we were attempting to put forward was that the cruises that have come past Cape Town / Cape Point have been sporadic, and tend to be focused on summer when the Southern Ocean is most accessible. A fixed sampling station in this location could be a cost effective method of addressing a large gap in our data, particularly in these winter months. Nonetheless, more ship cruises and/or airborne surveys in the area would of course be of great advantage. The reviewer is correct that this data set may be biased by local sources. A longer study possibly examining the anthropogenic sources in detail could resolve this. The fact that Cape Point is on occasion impacted by anthropogenic sources does not necessarily mean that this site is less useful. Furthermore, the GAW station at Cape Point was strategically positioned where it was as it is able to capture both the clean marine background and show local anthropogenic growth, through the different seasons and wind regimes. Moreover the measurements made there are setup to skillfully resolve the difference between the two (Brunke et al., 2004).

The impact of Cape Point bromoform on stratospheric ozone may be minimal, that is untested. It is possible in the summer months, under strong SE wind conditions, that the bromoform released may be transported to the ITCZ. We agree however that this is all speculative at this stage. The contribution to the global budget and the understanding thereof is, however, of great interest and importance.

Remedial action: The text has been revised to remove ambiguity over measurements. Making note that any measurements are beneficial. The reasons for the site being of specific interest have been clarified - please see comments to reviewer 1 for more details here.

3. *Sampling/Analytical: I would appreciate a bit more detail on the sampling and analytical methods. For example, was there some length of inlet tubing prior to the sample trap; how was water removed prior to sample trap; were aerosols removed in any way? For the GC analysis, presumably the carrier gas was operated at constant pressure?*

From the listed references, a system detection limit of 0.73 ppt bromoform is reported. This is surprisingly high for the conditions and GC system used. This DL should be included in the description since the "background" levels are only 3 x this amount. For calibration discussion, you should clarify the concentration of bromoform

> *coming from the permeation oven. It is not 100 ul of pure bromoform. It seems more like 350 ppb of bromoform based on the flows and mixing ratios reported. Was a total of 1.5 L of air added to the trap after loading the 1 – 3 loop injections of standard? Also, I am confused by the calibration curve and, related to that, how detector drift was calculated during the study. The peak area is determined for each known standard concentration; so the uncertainty is related to the peak area not the standard concentration. Why are the error bars associated with the known standard concentrations? Given the large uncertainty associated especially with the 3-loop standard injection (Fig, 2 and also in Kuyper, 2012 and 2014), how were intermediate detector drifts determined between samples? It seems that the individual uncertainties of a standard injection could add considerable uncertainty to the estimated drift and to the final mixing ratios reported.*

Response: This has all very useful and correct thank you. It has however been dealt with in our responses to the comments of reviewer 1. A chromatogram is also included in our response to reviewer 1 for reference. In summary, the methods section has been revised to better reflect the full operating parameters and include the requested information. Calibration standards and air samples were loaded on the trap independently. If a standard was loaded no air was introduced.

Remedial action: The calibration section of the methods has been rewritten to add clarity to the aspects raised here by the reviewer. This includes information regarding the detector drifts in which a standard (1-3 loops) was analysed after every 5 samples. These were compared to other standards of similar volume. Attention has also been paid to calibrant sample flow and trapped volume. We apologise for the calibration error in the manuscript as originally submitted. The sampling section in the revised manuscript reads as follows:

On the sampling method:

"... A 30 ml min^{-1} nitrogen flow was added directly to the ECD in the form of make up gas. Helium (Grade 5.0, Air Liquide) at a constant flow rate of 5 ml min^{-1} was maintained through the system. The oven was maintained at 35 ºC for 5 min following the injection of a sample. Thereafter the temperature was increased to 60, 90, 150, and 200 ºC every 5 min. The temperature in the oven was increased at 65 ºC min^{-1} and held isothermally once the temperature was reached."

Air samples were pre-concentrated in a custom built thermal desorption unit (TDU, Kuyper et al., 2012). Adsorbents (Carbopac X and Carboxen 1016, 9 mg each) held in a glass tube were cooled to -20 ◦C during the trapping phase. **To exclude air from the adsorbent trap a flow of helium (100 ml min^{-1}, Grade 5.0) was maintained both before and after sampling. Before being passed to the adsorbent trap, samples were dried using magnesium perchlorate held in glass moisture trap (Moore and Groszko, 1999).** Air was passed through the adsorbent trap at 100 ml min^{-1} for 15 min, resulting in a 1.5 l sample size. **The sampling flow rate was checked weekly by means of a digital flow meter.** The cooling of the system was achieved by a recirculating chiller filled with glycol. **An oil free piston pump was used to draw air through a 60 m Decabon sampling line and the trap.** This was routed through a T-piece with the excess gas vented to the atmosphere. A mass flow controller was used to regulate the gas flow through the adsorbent trap. The pump was operated at 400 ml min^{-1} and a needle valve on the exhaust was used to provide sufficient pressure for the mass flow controller to operate.

A built in resistance wire heated the glass tube to 400 ◦C to desorb samples for injection. A second stage cryo-focusing system was used at the head of the column, with liquid nitrogen to improve the chromatography. The liquid nitrogen was held at the head for the duration of the primary injection. Thereafter, boiled water was used to desorb the samples trapped at the head of the column."

On the calibration:

"An external calibration method was used to verify the system performance. A custom built permeation oven was used to deliver aliquots of bromoform at varying concentrations to the trap (Wevill and Carpenter, 2004; Kuyper, 2014). A bromoform permeation tube held at 70 ºC (permeating at 343 ng min^{-1}) was flushed with nitrogen (grade 5.0, Air Liquide) at 100 ml/min. This gas mixture was continually passed through a 100 µl sample loop and exhausted through a halocarbon trap. Aliquots of 100-300 µl (1 - 3 sample loops) of the resulting permeation gas (bromoform diluted in nitrogen), were introduced to the thermal desorption unit from the permeation oven. **The sample loop was flushed for 30 s to ensure complete transport of the calibrant onto the adsorbent trap.** Calibration samples were passed through the drying trap as for air samples, thus any loss would be consistent for air and calibration methods. The calibration points were analysed using on the same temperature programme as air samples to ensure identical retention times. These were also used for the identification of bromoform.

A complete calibration curve (Fig. 2) was measured prior to the start of the experimental period. The peak area was determined from the injection of 1 - 3 loops of diluted bromoform in nitrogen gas. Peak areas were calculated through the trapezoid method of integration (Poole, 2003). These areas were computed in MATLAB. The mixing ratios of the injected loops were calculated as the number of moles injected. Each loop injection **resulted in 0.1865 ng of bromoform being loaded on the trap, based on the calibrated rate of the permeation tube (**Weville et al. 2004; Kuyper 2014**). The number of moles of bromoform on the trap was calculated. Through the air number density and the number of molecules loaded on the trap, the number of moles (bromoform) was converted to a mixing ratio. Calibration standards and air samples were run through the system independently of each other**.

The variability of the peak areas measured based on repeated loop injections was converted to a 95 % confidence interval. This confidence interval was used to show the uncertainty in the conversion of measured peak area to mixing ratio. Since the peak area is proportional to the concentration in the sample, the measured peak area is controlled through the number of injected loops and thus calculated against mixing ratio (Fig. 2).

Thereafter, a calibration point of 1-3 loops was run every 5 air samples to account for system drift. Based on a linear regression between the introduced sample and peak area response a 99 % accuracy was achieved on this system. Analysis from repeated 2 loop injections indicated a system precision of **7.4** %. **Following an analysis of the calibration curve a limit of detection of 0.21 ppt was determined for this system. "**

4. *Note that Poole, 2003 not in reference list.*

Response: We would like to thank the reviewer for this observation and like to apologise for the oversight.

Remedial action: This reference has been added to the reference list.

Poole, C. F. (2003). *The Essence of Chromatography*. Elsevier B.V., Sara Burgerhartsraat 25, Amsterdam, The Netherlands.

5. *Repeat comment of Rev. #1: the polar plots are very confusing in what they are showing. Please consider alternate plots to illustrate relationships.*

Response: We thank the reviewer for this comment - it does appear that this plots caused much confusion.

Remedial action: The results have been presented differently as suggested by the reviewer. The majority of the polar plots have been removed. A revised time series plot has been added to the results as the main focus point. The revised results also includes a diurnal variation plot, time series plots of the bromoform events and a single polar plot of bromoform as a function of wind speed and direction, as the authors felt that this figure was still instructive.

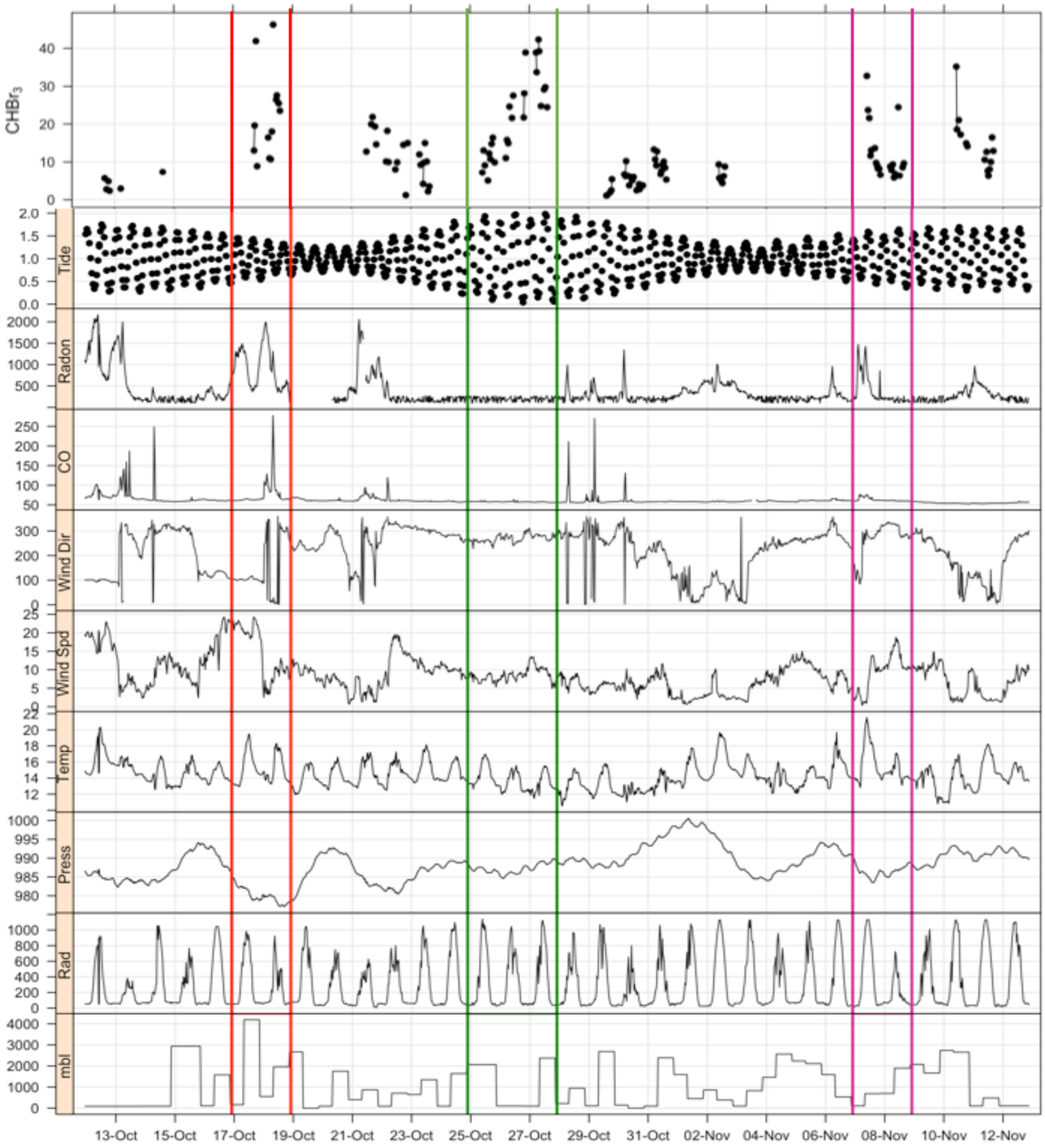

Figure: Time series plot of measurements at Cape Point during October / November 2011. Events are highlighted by the coloured lines: E1 = red, E2 = green, E3 = violet.

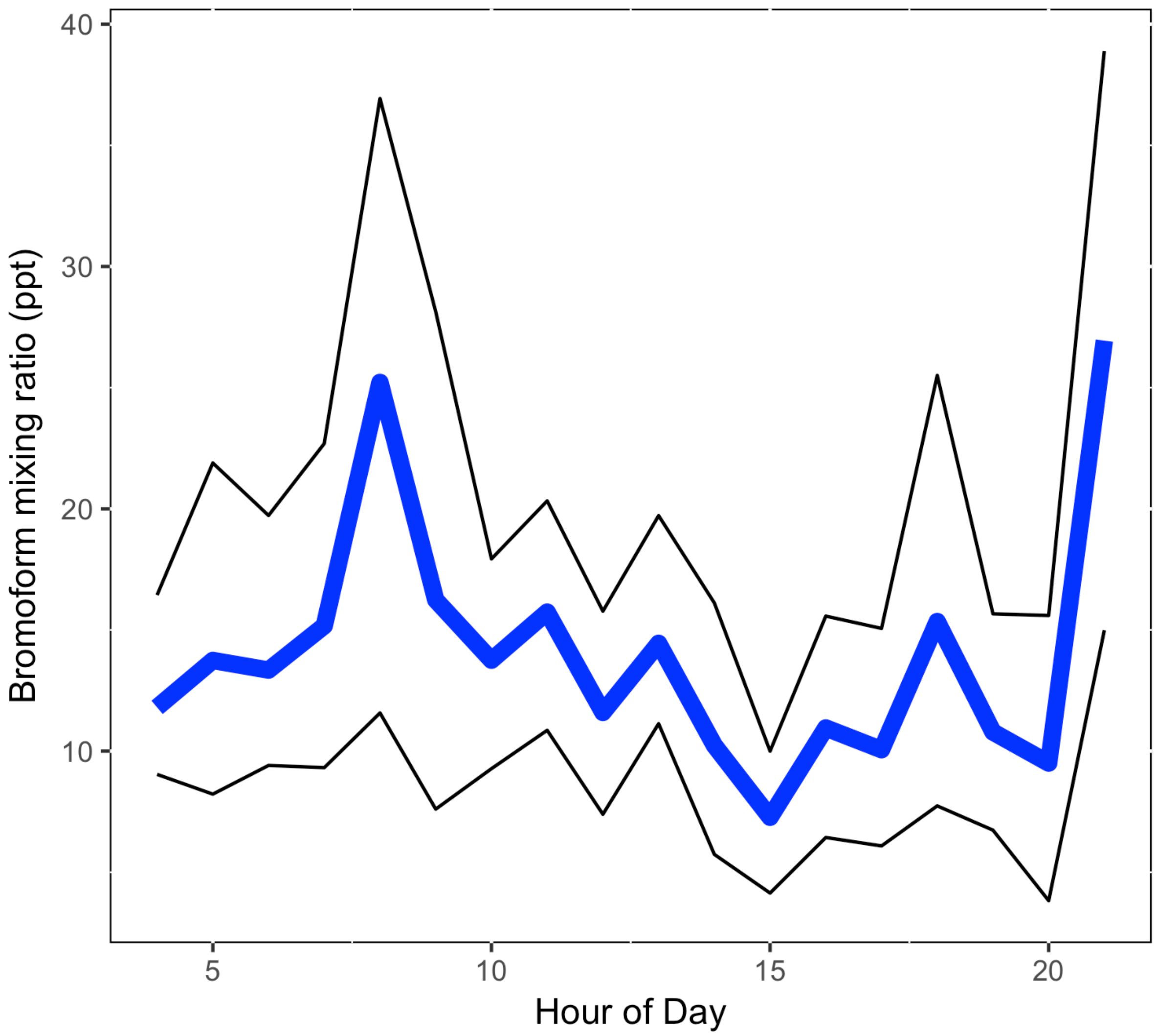

Figure: Mean diurnal cycle, calculated from all measurements binned by hour. The black lines above and below signify the 95 % confidence interval.

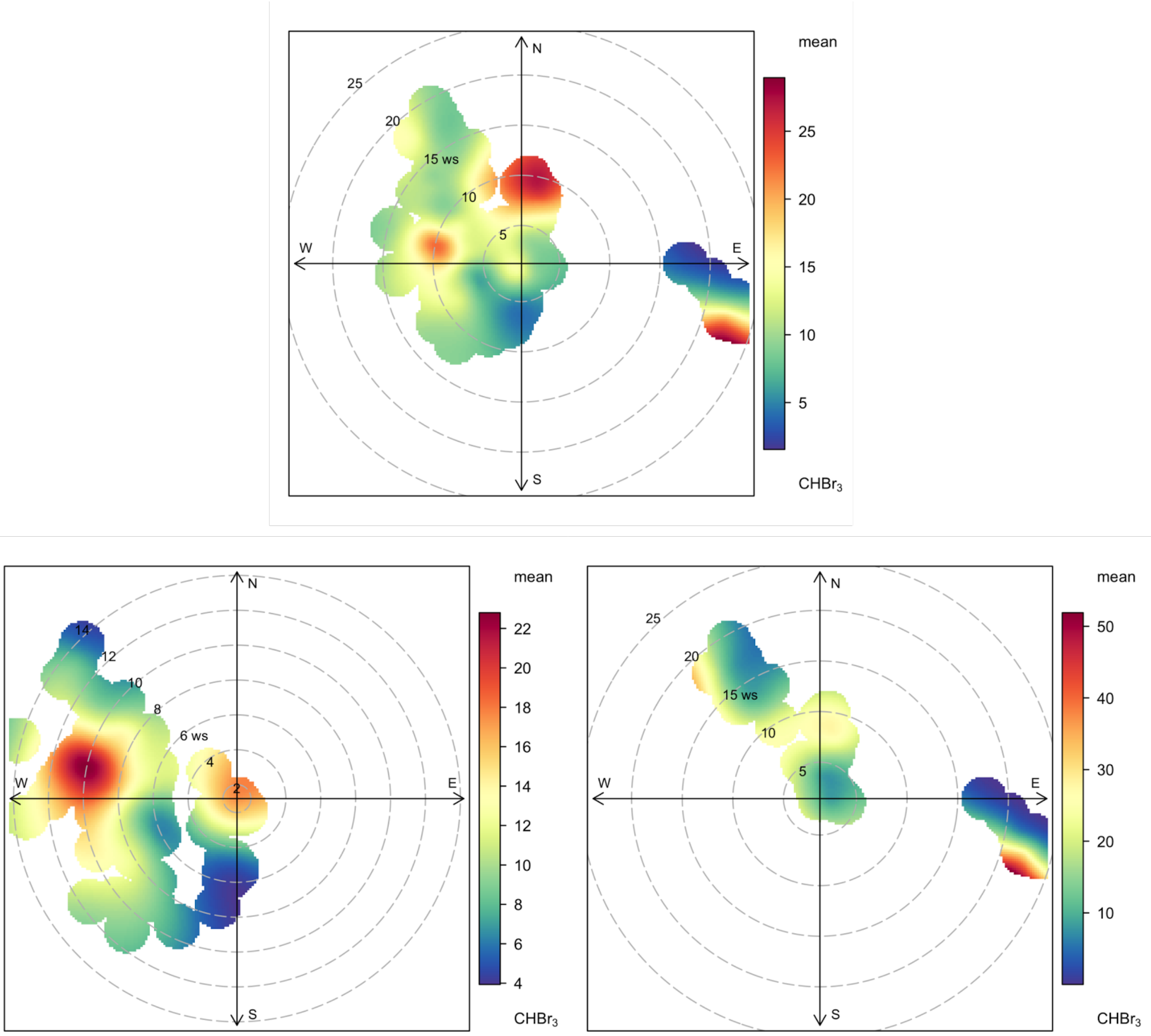

Figure: Polar plots of bromoform as a function of wind speed and direction. The top figure highlights all the data, while the lower plots show background and non-background respectively. These figures give an indication of possible source directions and distance.

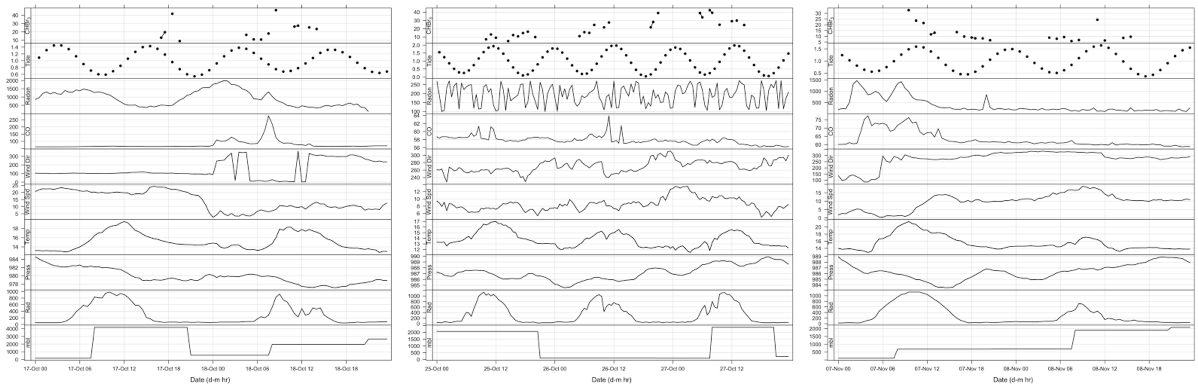

Figure: Time series sub-plots expanding the elevated bromoform event days. From left to right Events 1 - 3.

6. *P9, Bromoform time series. It is not clear what is the meaning of the standard deviation around the maximum and minimum (also in abstract). What is being averaged?*

Response: The ‘standard deviation’ reported in the text regarding certain measurements are a description of uncertainty based on the precision of the instrument.

Remedial action: The wording has been revised to be clearer.

7. *P 10. Line 1 Clarify. . .”the second and third events showed higher levels of bromoform compared to the first episode.*

Response: We thank the reviewer for pointing out the ambiguity of the statement. The maximum (and not specifically average) mixing ratios of bromoform were larger in events 2 and 3 than in event 1.

Remedial action: The results and discussion sections have been revised in light of this.

8. *P11, line 9 ; high 30s ppt? should be ppb?*

Response: We would like to thank the reviewer for noticing this. The reviewer is correct and it should be ppb.

Remedial action: This has been corrected.

9. *P13, fig. 10. I think Rev #1 is correct about wrong trajectories displayed for event #2. A question I have, though, is how the “event” trajectories compare to the “background” trajectories? Or if only local wind direction or 1 day trajectories are most relevant for this site?*

Response: The reviewer is correct that the wrong back trajectory had been inserted in error into the figure. From the revised figures (below) one can see some variability in the back trajectories. However, we do not feel that the variability is not to such an extent that 1 day trajectories are necessary.

Remedial action: The back trajectories have been corrected. In response to the reviewer’s comment about background trajectories, a background trajectory has been added to the figure. For reference.

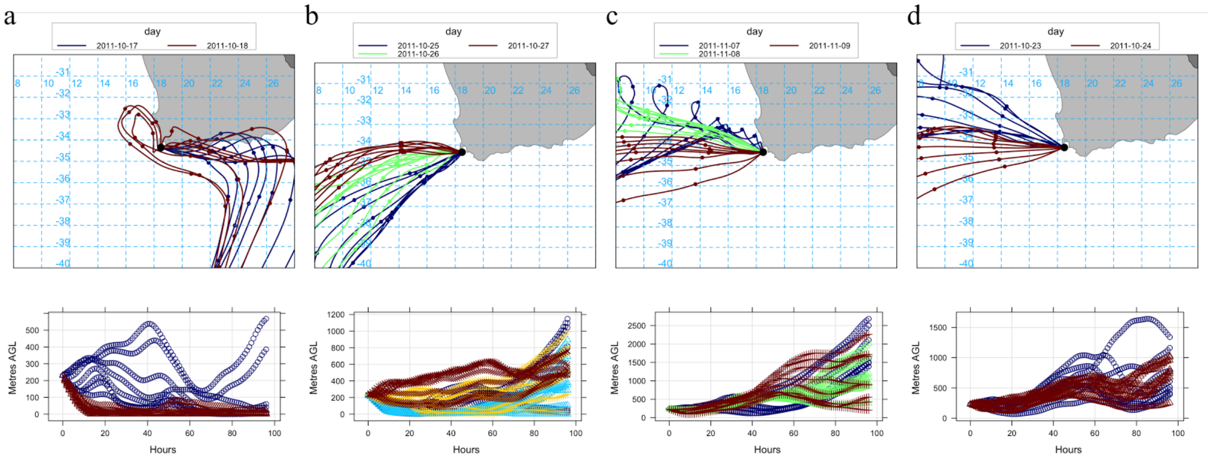

Figure: Composite daily back trajectories for the selected Events (a) E1 17 – 18 October 2011, (b) E2 25 – 27 October 2011, (c), E3 7 – 9 November 2011, (d) Background samples 23 - 24

October 2011. Trajectory heights for the events are displayed below. The colours and dates correspond respectively for each event.

10. *P14, line 18. As noted in my first comment, I disagree totally with this statement.*

Remedial action: The discussion has been revised as suggested by the reviewer and reviewer 1 to remove discussion about source attribution.

11. *P15, line 8. I don't understand what this sentence means.*

Response: We thank the reviewer for their observation regarding this sentence. That line should not have appeared in the final version, our sincere apologies.

Remedial action: The sentence has been removed in the revised discussion.

12. *P16, line 12, What is biogenic ozone?*

Response: What was meant by this term was ozone formed in the stratosphere and not from anthropogenic precursors.

Remedial action: This has been amended accordingly in the revised results and discussion.

13. *P16, Table 1, Since trajectories show potential sources from Southern Ocean, it would be informative to include data from cruises in the Southern Ocean. Plus, recent measurements have been reported from Peruvian upwelling regions (see ACP)*

Response: The authors would like to thank the reviewer for this useful and insightful comment and suggestion.
Remedial action: The Table has been updated including cruises from the Southern Ocean.

Table: Selected comparison measurements of bromoform in air samples above coastal, upwelling, open ocean and lower marine boundary layer regions.

			$CHBr_3$ (ppt)				
Location	Date	Latitude	Min	Max	Mean	Reference	Region
New Hampshire TF	Jun-Aug 2002-4	43.1 ºN	0.2	37.9	5.3-6.3	Zhou et al. 2008	Coastal
New Hampshire AI	Jun-Aug 2004	42.9 ºN	0.9	47.4	14.3	Zhou et al. 2008	Coastal
Hateruma Island, Island	Dec 2007 - Nov 2008	24 ºN	~0.5	7	0.91-1.28	Yokuchi et al 2017	Coastal
Mauritanian upwelling	Mar - Apr 2005	16-21 ºN	0.1	0.6	0.2	Quack et al. 2007	Upwelling
Cape Verde	May-Jun 2007	16.8 ºN	2.0	43.7	4.3-13.5	O'Brien et al. 2009	Coastal
R/V Sonne	July 2014	2-16 ºN	0.79	5.07	2.08	Fuhlbrugger et al. 2016a	Open ocean
R/A Falcon	July 2014	2-16 ºN	0.99	3.78	1.90	Fulbrugger et al. 2016a	MABL WASP
Atlantic Ocean	Oct - Nov 2002	10 ºN	0.5	27.2	-	Quack et al. 2004	Open ocean

SHIVA	Nov-Dec 2011	0-8 ºN	1.23	3.35	1.81	Sala et al. 2014	MABL WASP
Borneo	Apr-Jul 2008	4.70 ºN	2-5	~60	-	Pyle et al. 2011	Coastal
Strait of Malacca	Jun-Jul 2013	2-6 ºN	1.85	5.25	3.69	Mohd Nadzir et al. 2016	Coastal
Sulu-Sulawesi	Jun-Jul 2013	2-6 ºN	1.07	2.61	1.60	Mohd Nadzir et al. 2016	Coastal
Christmas Island	Jan 2003	1.98 ºN	1.1	31.4	5.6-23.8	Yokuchi et al. 2005	Coastal
San Cristobol Island	Feb - Mar 2002, 2003	0.92 ºS	4.2	43.6	14.2	Yokuchi et al. 2005	Coastal
Peruvian upwelling	Dec 2012	5-16 ºS	1.5	5.9	2.9	Fuhlbrugger et al. 2016b	Upwelling
Indian ocean	Jul-Aug 2014	2-30 ºS	0.68	2.97	1.2	Fiehn et al. 2017	Open ocean
Cape Point	**Oct - Nov 2011**	**34 ºS**	**1.10**	**46.2**	**13.2**	**This study**	**Coastal**
Cape Grim	2003	40.7 ºS	1.3	6.4	2.9	Yokuchi et al. 2005	Coastal
Coastal South America	Dec 2007 - Jan 2008	55 ºS	1.8	11	7.4	Mattsson et al. 2013	Coastal
Antarctic coast	Dec 2007 - Jan 2008	65 ºS	2.1	4.9	3.2	Mattsson et al. 2013	Coastal
Antarctic Ocean	Dec 2007 - Jan 2008	65-67 ºS	1.9	3.9	2.3	Mattsson et al. 2013	Open ocean

The authors would like to the reviewers for their time, efforts and comments which have helped to greatly improve the substance and quality of the paper.

References

Brunke, E. G., Labuschagne, C., Parker, B., Scheel, H. E., & Whittlestone, S. (2004). Baseline air mass selection at Cape Point, South Africa: Application of 222Rn and other filter criteria to CO2. *Atmospheric Environment*, *38*(33), 5693–5702. https://doi.org/10.1016/j.atmosenv.2004.04.024

Fiehn, A., Quack, B., Hepach, H., Fuhlbrügge, S., Tegtmeier, S., Toohey, M., Atlas, E., & Krüger, K. (2017). Delivery of halogenated very short-lived substances from the west Indian Ocean to the stratosphere during the Asian summer monsoon. *Atmospheric Chemistry and Physics,* 17, 6723-6741.

Fuhlbrügge, S., Quack, B., Tegtmeier, B., Atlas, E., Hepach, H., Shi, Q., Raimund, S., & Krüger, K. (2016a) The contribution of oceanic halocarbons to marine and free tropospheric air over the tropical West Pacific. *Atmospheric Chemistry and Physics,* 16, 7569-7585.

Fuhlbrügge, S., Quack, B., Atlas, E., Fiehn, A., Hepach, H., & Krüger, K. (2016b). Meteorological constraints on oceanic halocarbons above the Peruvian upwelling. *Atmospheric Chemistry and Physics*, 16, 12205-12217.

Kuyper, B. (2014). An investigation into source and distribution of bromoform in the Southern African and Southern Ocean Marine boundary layer. *PhD Thesis,* University of Cape Town. http://open.uct.ac.za/handle/11427/8804

Mattsson, E., Karlsson, A., & Katarina Abrahamsson, K. (2013). Regional sinks of bromoform in the Southern Ocean. *Geophysical Research Letters,* 40, 3991-3669.

Mohd Nadzir, M. S., 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., & Hanafiah, M. M. (2014). Bromocarbons in the tropical coastal and open ocean atmosphere during the 2009 Prime Expedition Scientific Cruise (PESC-09). *Atmospheric Chemistry and Physics, 14, 8137-8148.*

O'Brien, L. M., Harris, N. R. P., Robinson, A. D., Gostlow, B., Warwick, N. J., Yang, X., & Pyle, J. A. (2009). Bromocarbons in the tropical marine boundary layer at the Cape Verde Observatory – measurements and modelling. *Atmospheric Chemistry and Physics Discussion*, *9*, 4335–4379.

Poole, C. F. (2003). *The Essence of Chromatography*. Elsevier B.V., Sara Burgerhartsraat 25, Amsterdam, The Netherlands.

Pyle, J. A., Ashfold, M. J., Harris, N. R. P., Robinson, A. D., Warwick, N. J., Carver, G. D., … Ong, S. (2011). Bromoform in the tropical boundary layer of the Maritime Continent during OP3. *Atmospheric Chemistry and Physics*, *11*(2), 529–542. https://doi.org/10.5194/acp-11-529-2011.

Quack, B., Atlas, E., Petrick, G., Stroud, V., Schauffler, S. & Wallace, D. W. R. (2004). Oceanic bromoform sources for the tropical atmosphere, *Geophysical Research Letters,* 31, L23S05.

Quack, B., Peeken, I., Petrick, G., & Nachtigall, K. (2007). Oceanic distribution and sources of bromoform and dibromomethane in the Mauritanian upwelling. *Journal of Geophysical Research: Oceans*, *112*(10). https://doi.org/10.1029/2006JC003803

Sala, S., Bönisch, H., Keber, T., Oram, D. E., Mills, G., & Engel, A. (2014). Deriving an atmospheric budget of total organic bromine using airborne in situ measurements from the western Pacific area during SHIVA, *Atmospheric Chemistry and Physics, 14, 6903-6923.*

Wevill, D. J., & Carpenter, L. J. (2004). Automated measurement and calibration of reactive volatile halogenated organic compounds in the atmosphere. *Analyst*, *129*(7), 634–638. https://doi.org/10.1039/b403550j.

Yokouchi, Y., Hasebe, F., Fujiwara, M., Takashima, H., Shiotani, M., Nishi, N., … Nojiri, Y. (2005). Correlations and emission ratios among bromoform, dibromochloromethane, and dibromomethane in the atmosphere. *Journal of Geophysical Research Atmospheres*, *110*(23), 1–9. https://doi.org/10.1029/2005JD006303.

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

Zhou, Y., Mao, H., Russo, R. S., Blake, D. R., Wingenter, O. W., Haase, K. B., Ambrose, J., Varner, R. K., Talbot, R., Sive, B. C. (2008). Bromoform and dibromomethane measurements in the seacoast region of New Hampshire, 2002-

2004. *Journal of Geophysical Research Atmospheres*, *113*(8), 2002–2004. https://doi.org/10.1029/2007JD009103.