The authors response to the Reviewers. We have here addressed all the comments of the reviewers. As per the reviewer's' request the results and discussion have been entirely reworked and written. The completely revised manuscript with mark-up can be found at the end of the document.

Response to Reviewer #1

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 summerised 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

> *This paper presents some in-situ atmospheric measurements (~130 samples) of bromoform ($CHBr_3$) from Cape Point, South Africa over a 2 month period in 2011. These are the first reported measurement of this important halocarbon from the southern African continent (although some of the data has already been discussed in Kuyper et al. 2012) so do provide a useful, if limited, new dataset. The concentrations observed are, on occasion, at the higher end of those previously reported. I have a number of serious reservations about the measurements, the interpretation of the data and the conclusions which prevent me from recommending the paper for acceptance in its present form. I fully understand that sometimes it is difficult to draw firm conclusions from a limited set of measurements, but in this case I believe the authors are rather over-interpreting their data.*

Response: We believe that the comments and recommendations from the reviewer will greatly improve the quality and substance of this paper. The reviewer raises some concerns over the validity of the data and the conclusions. It is hoped that through these discussions / responses we can alleviate the reviewer's concerns. As the reviewer highlights it is difficult to draw firm conclusions from an inceptive dataset and limited dataset, which were on occasion at the higher end of those previously reported. In trying to bring our data to life, we have perhaps strayed into overinterpreting the data and we have tried to take on board the reviewers helpful suggestions to remedy this. As a result of the reviewer's comments, the entire calibration method was extensively re-examined and subsequently, an error identified. This has had a material impact on the data and this is reflected in the revised manuscript. Specifically, the error resulted in a systematic overestimation of the observed bromoform mixing ratios by a factor of 2. Finally, the results and discussion have thus been simplified and updated as per the reviewer's suggestions.

1. *The instrumental methods are not described particularly well. The authors refer to a previous publication which does have a lot more detail, but there are some outstanding questions related to the identification of bromoform (CHBr3) and the exclusion of possible co-eluting species. The electron capture detector (ECD) is not particularly specific so is subject to potential interferences in different types of air mass, particularly when trapping such large volumes of air or when sampling in more polluted environments. Have potential co-elutions been thoroughly tested for and ruled out?*

Response: The reviewer is correct that the ECD is not a an absolute detection method and this is a limitation of the technique. The ECD (in combination with an analyte -specific chosen chromatographic column) is however, highly specific to polar compounds and well suited for halocarbon measurements, as has been extensively demonstrated in the literature extending back to the early 1990s (e.g. Schall and Heumann, 1993). Moreover, analyte identification by using relative retention time is a reliable and well documented method found throughout the published literature (e.g. O'Brien et al., 2009; Poole, 2003; Wevill, 2005).

The literature is also unanimous and unambiguous in showing that, in unpolluted environmental air samples, bromoform can be separated with no co-elution problems (column dependant - see below). This is made clear in the EPA 8260B method, which discusses the separation of numerous halocarbons. There is some evidence that separating bromoform from water and in highly polluted gaseous mixtures can be problematic (EPA 504.1). The co-elution problem described above is entirely column dependant; in the study presented here a DB-624 column was specifically selected for its published ability to separate bromoform without co-elution (Mattson et al., 2012; Happell & Wallace,1997; Itoh et al., 1997; Andrews et al., 2016). Furthermore, Cape Point predominantly receives "clean" (i.e. with little/no detectable pollutants) marine air from the Southern Ocean and is only occasionally intruded by anthropogenically modified air from Cape Town (as is discussed in the paper). Given this the chances of co-elution would appear to be negligible for the majority of the data presented, which was recorded in pollution free air. Where the air being measured shows significant anthropogenic influence the possibility of co-elution may increase (although given the discussion above would still be expected to be low) and the discussion has been amended to reflect this potential source of uncertainty in those result which are affected.

Please see below an overlay figure of a calibration standard and an air sample taken from Cape Point. If there were co-elution occurring we would expect that the peak shape would be non-Gaussian, typically displaying tailing of the co-eluting peak. As one can see from the figure the peak shape of the calibration and the air sample for bromoform are almost identical. This gives us great confidence that the system was able to suitably separate and detect bromoform in air samples.

Remedial action: The methods section has been revised in the updated manuscript to be more explicit and unambiguous on all points raised. This includes the separation of samples as well as the calibration of GC-ECD system.
Following the reviewer's comments on co-elution, as a possible mechanism to explain the observed elevated mixing ratios, an exhaustive examination of our calibration method was performed. It was found that the trapped calibrant volume had not been correctly calculated.

The permeation tube emitted pure bromoform at 373 ng min^{-1} and this was diluted in nitrogen at 100 ml min^{-1}. The calibrant gas was loaded onto the trap for 30 s per sample loop. Our calculations had assumed a full minute of calibrant was loaded on the trap. Effectively a mass of 0.1865 ng of bromoform was loaded on the trap instead of the 0.373 ng previously calculated. As described in the text the number of moles of bromoform loaded in a calibration sample was calculated. This was then converted through the air number density and the number of molecules trapped to an atmospheric mixing ratio.

The net effect of the correction of the error effectively resulted in a halving of the reported bromoform mixing ratios. We apologise for this error. The data has been revised as per the new calibration parameters and presented below.

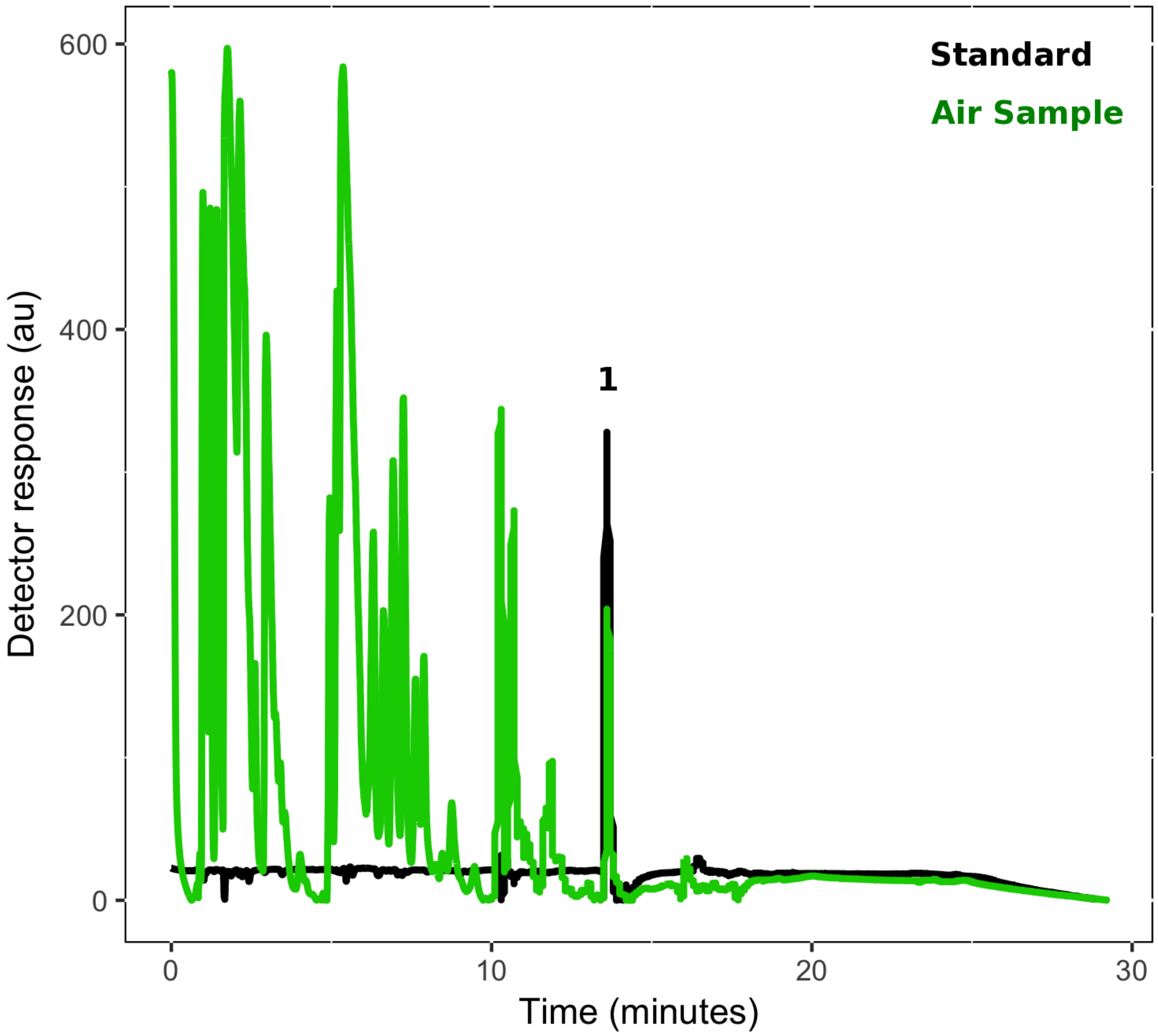

Figure: Overlay of air sample and calibration standard. Bromoform peak indicated by the number 1. The calibration standard reflects the injection of 2 loops of bromoform standard (23.6 ppt) from the permeation oven trapped on the adsorbent trap.

As this is not intended to be a methods paper and given the method was previously published elsewhere, we do not feel that publishing this graph in ACP adds enough to the work here to justify its inclusion. However, should the reviewer/editors deem it worthy of inclusion we would be happy to edit it and include for publication.

2. Much of the discussion is highly speculative and potentially wrong. For example the conclusions on (a) anthropogenic sources of CHBr3, (b) ozone stimulation of CHBr3 release from seaweeds, and (c) a CHBr3 source from the upwelling region, are all highly dubious. The authors present very little firm evidence to support these theories and, to some extent, they overlook a more likely, or simpler, explanation for the high levels of CHBr3 at the site. They state that Cape Point and the surrounding coast-lines for many kilometres to the north and west (and south?) support large, extensive seaweed beds. If this is true then surely the most likely origin of the high CHBr3 they observed is simply local (and regional) seaweed? The flux to the atmosphere would then be highly dependent on local tidal patterns, with large concentrations to be expected when the kelp becomes exposed to the air. Although this is mentioned briefly in one case study, which suggests that this process may be occurring further to the north, can the authors confirm that the same phenomena is not occurring closer to the site on a daily basis? Here a detailed description of the local /regional seaweed populations would be very helpful, ideally identified on a map of the area (Figure 1?). The authors need to convince the reader that the high levels of CHBr3 are not simply from very local sources.

There needs to be a wider discussion of the tidal phenomenon as it is very likely to be the reason for the high concentrations and some, if not all, of the spatial/temporal variation. Similar, and more extensive, studies have been carried out over different seaweed areas such as Mace Head and NW France so references to these should also be provided.

Response: The reviewer raises valid concerns over the discussion and the various attribution of bromoform sources. We would like to preface our response by addressing one important misconception. The three statements A-C the reviewer refers to as *conclusions* were not intended to be interpreted as conclusions. The purpose of A-C is to serve as *test hypotheses* used to frame the discussion of our results. These were chosen as a result of (i) a careful review of the literature, to identify the sources of bromoform in past studies, and then (ii) considering this review in the context of our specific knowledge of the local environment / climate and geography, to arrive at the stated test hypothesis. We are more than aware that this first tentative data recorded at the Cape Point site does not, and could not, falsify any of the test hypothesis in and of itself. We intended to use the hypothesis as a tool to frame the discussions as to which of these potential sources of bromoform this initial data is most consistent with, with a view to guiding future research. We apologise for any ambiguity here and will aim to make this more clear.

The reviewer suggests that the local kelp may explain the measurements observed at Cape Point and that we may have omitted this possibility from our discussion. This is in fact included in the manuscript, as a it effectively a restatement of hypothesis B above. We will aim to make this more clear in the text. To reiterate what we noted above, the result do not however clearly falsify any of A-C.

The reviewer highlights that there are examples in the literature where an increase in measurement signal is associated with low tides, specifically at Mace Head (Carpenter and Liss 2000). This literature argues that this is from the fact that at low tide the kelp is exposed (entirely or partially) to the atmosphere. While the tidal range in the vertical at Cape Point is similar to that of Mace Head (1 – 2 m), the horizontal extent of its range is vastly different. The horizontal change in tide at Cape Point is ~10 m, while at Mace Head the horizontal extent can be many 10s to 100 m (D. Shallcross, pers. comm.). Therefore, at Cape Point the kelp remain submerged throughout the tidal cycle. Thus, as the local kelp remain submerged we do not expect a large tidal signal at the Cape Point site.

In terms of the distribution and species composition of seaweed, the work of Anderson et al. (2007) divided the area in shown in the location map (Figure 1) into 19 areas and used a variety of remote sensing technique to assess the extent of kelp beds in each of those areas. The result show that kelp beds are present in all 19 areas ranging from a minimum of 11 ha coverage in Table Bay to a maximum of just under 1000 ha towards Port Nolloth. The species composition was predominantly Ecklonia maxima Papenfuss south of Yzerfontein but transition to predominantly Laminaria pallid Greville north of Yzerfontein.

Furthermore, whereas we are not excluding the local sources by any means there are arguments to support a (additional) source further afield. The bromoform signal as a function of wind speed and direction as displayed in the polar plot (Fig. 8.) suggests two sources of bromoform, one to the north and a second to the west. Although interpretation of these figures can be problematic, the figure indicates that the dominant sources are at higher wind speed thresholds and consequently from farther afield. Concurrent measurements of ^{222}Rn and CO at Cape Point were used in an attempt to isolate sources. Some of the cases the air mass can be traced to areas influenced by anthropogenic activity, and other times not. If the wind is clean (no or very low ^{222}Rn) and a high wind speed is present then we can assume that the bromoform is not local.

Remedial action: The discussion as a whole, along with the results, have been revised to clarify our position and further explain the points raised by the reviewer. The time series plots have been revised and includes a plot of the tide and meteorological measurements as requested. See time series figures and the sub-plot figures below.

3. *Results section: The order seems wrong. Why not start the results section by discussing the CHBr3 time series before going into the chemical climatologies? I would further suggest that you show the radon and wind direction data on the same plot as Figure 7 as this would make it much easier to spot patterns, etc. Similarly, when discussing the 3 individual episodes it would be helpful to see the same Figure expanded for the periods of interest.*

   I found some of the diagrams rather difficult to interpret. In particular the various polar plots (Figs 5, 6, 8). These types of diagram can sometimes be a little over-complicated. A better explanation, if not a full rethink, is required. For example, in the case of Figure 5, what do the individual circles represent? Are they individual samples or averages in a particular sector? Why is the red circle to the NE not represented somewhere in Figure 6. I would expect to see a red circle, albeit

> > *closer to the origin, in Figure 6. Perhaps this is because the colour scaling in the 2 Figures is different?*
> >
> > *Why not show Figure 8 before Figs 5 and 6, perhaps after discussing the time series (see earlier comment).*
>
> *However, before using these polar plots the authors need to explain why they would be expecting to see correlations of CHBr3 with tracers like CO and ozone. Furthermore, the argument that ozone increasing from, say, 25 to 35 ppb represents a significant enhancement of ozone is contentious. Can you really label this as "enhanced ozone" and would you really expect such a small enhancement to have any significant effect on CHBr3 release from seaweeds? Please provide a reference to support this. Surely any ozone effect will be much smaller than the local tidal effect (which has not been discussed)?*
>
> *There is no discussion of any diurnal pattern in the data. Were there measurements at night? Can boundary layer height or temperature have an impact on the observed concentrations?*

Response: The reviewer expressed concern over the order and in particular some of the figures found within the results section. After consideration, we concur that some of the polar plots and their interpretation proved to be problematic. Whereas we thought these figures offered valuable information, we accept the reviewer's criticism that interpretation of the figures is difficult and therefore it would be better to try and tell the story without them. Thus, these the majority of these figures have been removed. As noted we now have the tracer data plotting in times series alongside bromoform as the reviewer requested.

In terms of why CO is expected to be related in some way to bromoform, it is here being used as a potential proxy for anthropogenic emissions. Bromoform has some known anthropogenic sources such as water chlorination and nuclear power generation (Quack and Wallace, 2003). While, the anthropogenic sources are on the whole small in comparison to natural sources they can, however, be significant on a local or regional scale (Quack and Suess, 1999). Since CO is a known tracer of anthropogenic influence, measurement of elevated CO in an air mass strongly suggests some type of anthropogenic mixing. A correlation of elevated CO and bromoform was expected, if the bromoform was anthropogenic in origin. The absence of a correlation being observed helps demonstrate that the bromoform measured here was not predominantly anthropogenic in origin.

In terms of the reasons for measuring ozone, the presence of ozone has been shown to elicit a bromoform release in species of *Laminaria* kelp (Palmer et al., 2005). Palmer et al. (2005) show that ozone can elicit a significant and rapid response from kelp when ozone is introduced. Although the kelp was covered for most of the tidal range, the tops of the kelp fronds at Cape Point were exposed. The ozone measurements were intended to help investigate whether exposure of the fronds to sunlight and ozone would notably impact the bromoform observed. Work was done in Kuyper (2014) in which these multivariate comparisons were performed. The net result was that there were too few data to conclusively explore this. The analysis was thus simplified to examine these in isolation.

We thank the reviewer for bringing up the diurnal cycle as this was something of an omission and appears to provide some interesting insight.

Remedial action: The Results and Discussion section has been rearranged and reordered to make the flow more logical as per the reviewer's comments. Furthermore, most of the polar plots have been removed as they appear to be a source of confusion. Discussion about 'enhanced ozone' has been removed or revised. The reasons for investigating a correlation between bromoform and other tracers have been made clear. A discussion of the diurnal cycle and any possible impacts from temperature and marine boundary layer height have been included in the updated manuscript.

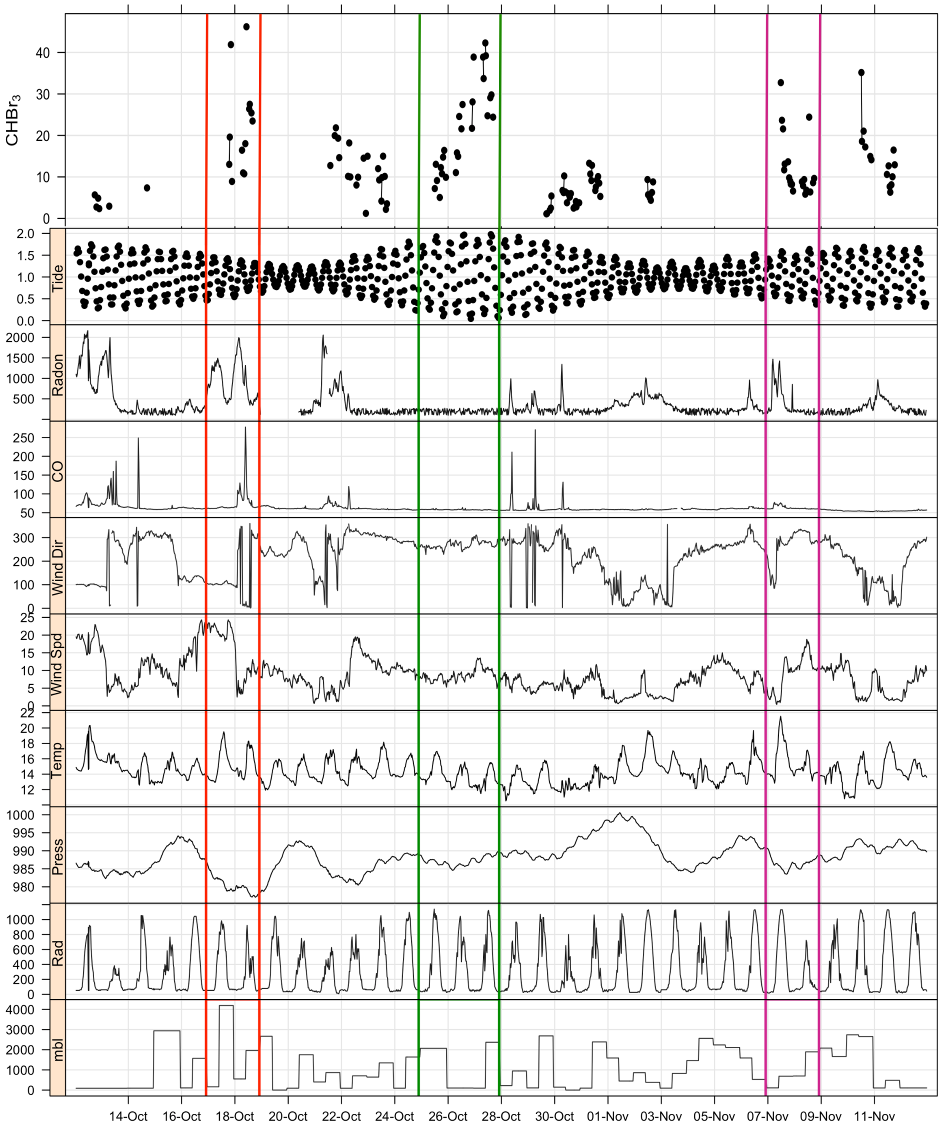

Figure: Time series plot of measurements at Cape Point during October / November 2011. Events are highlighted by the coloured lines: E1 = red, E2 = green, E3 = violet.

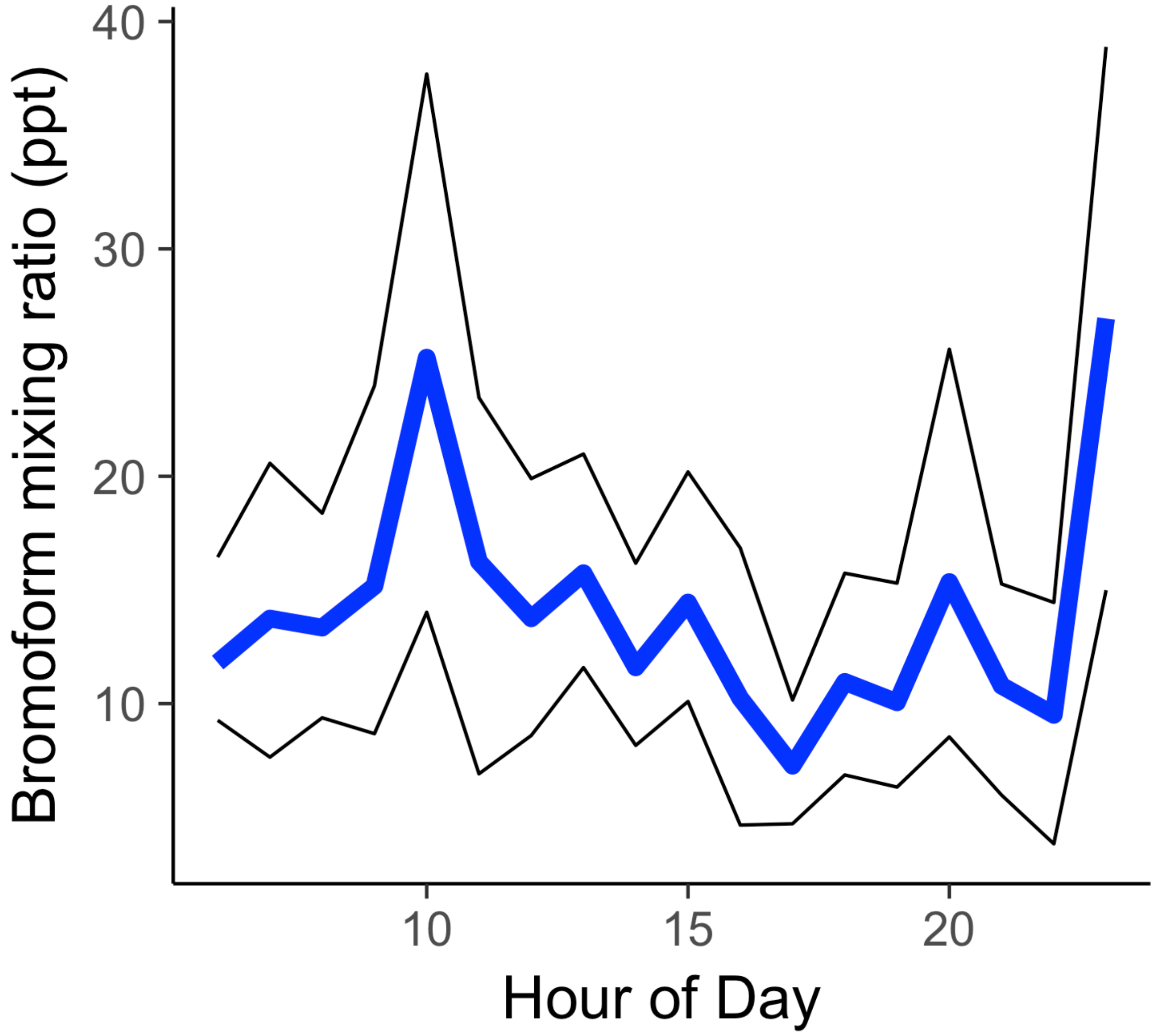

Figure: Mean diurnal cycle, calculated from all measurements binned by hour. The black lines above and below signify the 95 % confidence interval.

> 4. *The references to previous measurements (e.g. in Table 1) are not up-to-date. There have been a number of new studies in recent years that should be included (including a possible reference to the HALOCAT database).*

Response: The reviewer kindly noted that the Table of observations included in the paper is not up to date. We thank the reviewer for highlighting this oversight on our part.

Remedial action: The table has been updated to include some recent measurements. The updated measurements from Cape Point have been included in this table.

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	Yokouchi 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	Fuhlbrugge et al. 2016a	Open ocean
R/A Falcon	July 2014	2-16 ºN	0.99	3.78	1.90	Fuhlbrugge 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	Yokouchi et al. 2005	Coastal
San Cristobol Island	Feb - Mar 2002, 2003	0.92 ºS	4.2	43.6	14.2	Yokouchi et al. 2005	Coastal

Peruvian upwelling	Dec 2012	5-16 ºS	1.5	5.9	2.9	Fuhlbrugge 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 (revised)**	**Coastal**
Cape Grim	2003	40.7 ºS	1.3	6.4	2.9	Yokouchi 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

In response to the reviewer's specific comments please see below.

P1, L2: why is the location "unique"?

Response: Cape Point is unique in receiving clean air from the Southern Ocean and occasional influences from urban-anthropogenic sources.

Remedial action: The word unique has been removed.

P1, L13-14: the "sweet odour similar to chloroform" is irrelevant

Remedial action: This has been removed.

P1, L14: what are these anthropogenic sources of bromoform? Please list with references. What fraction of global emissions are likely to be anthropogenic?

Response: The likely anthropogenic sources in Cape Town are the nuclear power plant north of Cape Town and the numerous water treatment plants throughout the city that relies heavily on chlorination processes. From Quack and Wallace (2003) and Carpenter and Liss (2000), the estimated global budget of bromoform is total and divided into 1.6 (0.4–2.7) Gmol Br yr^{-1} for kelp, ~2 Gmol Br yr^{-1} phytoplankton and 0.346 Gmol Br yr^{-1} anthropogenic (Quack and Wallace, 2003).

Remedial action: These have been added to the text which now reads:

Bromoform, apart from the few anthropogenic sources including water chlorination, nuclear power and rice paddies, is naturally produced by kelp and phytoplankton in the upper layers of the ocean (Quack and Wallace, 2003). It is estimated that globally between 2.2 x 10^{11} – 2.5 x 10^{12} g CHBr3 yr^{-1}i is produced of which only 3.0 x 10^{10} g CHBr3 yr^{-1} is anthropogenic, the rest being from natural sources, including 1.3 x 10^{11} g CHBr3 yr^{-1} from brown algae and 1.7 x 10^{11} g CHBr3 yr^{-1} from phytoplankton (Quack and Wallace, 2003, Carpenter and Liss, 2000).

> *P1, L16: "Outgassing to the atmosphere" sounds better than "Atmospheric outgassing" P2,*

Remedial action: This has been changed as requested.

> *L20: replace "within this region" with "in the tropics" P2, L22: same as above*

Remedial action: These have been replaced as requested.

> *P2, L22: What is meant by "discrete shipboard measurements"?*

Response: In this we intended to imply measurements that occur only when there are cruises which happen to pass through the region/ area of interest. They are not fixed point measurements and have not been made over long periods of time. I.e. they are highly irregular.

Remedial action: The sentence has been revised to read:

"Existing data in this region tend to be from transient ship cruises, which only provide a discrete snapshot at the point in space/time that the cruise transects the area of interest."

> *P2, L23-24: "No time series . . .. Like Cape Point.". The authors need to be careful with this sentence. Do they mean there are no time series in Africa, the tropics or globally? The latter 2 would both be wrong. Cape Point of course is also not in the tropics.*

Response: We thank the reviewer for highlighting this potential ambiguity.

Remedial action: The sentence has been revised to be more accurate. It now reads:

"No time series of measurements at a fixed point currently exists for a coastal site in southern Africa. Furthermore, the Cape Point monitoring station fills a critical Southern Hemisphere latitudinal gap between Cape Matatula, American Samoa (14 ºS) and Cape Grim, Tasmania (41 ºS; Brunke and Halliday, 1983)."

> *P2, L27-28: please explain why these gases might play a significant role in climate change.*

Response: Ozone in the upper troposphere is a potent greenhouse gas and bromine initiated destruction of ozone occurs in this region.

Remedial action: An explanation of the role of ozone in the upper troposphere and it greenhouse potential in this region have been added to in the text.

> *P2, L31: delete "to", i.e. "a unique location from which to measure. . .."*

Remedial action: This has been deleted.

> *P2, L33: what is meant by an "intermediate air sample"?*

Response: An intermediate air sample is a marine air sample that has become modified with continental air masses (as defined in Brunke et al., 2004.). This is indicated by the radon concentration; marine air typically has a radon concentration below 350 mBq m^{-3}, intermediate (or mixed) air samples between 800–1500 mBq m^{-3} and continental air at above 1500 mBq m^{-3}. mixed air contains marine, continental and urban influences (Brunke et al., 2004).

Remedial action: The text has been updated to: mixed air as defined in Brunke et al. 2004.

> " … ranging from marine sources (baseline), to continental and mixed air (baseline, continental and urban influences; Brunke et al 2004)."

> *P3, L1: Why might the subtropical location of CP make the region be an important source bromoform? Do you mean that if the region were a strong source of bromoform then this would be significant globally? I assume this is because it is relatively close to the tropics where convection could potentially transport it to the stratosphere? Please explain this sentence more clearly.*

Response: A bit of both. That this could be a large contribution to the global budget of bromoform. Although in all likelihood the contribution from the sub-tropics is going to be small, the significance of its proximity to the tropics and the deep convection cannot be overlooked.

Remedial action: The paragraph has been revised to redress this ambiguity. It now reads:

"The subtropical location of Cape Point may make this region a particularly significant source of bromoform to the atmosphere, specifically when considering potential impact on global ozone budgets; the region lies in close proximity to the tropics where deep convection is able to rapidly transport the outgassed bromoform into the UT/LS. It is here that bromine initiated catalytic ozone destruction occurs. Moreover, data recorded here is of particular value as the size of the contribution from Cape Point region is to date largely untested."

> *P3, L5: "biologically active" or similar is possibly better than "highly productive". Is the Southern Ocean active everywhere or just in certain regions? I assume the authors are referring to phytoplankton rather than macroalgae?*

Response: The Southern Ocean is well recognised as a high productivity low nutrient ecosystem and to a first approximation exhibits homogeneously high phytoplankton growth. There are of course fine scale various in time and space, but for the purposes of this work we suggest that the approximation of homogeneous high biological activity is sufficient. In this pelagic environment we are of course referring to microalgal productivity and not kelp.

Remedial action: The terms have been replaced as suggested by the reviewer. The text has been amended to remove any ambiguity.

> *P3, L11: The location of the local and regional kelp beds is highly relevant to the arguments used later in the paper. Is it possible to indicate on Figure 1 where the main kelp beds are?*

Remedial action: The discussion has been modified to expand on location and type of kelp found in area surrounding Cape Point and to the north up the coast. Please also see earlier comment.

> *P4, L5: define the term "GC-ECD"*

Remedial action: This has been done.

> *P4 L7: insert "the", i.e. "as per the method"*

Remedial action: This has been done.

> *P4, L12: What is meant by a "quasi-discrete sampling pattern"? "Quasi-continuous would be more appropriate, although you could simply say that 131 samples were collected during the period xxx to yyy.*

Response: Later the reviewer asks for the description of 'quasi-discrete' to be changed to 'quasi-continuous'.

Remedial action: We have followed the reviewers' suggestions here and later.

> *P4, L18: Please explain what the relevance of the sentence about gas viscosity is.*

Response: As the temperature of a gas increases so does it's viscosity and so the flow rate decreases. In modern GC systems an electronic pressure controller regulates the pressure at the head of the column to ensure a constant flow. The simplicity of the GC-ECD used here system meant that no adjustment could be made to account for changes in gas viscosity. This can have an effect on the separation of samples. Since this was consistent through all our samples this does not pose a problem, but the authors initially thought this fact should be noted for completion sake.

Remedial action: The sentence has been removed as it appears to be causing more confusion than clarity of understanding. A statement about the gas pressure being run at constant pressure has been added to the text as follows:

“Sampling

... 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 maintained through the column at the start of the each analysis. The oven was held 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 new temperature was reached.”

> *P4, L20: a ramp rate of 65 degrees per minute is very fast. Why was this necessary as it surely doesn’t help with peak separation?*

Response: The simple answer is that the GC model was not able to ramp at any other rate. A temperature could be programmed into the controller, resulting in a current being applied to the element and heating the oven. It was determined experimentally that this heating occurred at 65 ºC per minute. Once each ‘ramp’ or increase was complete, the oven was maintained at the new temperature for a period of 5 minutes, allowing for separation at that temperature to occur.

Remedial action: The paragraph has been rewritten to remove mention to a temperature ramp. The word ramp is a technical term that is not appropriate in this context. Please see the updated text above.

> *P4, section 2.3: there are a few details missing in this section which should be included. Was the air stream dried before pre-concentration? How did you measure the volume of air trapped? Did the system trap CO_2 and, if so, how did this affect the chromatography? An example chromatogram would also be helpful as well as some discussion on possible co-elutions (see earlier comment).*

Remedial action: The text in the methods section has been revised and expanded. As per the text sample volume was calculated based on sampling rate and time. A flow rate of 100 ml min^{-1} through the trap was measured on a digital flow meter. Since the trap adsorbents and desiccant remained constant so did the gas flow rate. This was checked on a weekly basis. A time of 15 minutes was used to collect the sample resulting in a 1.5 l sample volume.

The trap was flushed with helium (grade 5.0) before and after trapping and adsorbents were picked specifically such that they did not retain CO_2 . The relevant paragraphs now read as follows:

“Sampling …

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 trap, samples were dried using magnesium perchlorate held in glass moisture trap, as per 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 adsorbent 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."

See above for for discussion of co-elution and note that as this is not intended to be a methods paper and given the method was previously published elsewhere, we do not feel the publishing this graph in ACP adds enough to the work here to justify its inclusion. However should the reviewer/editors deem it is worthy of inclusion we would be happy to edit it and include for publication.

> *P5, calibration section: this section needs some further clarification as it is not clear how the calibration was done. How does 100-300 μl of pure bromoform equate to a concentration? Was it diluted prior to trapping? What is meant by a calibration loop? How were the 99% accuracy and 12% precision estimates derived?*

Response: We would like the thank the reviewer for bringing our attention to the ambiguity in this section and hope our description below is now clear. **Attention has also been paid to calibrant sample flow and trapped volume. We apologise for the calibration error in the manuscript as originally submitted.**

Remedial action: The calibration section in the methods has been rewritten and now reads as follows:

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 (**Wevill 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. "**

> *P5, Figure 2: Normally the fixed entity (mixing ratio) would be on the x-axis and the variable entity (peak area) would be on the y axis? What do the error bars represent*

(how many samples)? Why is the uncertainty given in the mixing ratio rather than the peak area?

Response: The calibration is done by the injection of a known number of loops. The number of loops is an arbitrary measure however. What is of much more interest is the measured peak area and how this relates to actual mixing ratios since the peak area is related to the concentration or mixing ratio. By controlling the number of loop injections we effectively control the peak area so this goes on our x axis. The mixing ratios are then calculated from the measured peak areas. The uncertainty displayed through the error bars reflects variations in the measured peak area from repeated injections. **An example of the calibration curve calculated in this manner can be found in Wevill and Carpenter (2004).**

Remedial action: As far as we can determine this figure is correct. The text has been revised to better explain the calibration curve.

P6, L6: "flow path" not "flow pass".

Remedial action: This has been corrected in the revised manuscript.

P6, L31: What is meant by "rapid shifts" on the 19th, 29th and 30th?

Response: The rapid shifts referred to the rapid changes in wind direction.

Remedial action: The text has been amended to reflect this.

"The transit of weaker cold fronts caused the occasional rapid shift in wind direction …"

P6-7: what is the significance of wind speed?

Response: Wind speed is important in gas measurements for a number of reasons. The bromoform sea-air gas flux rate may be approximated as a function of either the square or cube of the wind speed; e.g. Nightingale et al., (2000): $k = 0.31u^2(Sc/660)^{-1/2}$. The rate of atmospheric dilution also increases with wind speed. The wind speed can also be an indication of wind fetch. These factors combined play a role in determining the observed mixing ratio at any given point in time.

Remedial action: A discussion about the role of wind speed in the variation of bromoform mixing ratios has been added to the results and discussion.

P8, L7: "Measurements of bromoform at all ranges were recorded at CO levels below 100 ppb". If this is the case why are there no red or orange circles in this CO range?

Response: One of the difficulties of polar plots is that the data are binned by wind direction and averaged. In this case the smaller measurements biased the few high measurements that occurred at below 100 ppb.

Remedial action: This figure has been removed and the sentence revised to be more accurate in the updated results section.

> *P8, L11: I fail to see the 2 periods of elevated ozone referred to.*

Remedial action: The time series figure has been updated and annotated to highlight the event periods. The discussion regarding ozone and in particular elevated ozone have been revised.

> *P9, Fig.6: What is the impact of boundary layer height on the measurements? This might also explain some of the variability. I am not convinced that the observed variation in ozone is sufficient to be able to get any real meaning from the analysis in Fig. 6.*

Response: The marine boundary layer height at Cape Point was calculated from twice daily radiosonde measurements made at Cape Town International airport, 60 km northeast. This is a rough approximation of the MBL at Cape Point. The height of the MBL was determined by the surface and elevated temperature inversion methods (Seibert et al., 2000; Seidel et al., 2010). The calculated heights ranged from a minimum of 91 m to a maximum of over 4000 m (Kuyper 2014).

Changes in the MBL height have in past studies been reported to influence the measured concentration of bromoform (Fuhlbrügge 2013). Despite this strong relationship reported by Fuhlbrügge et al (2013), no such relationship between bromoform and MBL at Cape Point could be established in the data presented here This could be explained due to a variety of factors. Firstly uncertainties may arise due to the approximation of MBL from Cape Town International Airport (some 60km away), as this might not be representative of conditions at Cape Point. In addition to this, if the bromoform measured at Cape Point was not locally sourced it would therefore independent of local MBL height and no effect would be expected. It could be that the MBL height as ascertained at Cape Town International airport is independent of the MBL at Cape Point and therefore not significant. At this stage we do not have enough information to separate or elaborate further on these speculations.

Remedial action: We have added information relating to the MBL at Cape Town International Airport to results and discussion sections.

> *P9, L9: What are the stated uncertainties in the reported maximum and minimum measurements and how do these differ from the somewhat lower uncertainties in the mean?*

Response: The uncertainties were calculated as a function of the precision of the measurements. The uncertainty in the mean is the standard deviation from the calculation of this value.

Remedial action: The uncertainties of the measurements have been reported as the percentages in the text rather than the calculated values.

> *P10, Fig.7: It would help if the 3 periods of interest were highlighted (shaded?) on the Figure. Can the authors say something about the very low values of bromoform on the Figure? There are a number of points very close to zero. Where does the air come from at these times? Can the authors be sure that this is not a measurement problem – it seems unlikely that values would drop to zero in a region where bromoform is generally rather high?*

Response: The values reported are around 4-5x above the calculated LOD and therefore are unlikely to be an artifact. We see similar low "background" concentrations reported in the literature making these observations consistent with similar studies elsewhere.

The calibration curve indicates that the system displayed a linear response to bromoform over a range of **0-40** ppt. An injection of 100 l equates to **11.8 ppt**. As to the rapid changes, yes this can be expected. We see this in other regions (Pyle et al. 2011).

Based on the original calibration data, the wind direction at Cape Point when the bromoform mixing ratios were less than 5 ppt (n = 5) was predominantly from the west to northwest (245-320º). This is entirely within the background air sector, and further confirmed by radon concentration (< 250 mBq m^{-3}). These measurements typically occurred late in the afternoon/ early evening or in one case, before sunrise. This has been revised in the results and discussion using the updated figures and data.

Under the revised dataset there were 20 (14.8 %) measurements of bromoform less than 5 ppt. The wind direction was predominantly from the south (30 %), southwest and northwest (20 and 15 %, respectively). There was also a significant contribution from due east (20 %) of Cape Point. Of these measurements 4 had radon concentrations above 750 mBq m^{-3} and made up the observations from the east. The remainder of the measurements were all or marine origin (radon < 350 mBq m^{-3}).

Remedial action: The figure has been updated to include vertical lines to mark the events. See time series plot earlier.

> *P10, L4-5 and Fig.8: The wind speed associated with the higher concentrations to the NE and West seem very similar to me (one is described as "high" and the other as "intermediate to low"). I cannot really see any difference.*

Response: The reviewer is correct in their assessment. The wording of this sentence has been updated to be correct and less ambiguous.

Remedial action: The results and discussion sections have been completely revised. As per the reviewer's comments we have removed the polar plots.

P10, L6: This sentence needs rephrasing. I assume the authors mean that at low wind speeds the average concentration was 30 ppt and they are speculating that this is maintained by some "low level" local sources? What does low level actually mean and perhaps showing wind speed in Fig. 7 would help the reader to see this more clearly.

Remedial action: This sentence and figure have been updated in the new results section.

P10, L12: "a background of low mixing ratios were observed from all wind directions". How does this relate to what was said in my previous comment? Was the "background" signal 10 ppt or 30 ppt? There are no data less than 10 ppt in the N, NE and SE sectors.

Response: The reviewer is correct, we had introduced ambiguity through these statements. **The reviewer is correct that the binned, mean data were greater than 10 ppt in the sectors N, NE and SE. The figure has been over-interpreted by the authors; especially in light of the fact that the values represented are binned means and not the actual observations.**

Remedial action: The figure and text have been revised in the updated manuscript.

P11, episodic events: it would help to have a repeat time series for these events so the reader can see the patterns/correlations more clearly. Alternatively please put all data in one Figure (Fig 7) and perhaps some more axis markers to help distinguish between days.

Remedial action: An updated figure 7 has been added to the text. This has also been annotated to highlight the three events.

Time series plots of the three events have also been added to the text in the results and discussion of the updated manuscript.

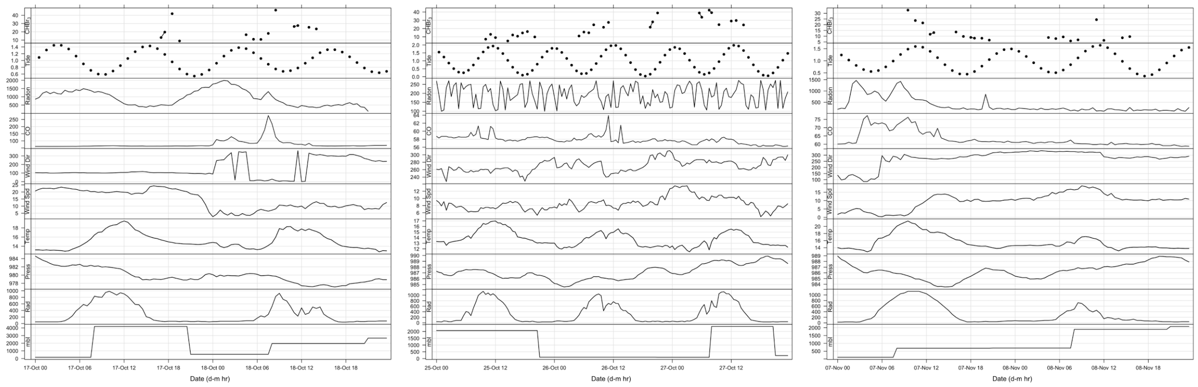

Figure: Time series sub-plots expanding the elevated bromoform event days. From left to right Events 1 - 3. (Figures shown separately in the revised manuscript)

> *P11, L11 – P12, L1: The authors state that the concentration of bromoform decreased slowly between the maximum on the 18th until the 23rd. The only problem here is that there is a large gap (several days?) in the data when we have no idea what is happening. To describe this period as a single “event” is therefore a little odd.*

Response: We thank the reviewer for raising this point regarding assumptions of data over gaps.

Remedial action: The event windows have been refined to exclude the data gaps. The text has been amended to reflect that event 1 terminates with the cessation of sampling at the end of the 18th. The same applies for the third event where a data gap existed in the earlier defined window. **Please also see the earlier time series plot.**

> *P12-13, Event 2: The winds are predominantly from the west-north-west but the back trajectories suggest that the air is coming from the south and east. This apparent contradiction needs to be explained. In fact the trajectories in Figure 10 for Event (b) are dated November 2011, not October. Have the authors used the correct trajectories?*

Response: The reviewer is correct, the incorrect back trajectories in figure b were inserted. The authors would like to thank the reviewer for the observation.

Remedial action: The back trajectories have been updated and corrected.

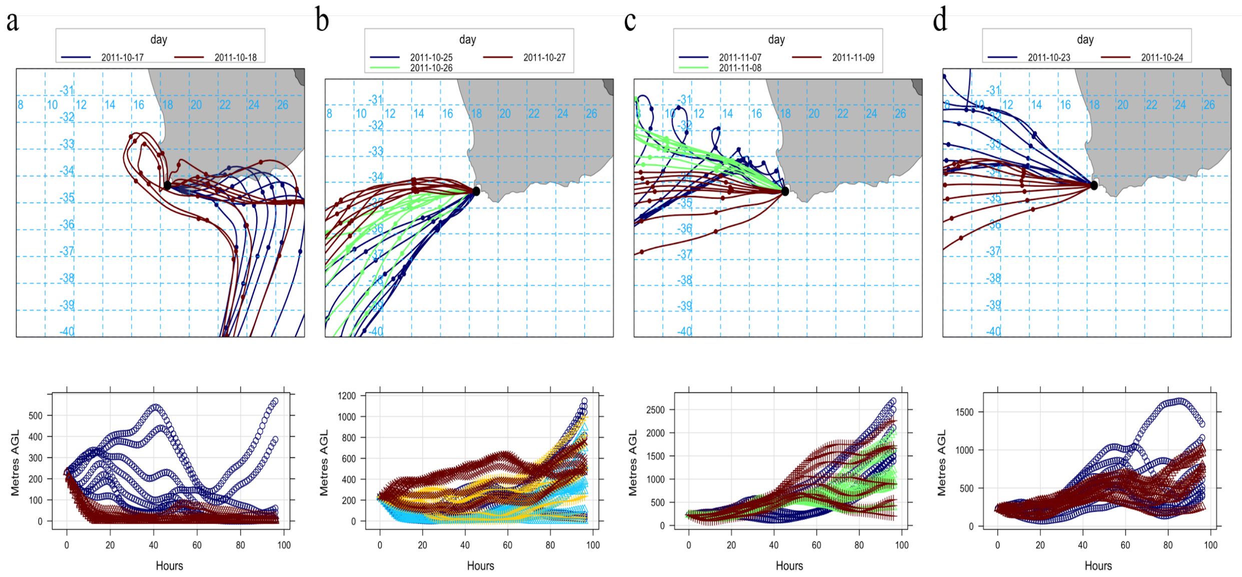

Figure: Composite daily back trajectories for the selected Events (a) E1 17 – 18 October 2011, (b) E2 25 – 27 October 2011, (c), E3 7 – 9 November 2011, (d) Background samples 23 - 24 October 2011. Trajectory heights for the events are displayed below. The colours and dates correspond respectively for each event. (Only events 1 and 3 shown, separately in the revised manuscript)

> *P13, Event 3: again it is very difficult to follow the ups and downs in the various parameters. I find it hard to pick out 2 events in elevated ozone (line 11). Again there is a large gap with no data which makes linking the period more difficult. The authors cannot say that "bromoform rose to a maximum of 70.2 ppt" because there is a gap.*

Remedial action: The text has been revised to reflect the gaps in the bromoform data. The time series plot has been updated and annotated to highlight the events. Please see the time series figure above.

> *P14, Section 4.1: this section is highly speculative using such terms as "circumstantial evidence" and "tentatively appear"*

Response: Given the limited data set it is not easy to be decisive. The words 'circumstantial evidence' and 'tentatively appear' are entirely appropriate in the context of the data on which they are based.

> *P14, L14-15: If air is flowing from the Southern Ocean in a "north-westerly direction" over Cape Town, how is it possible for this air to then pass over Cape Point which is due south of Cape Town?*

Response: As a result of the Coriolis effect, anticyclones rotate in a clockwise direction in the Southern Hemisphere. A quick look at a typical synoptic chart (url) for a NW wind in winter in Cape Town will hopefully convince the reviewer that as the anticyclone passes south of the African continent, air flows from the Southern Ocean, over Cape Town and then down to Cape Point. These are the conditions which are typical in Cape Town winter and are those experienced in the description above.

Remedial action: The text has been revised to be more clear and accurate. The discussion has been entirely revised.

> *P14, L18-20: there is really very little concrete evidence for this anthropogenic source and its impact on the measurements at Cape Point. There is more coast directly to the north of Cape Town so even if the air was coming from this direction and picking up anthropogenic emissions, what is to say that the bromoform and CO/radon are not coming from completely different sources?*

Response: Nothing; it is entirely possible the $CHBr_3$ was entrained over the coast and then the CO over the city later. We intended to imply here that an Anthropogenic source could not be ruled out in these samples as the air had been influenced by human activities and will revise the wording accordingly.

Remedial action: Speculative text regarding source attribution has been removed.

> *P14, L21-22: how well do CO and Radon correlate for the entire period. It is hard to tell when they are on separate graphs using different axis ranges. It seems there are periods of high radon and low CO, but what about low radon and high CO? I assume*

> *this is unlikely if you assume a continental source for both, but it is very difficult to tell from separate figures.*

Response: Over the sampling period CO and radon measurements agree well. There are a couple of events where elevated CO can be observed while radon is low. These brief CO 'peaks' are potentially experimental artifacts but that discussion is beyond the scope of the work presented here. **Brunke et al. (2004) show the source regions of CO and radon at Cape Point, based on numerous years of measurements.**

Remedial action: The time series figure has been updated to include the radon measurements as well as the CO on the same time scale. Please see the time series figure above.

> *P14, L30: why have you not investigated the impact of tides at the local site? (see major comment above and the next comment below).*

Response: Please see the major response above. An investigation of the tides was performed. For more complete details on the tide analysis please see Kuyper, 2014. The conclusion from Kuyper (2014) were that the tides played no significant role on the variability of the measurements at Cape Point.

> *P15, L4-5: "The extensive kelp beds at CP may contribute bromoform to both the consistent baseline and extreme events observed". If this is the case, can the presence of local kelp beds not explain the entire set of measurements? Without ruling this out, the majority of the preceding discussion is surely obsolete? Where are the local kelp beds? Are they underwater or exposed at low tide? If the latter, do you see an impact of local tide time with bromoform concentration?*

Response: Please see the major response above. The kelp beds are not totally exposed at low tide. It is possible that emissions from the local kelp beds explain the majority of the variability. From the updated time series plots, it is suggested that the tide height may be a contributing factor in the elevated bromoform events, but not an independently sufficient factor. As was noted above the data presented here do not conclusively refute any of the test hypothesis A-C. The kelp beds, as the dominant bromoform source, may have also been overlooked on an event scale basis as the published emission rates were not sufficiently large enough to explain the observed elevated bromoform mixing ratios.

Remedial action: Source attribution has been removed from the discussion. The possible tidal influence has been added to the discussion, more completely. The role of tidal height and kelp exposure as a dominant source of bromoform to the atmosphere at Cape Point has been carefully explored in the revised manuscript.

> *P15, L6: what is meant by "other typical meteorological conditions"?*

Remedial action: We have added to the text:

"…such as air temperature, pressure, rainfall and global downward radiation…"

> *P15, L8: "quasi-continuous" is better than "quasi-discrete".*

Remedial action: As per the reviewer's suggestion this has been changed throughout the updated manuscript.

> *P15, L21-22, and Table 1: Why not report some median values as well as means?*

Response: None of the authors of the papers from which the values were drawn report the median values of the measurements made. We have report past results exactly as per Quack and Wallace (2003), who also report only mean values in their extensive and authoritative review.

Remedial action: The table has been updated to include more recent measurements from coastal as well as open ocean reports.

> *P15, L25-26: the evidence for an anthropogenic source of bromoform is not really apparent (see earlier comments).*

Response: The reviewer is correct and thanked for pointing this out to us. The updated figure (time series) in the results and discussion should better highlight the evidence of an anthropogenic enhancement.

Remedial action: The results and discussion have been revised as detailed above.

> *P15, L26-27: radon CO and ozone were not all elevated throughout Event 1. CO and radon were elevated at times during the period, and it is hard to say whether ozone was elevated or not. Higher ozone wouldn't necessarily be an indicator of recent anthropogenic influence. Were there no other tracers in the GC output that might help?*

Response: The only compound calibrated for at the time of the measurements, was bromoform.

Remedial action: The discussion surrounding O_3 has been revised.

> *P16, L1-7: this section is highly speculative and rather confirms that no conclusions can be drawn as to the importance of any anthropogenic source. It would be helpful if some measurements could be made near to the water processing plants to confirm the levels of bromoform.*

Response: Conducting studies into the kinetics of the bromoform production from water chlorination and the resulting budgets to the atmosphere is a whole field of research in and of itself. This however falls beyond the scope of the work presented here which sets out to try and investigate the concentrations in unpolluted baseline air from biogenic sources. The anthropogenic contribution is discussed as a potential additional source, and it may become an important factor in the rare circumstances we have evidence to show the air being sampled is anthropogenically influenced but, this is not the main thrust of the work. As noted above we do claim to conclude that there is an anthropogenic source.

Remedial action: The discussion has been revised to focus on the relationships between the bromoform measurements and the GAW measurements in background air masses. Source attribution has been limited to speculation and this has been made clear in the revised text.

> *P16, L11: I cannot easily identify a period of "moderately elevated ozone"*

Remedial action: The line has been removed. Ozone has no significant departures.

> *P16, L12: How was the ozone "biogenic in origin"?*

Response: The authors were attempting to imply that the ozone was stratospheric in origin and it was not formed from anthropogenic precursors.

Remedial action: The line regarding '*biogenic in origin*' has been removed.

> *P16, L15: "from the west" - see point earlier about the discrepancy between measured wind direction and the back trajectories.*

Remedial action: We would like to thank the reviewer again for this observation and the back trajectories have been amended accordingly.

> *P16, L16: there is no clear evidence in this analysis that supports the theory of ozone- induced bromoform release.*

Response: The authors would like to thank the reviewer for their comments on this.

Remedial action: The results and discussion have been rewritten.

> *P17, L6: the Benguela current is far to the north of CP according to Figure 1. How will this affect the concentrations at CP during Event 2? I do however agree that a study of the local kelp would be a sensible thing to do.*

Response: The Benguela Current is not exclusively far to the North, but extends all the way down to Cape Town. Moreover, with an atmospheric lifetime of 24 days it is quite possible for bromoform formed in the Northern (and more intense) Benguela to travel to Cape Point. Under north-westerly winds air is drawn from the Benguela region over Cape Town and to Cape Point. Species composition of seaweeds in the region has been discussed above. The over interpretation of the data may have been a function of stretching all known sources to the limit to explain the elevated mixing ratios. This should be mitigated with the revised data, which is much more inline with previous measurements.

> *P17, L19: It has not been proven that the anthropogenic source of bromoform was strong during Events 1 and 2. This statement is inaccurate. In fact the whole of this final paragraph is highly speculative.*

Response: We agree with the reviewer. That line should not have appeared in the final version.

Remedial action: The discussion text has been entirely revised to indicate that this is our speculation and not a fact.

> *P17, conclusions: The whole section will need to be rewritten once the various issues above have been addressed. I do also note that the extremely high values reported from Gran Canaria were measured many years before the majority of data in Table 1, so, with due respect to the original authors, I would perhaps treat these data carefully. There have been substantial improvements in analytical technology and calibration since these measurements were obtained.*

Response: The reviewer is correct that the conclusions need to be updated along with the results and discussion sections.

Response: The conclusions have been revised accordingly with the Results and Discussion sections as per the reviewer's comments and suggestions. The Gran Canaria data will be treated with some caution.

The authors would like to again thank the reviewer for their time and effort in examining the paper. Their comments have been helpful in greatly improving the quality of the paper.

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Response to Reviewer #2

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 2. 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 skilfully 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 error caused here earlier.** 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 (**Wevill 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.

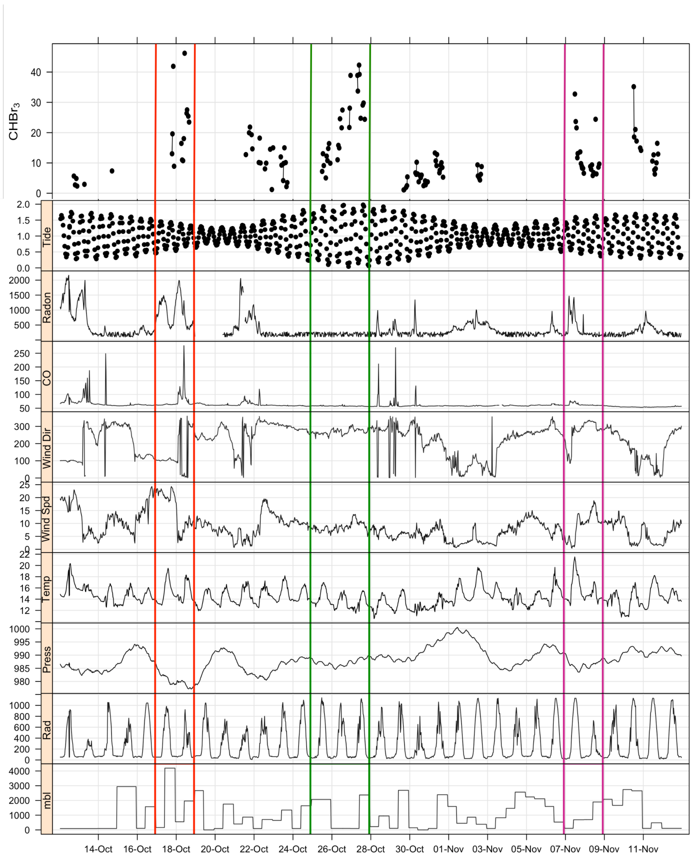

Figure: Time series plot of measurements at Cape Point during October / November 2011. Events are highlighted by the coloured lines: E1 = red, E2 = green, E3 = violet.

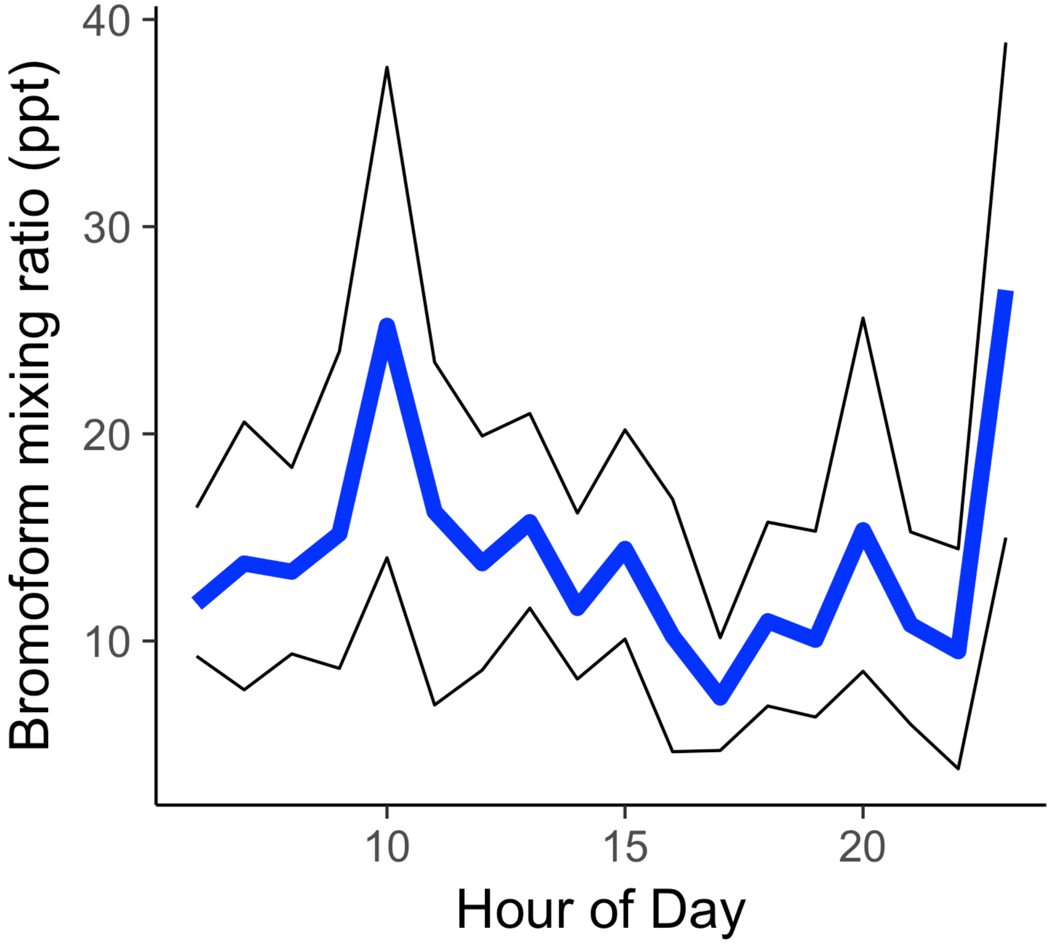

Figure: Mean diurnal cycle, calculated from all measurements binned by hour. The black lines above and below signify the 95 % confidence interval.

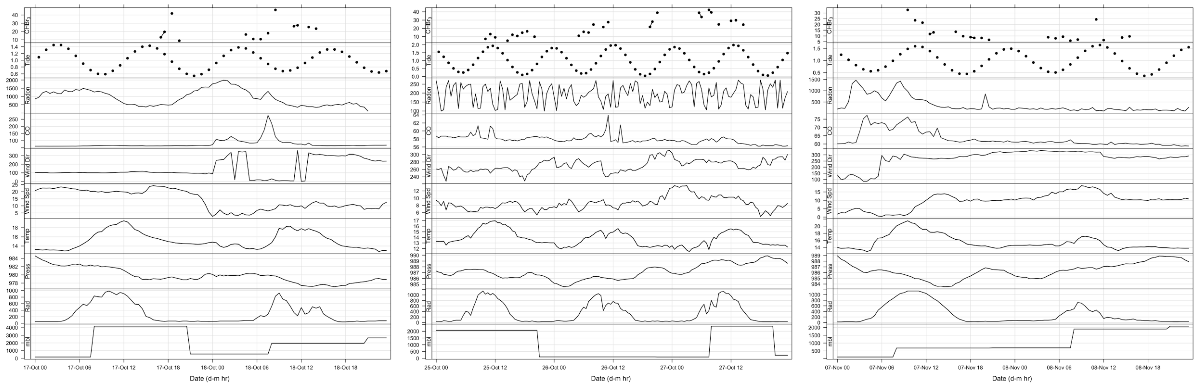

Figure: Time series sub-plots expanding the elevated bromoform event days. From left to right Events 1 - 3. (Expanded in the text)

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.

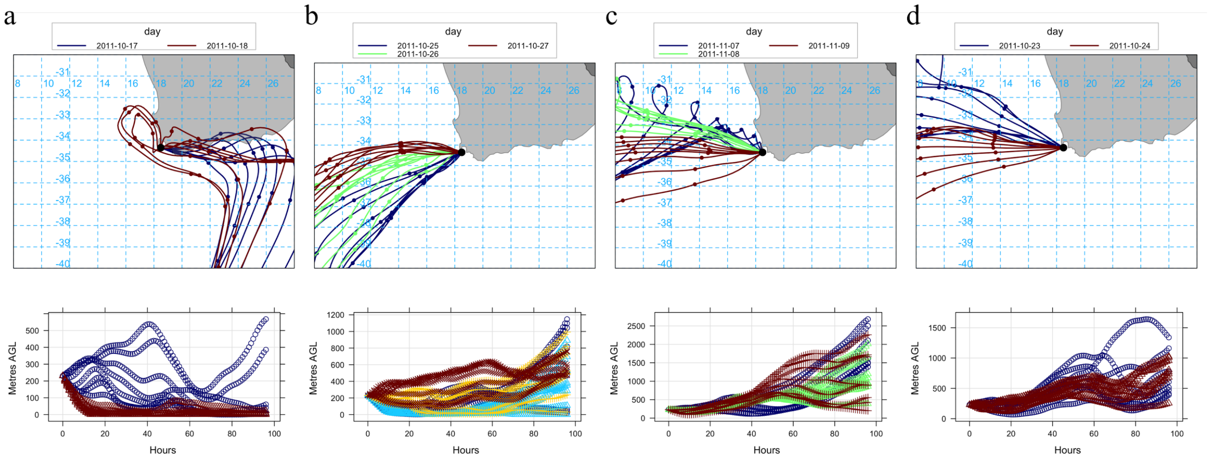

Figure: Composite daily back trajectories for the selected Events (a) E1 17 – 18 October 2011, (b) E2 25 – 27 October 2011, (c), E3 7 – 9 November 2011, (d) Background samples 23 - 24 October 2011. Trajectory heights for the events are displayed below. The colours and dates correspond respectively for each event. (Events 1 and 3 shown separately in the revised manuscript)

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	Yokouchi 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	Fuhlbrugge et al. 2016a	Open ocean
R/A Falcon	July 2014	2-16 ºN	0.99	3.78	1.90	Fuhlbrugge 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	Yokouchi et al. 2005	Coastal
San Cristobol Island	Feb - Mar	0.92 ºS	4.2	43.6	14.2	Yokouchi et al.	Coastal

	2002, 2003					2005	
Peruvian upwelling	Dec 2012	5-16 ºS	1.5	5.9	2.9	Fuhlbrugge 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**	**Kuyper et al. 2012; Kuyper 2014 (revised)**	**Coastal**
Cape Grim	2003	40.7 ºS	1.3	6.4	2.9	Yokouchi 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.

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

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Abstract. Bromoform mixing ratios in marine air were measured at Cape Point Global Atmospheric Watch Station, South Africa. This represents the first such bromoform data set recorded at this location. Manual daily measurements were made during a month long field campaign (austral spring 2011) using a GC-ECD with a custom built front end thermal desorption trap. The measured concentrations ranged between 1.1 and 46.2 (± 7.4 %) ppt with a mean of 13.2 ± 9.7 ppt. The highest mixing ratios recorded here occurred at, or shortly after, low tide. The diurnal cycle exhibited an morning and evening maximum with lower concentrations throughout the rest of the day. Initial analysis of the data presented indicate that the local kelp beds were the dominant source of the bromoform reported, a small anthropogenic contribution can not however be entirely excluded.

1 Introduction

1.1 Bromoform in the marine environment

Bromoform ($CHBr_3$) is a brominated methane-like hydrocarbon which is a volatile liquid at room temperature. Bromoform, apart from the few anthropogenic sources including water chlorination, nuclear power and rice paddies, is naturally produced by kelp and phytoplankton in the upper layers of the ocean (Quack and Wallace, 2003). It is estimated that globally between 2.2 x 10^{11}-2.5 x 10^{12} g $CHBr_3$ yr^{-1} is produced of which only 3.0 x 10^{10} g $CHBr_3$ yr^{-1} is anthropogenic, the rest being from natural sources, including 1.3 x 10^{11} g $CHBr_3$ yr^{-1} from brown algae and 1.7 x 10^{11} g $CHBr_3$ yr^{-1} from phytoplankton (Carpenter and Liss, 2000; Quack and Wallace, 2003). Outgassing to the atmosphere constitutes the largest known oceanic loss of bromoform, which is relatively stable to chemical loss pathways (hydrolysis and nucleophilic substitution) in seawater at ambient temperatures (Carpenter and Liss, 2000; Quack and Wallace, 2003; Jones and Carpenter, 2005). The production of bromoform in the oceans forms an important step in the biogeochemical cycling of bromine through the Earth system (Warwick et al., 2006; Hossaini et al., 2010).

The production of bromoform by phytoplankton and kelp has been shown to be stimulated through oxidative stress (Quack and Wallace, 2003; Palmer et al., 2005; Küpper et al., 2008) and a maximum rate of bromoform production has been linked with the photosynthetic cycle (Collén et al., 1994). However, the specific reasons for bromoform production in these organisms remains unknown (Moore et al., 1996; Paul and Pohnert, 2011; Kuyper, 2014). Production by kelp is thought to be the dominant natural bromoform source to the marine environment, (Carpenter and Liss, 2000). Different species of kelp are known to produce bromoform at varying rates (e.g. Nightingale et al., 1995). Laboratory studies have measured significantly higher mixing ratios from kelp, per weight, when compared to phytoplankton (Tokarczyk and Moore, 1994; Moore et al., 1996; Carpenter and Liss, 2000). However, kelp species are coastally constrained, while phytoplankton are able to cover hundreds of square kilometres (Jennings et al., 2001; Kudela et al., 2005). A question remains regarding the dominant contribution to the global bromoform budget.

1.2 Implications for atmospheric chemistry

The rate of outgassing to the atmosphere, gas flux rate, is proportional to the wind speed and the solubility of the gas (Liss and Merlivat, 1986; Wanninkhof, 1992; Nightingale et al., 2000). The wind speed is also a measure of dilution in the atmosphere. Increasing wind speeds result in a larger fetch and atmospheric dilution (Quack and Suess, 1999). The majority of the outgassed bromoform remains below the tropopause, with a small amount escaping to the stratosphere (Warwick et al., 2006; Hossaini et al., 2010; Saiz-Lopez et al., 2012). Photolysis of bromoform is the dominant sink once in the atmosphere, which results in an atmospheric lifetime of 2-3 weeks (Carpenter and Liss, 2000; Quack and Wallace, 2003). The photolysis of bromoform releases bromine radicals into the atmosphere. These bromine radicals are an important catalyst in the destruction of ozone in the upper troposphere and lower stratospheric region (Warwick et al., 2006; Hossaini et al., 2010). Ozone in this region plays two key functions: in the upper troposphere (UT) ozone is a potent greenhouse gas, whereas in the lower stratosphere (LS) it forms part of the ozone layer, absorbing incoming UV radiation (Saiz-Lopez et al., 2012). In the UT bromine radicals, released predominantly from bromoform, are known to catalytically react with ozone. This results in the destruction of the ozone and subsequent loss from the region (Ashmann et al., 2009; Hossaini et al., 2010; Saiz-Lopez et al., 2012). Thus, bromine chemistry could play a significant role in climate change (Hossaini et al., 2010; Saiz-Lopez et al., 2012).

Estimates have been made of both the amount of bromoform reaching the upper troposphere and the magnitude of the impact this has on climate change. These estimates are based on poorly constrained source emissions from the global ocean (Warwick et al., 2006; Hossaini et al., 2010). It is estimated that between 1.6 and 3.0 ppt of inorganic bromine is contributed directly from bromoform to the lower stratosphere (Ashmann et al., 2009). The background atmospheric bromoform mixing ratios are estimated to be 1-2 ppt. However, local mixing ratios can be elevated above this. This typically occurs in areas of strong upwelling and in tropical coastal regions (Quack and Wallace, 2003). The skill of atmospheric chemistry models would be greatly enhanced if there was better quantification of the source strength of bromoform, and in turn, its impact on bromine radicals and ozone chemistry in different regions. Such enhancement of modelling capacity would lead to a vastly improved understanding of the roles of source and product gases in the UT/LS region.

Quantifying inventories of bromoform emissions is thus critical in better characterising the oxidative capacity of the atmosphere. This is particularly pertinent in the tropics, where deep convection results in a greater percentage of bromine radicals reaching the UT/LS region (Hossaini et al., 2010; Saiz-Lopez et al., 2012). Understanding the sources in the tropics is therefore of great specific scientific interest (Palmer and Reason, 2009). However, there exists a paucity of measurements of bromoform in the tropics (Palmer and Reason, 2009). Existing data in this region tend to be from transient ship cruises, which only provide a discrete snapshot at the point in space/time that the cruise transects the area of interest. No time series of measurements at a fixed point currently exists for a coastal site in southern Africa. Furthermore, the Cape Point monitoring station fills a critical Southern Hemisphere latitudinal gap between Cape Matatula, American Samoa (14 °S) and Cape Grim, Tasmania (41 °S) (Brunke and Halliday, 1983).

1.3 Significance of Cape Point location

Here we present the first ever bromoform dataset recorded at the Cape Point Global Atmospheric Watch (GAW) station (34.3 °S 18.5 °E, Fig. 1). This station offers a unique location from which to measure bromoform mixing ratios in a subtropical region, but is also suitable to sample air from the south Atlantic and Southern Ocean. Wind direction and radon concentration ($^{222}\mathrm{Rn}$) at Cape Point have been extensively used to classify the arriving air masses (Brunke et al., 2004; Whittlestone et al., 2009). A mixture of air sources have been recorded at Cape Point; ranging from 100 % clean marine (baseline, $^{222}\mathrm{Rn}$ <350 $\mathrm{mBq\,m^{-3}}$) to 100 % continental (with/without anthropogenic influence, $^{222}\mathrm{Rn}$ >1500 $\mathrm{mBq\,m^{-3}}$) and intermediate (mixture of baseline and continental, 800 < $^{222}\mathrm{Rn}$ < 1500 $\mathrm{mBq\,m^{-3}}$) adapted from Brunke et al. (2004). The subtropical location of Cape Point may make this region a particularly significant source of bromoform to the atmosphere, specifically when considering the potential impact on global ozone budgets. The region lies in close proximity to the tropics where deep convection is able to rapidly transport the outgassed bromoform into the UT/LS. Where bromine initiated catalytic ozone destruction occurs. Moreover, data recorded here is of particular value as the size of the contribution from Cape Point region is to date largely untested. The Cape Point data presented here represent the first of their kind in Africa, or for the South Atlantic region (Cox et al., 2003).

The Southern Ocean is largely regarded as a highly biologically active region, especially during the spring and summer (Arrigo et al., 2012). This region may provide a significant contribution to the global atmospheric loading of bromoform. However, the Southern Ocean is widely under-sampled when it comes to bromoform measurements. Although there have been sporadic ship cruises to the Southern Ocean (Ziska et al., 2013), no long term work has been done in the Atlantic sector of the Southern Ocean. The data presented here therefore offer the first fixed point measurements of bromoform in air from the Atlantic sector of the Southern Ocean.

In addition to receiving baseline air from the south Atlantic and Southern Ocean, Cape Point also sits above extensive kelp beds. The extensive kelp beds extend along the South African coast to the north and east of Cape Point. A variety of remote sensing techniques were used to assess the extent and composition of kelp beds in 19 predefined areas along the Cape coast (Anderson et al., 2007). Their results show that kelp beds are present in all 19 areas ranging from a minimum of 11 ha coverage in Table Bay to a maximum of just under 1000 ha north towards the Namibia border. The species composition was

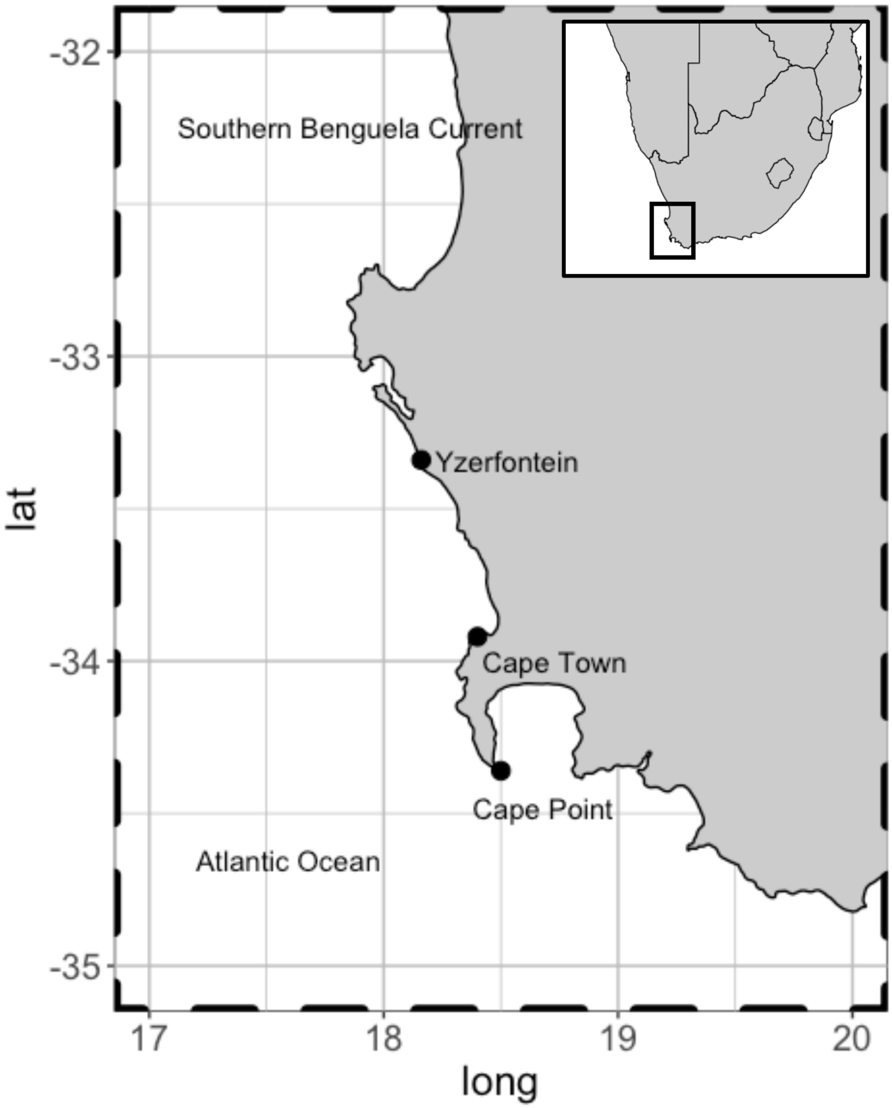

Figure 1. Location of Cape Point in relation to Cape Town. Kelp range along the entire coast. These are dominated by *Ecklonia maxima Papenfuss* south of Yzerfontein but transition to predominantly *Laminaria pallid Greville* north of Yzerfontein. Adapted from Kuyper 2014

predominantly *Ecklonia maxima Papenfuss* south of Yzerfontein, but transitioned to predominantly *Laminaria pallid Greville* north of Yzerfontein (Fig. 1). Thus, Cape Point is an ideal location to sample the open ocean, local tidally affected kelp beds, as well as the occasional anthropogenic pollution event from the greater Cape Town region; based on the seasonally varying wind direction. Addressing the paucity of data from this region will be instrumental in separating the persistent conundrum as to the major source of bromoform in the atmosphere.

2 Methods

The separation, identification and quantification of bromoform was achieved using a gas chromatograph (GC) with an electron capture detector (ECD) system. This featured a custom built thermal adsorption/desorption trap for the pre-concentration of atmospheric samples and delivery of analytes onto the GC column (Kuyper et al., 2012; Kuyper, 2014). Specific details of the sampling method in this campaign are described below.

2.1 Sampling

The measurements of bromoform were made at the Cape Point Global Atmospheric Watch station (GAW) in the austral spring of October and November 2011. The manual nature of the GC system, coupled with periods of instrument downtime, resulted in a quasi-continuous sampling pattern with a measurement frequency of approximately 45 min to 1 hour. A total of 135 discrete bromoform measurements were made in air samples during this period.

A Shimadzu GC-8A with a Perkin Elmar F-22 ECD was used to record the bromoform concentrations. A J & W Scientific DB-624 (30 m x 320 x 1.8 µm, 5 % polarity film) capillary column was used in the oven to achieve the separation of samples (Itoh et al., 1997). A 30 $\mathrm{ml\,min^{-1}}$ 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 $\mathrm{ml\,min^{-1}}$ was maintained maintained through the column at the start of the each analysis. The oven was held at 35 °C for 5 min following the injection of a sample. Thereafter, the temperature was increased to 60, 90, 150, and 200 °C every 5 min. The temperature in the oven was increased at 65 $\mathrm{°C\,min^{-1}}$ and held isothermally once the new 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. The cooling of the system was achieved by a recirculating chiller filled with glycol. To exclude air from the adsorbent trap a flow of helium (100 $\mathrm{ml\,min^{-1}}$, Grade 5.0) was maintained both before and after sampling. Samples were dried using magnesium perchlorate, held in a glass moisture trap, before being passed to the trap, as per Groszko and Moore (1998). Air was passed through the adsorbent trap at 100 $\mathrm{ml\,min^{-1}}$ for 15 min, resulting in a 1.5 l sample volume. The sampling flow rate was checked weekly by means of a digital flow meter. An oil free piston pump was used to draw air through a 60 m Decabon sampling line and the adsorbent 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 $\mathrm{ml\,min^{-1}}$ and a needle valve on the exhaust was used to ensure sufficient pressure in the sampling line for the mass flow controller to operate.

A built in resistance wire heated the TDU 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 of the column for the duration of the primary injection. Thereafter, boiled water was used to desorb the samples trapped at the head of the column.

2.2 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 °C (permeating at 343 $\mathrm{ng\,min^{-1}}$) was flushed with nitrogen (grade 5.0, Air Liquide) at 100 $\mathrm{ml\,min^{-1}}$. 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 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 integration method and were computed in MATLAB (Poole, 2003). The mixing ratios of the injected loops were calculated from the number of moles of bromoform injected, as follows. Each loop injection resulted in 0.1865 ng of bromoform being loaded on the trap, based on the calibrated rate of the permeation tube (Wevill and Carpenter, 2004; Kuyper, 2014). The number of moles of bromoform on the trap was calculated from this mass. Then 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.

Since the peak area is proportional to the concentration in the sample, the measured peak area is controlled through the number of injected loops. Thus the peak area is plotted against the calculated mixing ratio (Fig. 2). 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.

A complete system calibration was run at the start of the sampling at Cape Point. 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 99.7 % accuracy was achieved on this system (Fig. 2). An analysis of 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.

2.3 Ancillary measurements: Cape Point, Global Atmospheric Watch

The Global Atmospheric Watch (GAW) station at Cape Point is operated by the South African Weather Service. In addition to the standard meteorological parameters, numerous climate relevant gases are quantitatively measured here, including: $\mathrm{CO_2}$, $\mathrm{CH_4}$, CO, radon ($^{222}\mathrm{Rn}$) and $\mathrm{O_3}$ (Whittlestone and Zahorowski, 1998; Brunke et al., 2004; Whittlestone et al., 2009).

Air samples were drawn in at the top of a 30 m high sampling mast. A continuous flow system was used in the laboratory to exclude the accumulation of any contamination. Sequential cold trapping at -5 and -40 °C along the flow path was used to dry air samples prior to measurement. A 30 min mean was applied to all data to standardise different sampling periods.

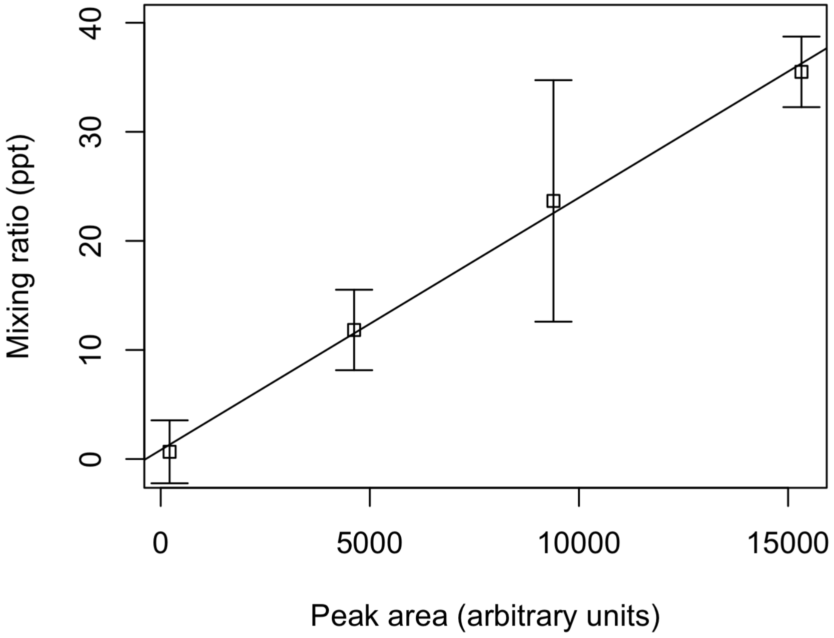

Figure 2. Calibration of the GC-ECD system for bromoform, based on multiple loop injections. Peak area calculated on the trapezoid method. (Adapted from Kuyper 2014)

The ozone measurements were made on a Thermo Electron 49C analyser. These analysers are based on the UV absorption technique and calibrated every two months. Daily zero and span measurements were used to assess long-term stability of the detectors. A Trace Analytical RGA3 was used to measure atmospheric CO mixing ratios. The detector uses a reduction of mercuric oxide (HgO) to determine the concentration of CO (Brunke et al., 2004). A measurement was made every $15\,\mathrm{min}$ with a calibration occurring every 2 hours. Radon ($^{222}\mathrm{Rn}$) measurements were made in an ANSTO-build, two-stage α-decay system which detects the collected radon daughter products (Whittlestone and Zahorowski, 1998; Whittlestone et al., 2009). A sample was measured half-hourly and calibrated monthly.

2.4 Ancillary measurements: NOAA HYSPLIT model, Marine boundary layer height and Diurnal cycle

NOAA Hysplit model

The HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT: http://www.ready.noaa.gov/) model was used in addition to the chemical tracers to examine the source of air masses being sampled (Stein et al., 2015). These trajectories were generated using the NCEP Global Data Assimilation System (GDAS) model output as the meteorological data. The back trajectories were run for 72 hours prior to bromoform measurement.

Marine boundary layer (MBL) height

Twice daily radiosondes were released from Cape Town international airport at local midnight and noon. The airport lies approximately 60 km northeast of Cape Point. The height of the MBL was determined by the surface and elevated temperature inversion methods from the radiosonde data (Seibert et al., 2000; Seidel et al., 2010). The calculated boundary layer height at the airport was used as a proxy for the marine boundary layer at Cape Point.

Diurnal cycle

A mean diurnal cycle was calculated from the full range of Cape Point measurements. The data was sorted into 24 hourly bins. The start time of the sampling was used to assign an hourly bin to each measurement. The mean and 95 % confidence interval of the bins were then calculated. The diurnal cycle is shown as the mean of each hourly bin with the confidence intervals.

3 Results and Discussion

The bromoform mixing ratios at Cape Point were measured in the range 1.1-46.2 ppt with a mean of 13.2 pm 9.7 ppt (Fig. time-series). The measurements were largely consistent within a few days, however could vary by 10s of ppt between days (Fig. 3). The range of variability observed at Cape Point is comparable to previously published work, specifically with reference to coastal sites (Table 1).

The measurements were made in a variety of air masses ranging from clean marine to continental air. This suggests that a number of sources may have impacted on the bromoform mixing ratios at Cape Point. Nearly 66 % of bromoform measurements recorded here, were below the mean. This indicates that the mean value is skewed by a few elevated bromoform mixing ratios. When examined over the whole data set the bromoform mixing ratios showed only weak correlations with the meteorological and physical measurements ($r^2 < 0.4$). However, on an event scale it appears that elevated bromoform concentrations tend to occur only when certain factors coincide.

Link to tidal cycle

The full tidal spectrum was captured at Cape Point during the bromoform sampling period, including two neap tides and a spring tide. A maximum tidal range of approximately 2 m was observed during the spring tide. This range decreased to a maximum of 1 m during the neap tides (Fig. 3. Exposure of kelp (which as discussed is present in abundance at Cape Town) to the atmosphere at low tide has been linked with an increase in atmospheric bromoform mixing ratios, for example, a site at which this has been observed is Mace Head on the west coast of Ireland Carpenter et al., 1999. An increase in the oxidative stress on the kelp initiated by solar radiation is thought to drive this correlation (Carpenter et al., 1999; Palmer et al., 2005). However, the measured bromoform mixing ratios do not correlate well with the tidal pattern, with higher mixing ratios being

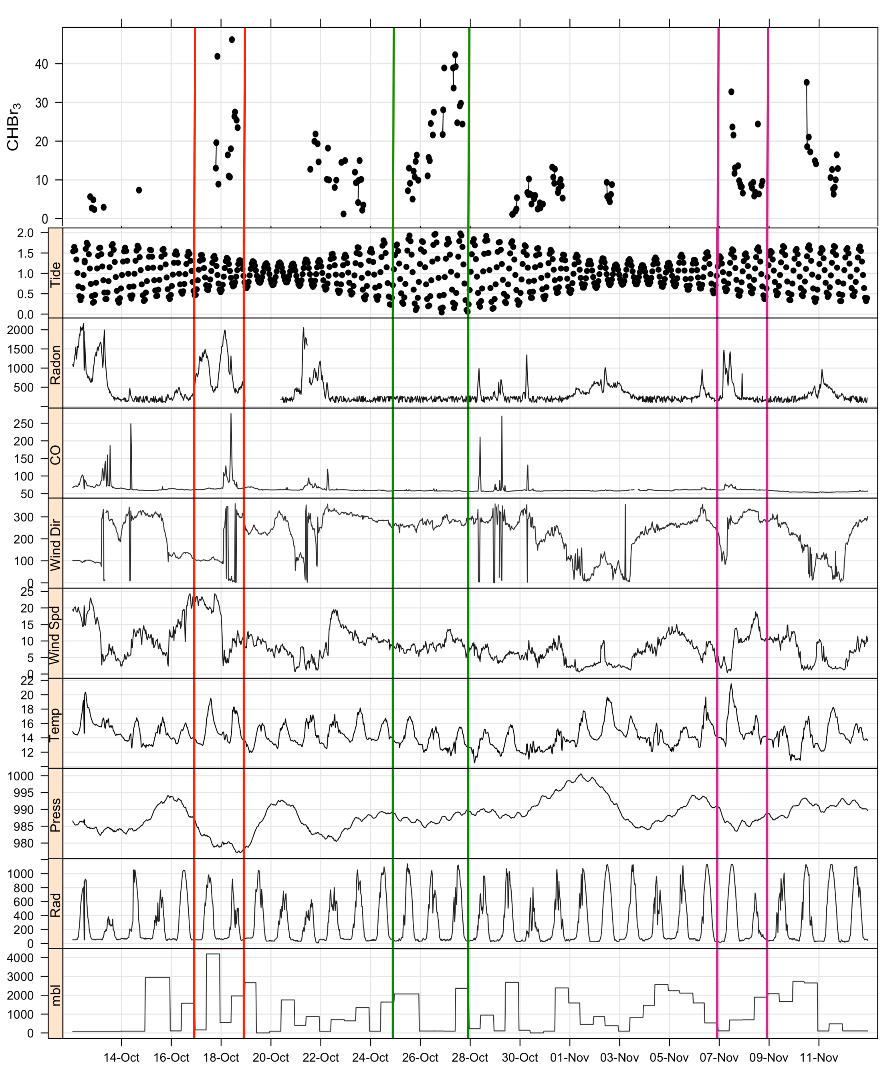

Figure 3. Time series plot of bromoform and meteorological measurements at Cape Point during October/November 2011. Events are highlighted by the coloured lines: E1 = red, E2 = green, E3 = violet.

recorded regardless of the tidal range. This lack of correlation may be explained as, while the maximum tidal range in the vertical at Cape Point is comparable to that at Mace Head, the horizontal extent is much smaller. Consequently during low tide at Cape Point, only the tops of the kelp fronds become exposed to the atmosphere. Nonetheless, the elevated bromoform events with the highest mixing ratios all appear to mostly occur shortly after low tide (Fig. 3). This suggest that the tidal height is a necessary but not sufficient factor in detection of extended periods of elevated bromoform mixing ratios at the Cape Point site. It is therefore likely that the extensive local kelp beds are an important source of the bromoform observed at the station.

Table 1. 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 2002-2004	43.1 °N	0.2	37.9	5.3-6.3	Zhou et al., 2008	Coastal
Hateruma Island, Island	Dec 2007-Nov 2008	24 °N	0.5	7	0.91-1.28	Yokouchi et al., 2017	Coastal
Mauritanian upwelling	Mar-Apr 2005	16-21 °N	0.1	0.6	0.2	Quack et al., 2007	Upwelling
Cape Verde	May-Jun 2007	16.8 °N	2.0	43.7	4.3-13.5	O'Brien et al., 2009	Coastal
R/V Sonne	July 2014	2-16 °N	0.79	5.07	2.08	Fuhlbrügge et al., 2016b	Open ocean
R/A Falcon	July 2014	2-16 °N	0.99	3.78	1.90	Fuhlbrügge et al., 2016b	MABL WASP
Atlantic Ocean	Oct-Nov 2002	10 °N	0.5	27.2	-	Quack et al., 2004	Open ocean
SHIVA	Nov-Dec 2011	0-8 °N	1.23	3.35	1.81	Sala et al., 2014	MABL WASP
Borneo	Apr-Jul 2008	4.70 °N	2-5	60	-	Pyle et al., 2011	Coastal
Strait of Malacca	Jun-Jul 2013	2-6 °N	1.85	5.25	3.69	Mohd Nadzir et al., 2014	Coastal
Sulu-Sulawesi	Jun-Jul 2013	2-6 °N	1.07	2.61	1.60	Mohd Nadzir et al., 2014	Coastal
Christmas Island	Jan 2003	1.98 °N	1.1	31.4	5.6-23.8	Yokouchi et al., 2005	Coastal
San Cristobol Island	Feb-Mar 2002, 2003	0.92 °S	4.2	43.6	14.2	Yokouchi et al., 2005	Coastal
Peruvian upwelling	Dec 2012	5-16 °S	1.5	5.9	2.9	Fuhlbrügge et al., 2016a	Upwelling
Indian ocean	Jul-Aug 2014	2-30 °S	0.68	2.97	1.2	Fiehn et al., 2017	Open ocean
Cape Point	**Oct-Nov 2011**	**34.5 °S**	**2.29**	**84.7**	**24.7**	**This study**	**Coastal**
Cape Grim	2003	40.7 °S	1.3	6.4	2.9	Yokouchi et al., 2005	Coastal
Coastal South America	Dec 2007-Jan 2008	55 °S	1.8	11	7.4	Mattsson et al., 2013	Coastal
Antarctic coast	Dec 2007-Jan 2008	65 °S	2.1	4.9	3.2	Mattsson et al., 2013	Coastal
Antarctic Ocean	Dec 2007-Jan 2008	65-67 °S	1.9	3.9	2.3	Mattsson et al., 2013	Open ocean

Air mass characterisation

Radon ($^{222}\mathrm{Rn}$) and CO have been extensively used as tracers for continental and anthropogenic contamination, respectively, in air mass characterisation particularly at Cape Point (Brunke et al., 2004). The measurements of radon ($^{222}\mathrm{Rn}$) and carbon monoxide (CO), which were generally extremely low, show short elevated periods in the observations (Fig. 3). This indicates that majority of the bromoform measurements made at Cape Point were under clean marine conditions. Of the 1535 half hourly measurements that make up the meteorological data observed at Cape Point during October/November 57 % were of clean marine origin. The bromoform mixing ratios in this clean air displayed a mean 12.8 ppt and ranged between 1.10 and 42.3 ppt (Table 2). The variations in $^{222}\mathrm{Rn}$ and CO concentrations occurred concurrently and mostly when the wind is from a northwesterly direction. Which suggests a continental and anthropogenic source. The continental contaminated air made up 3 % of the total measurements, with intermediate air masses accounting for 7.5 % of the measurements.

Table 2. Comparison of bromoform mixing ratios from different air mass sources, sorted by radon concentration.

	Clean Marine	**Intermediate**	**Continental**
$^{222}\mathrm{Rn\ mBq\,m^{-3}}$ (number)	< 350 (881)	800-1500 (115)	>1500 (45)
Mean $\mathrm{CHBr_3}$ ppt (number of samples)	12.8 (75)	16.0 (12)	2.93 (1)
Range $\mathrm{CHBr_3}$ (ppt)	1.10-42.3	2.35-46.2	-

The bromoform mixing ratios in intermediate air samples showed a similar mean to that of clean marine air (Table. **??**). The introduction of this intermediate or continental air at Cape Point allows for a determination of scale of the anthropogenic contributions in this region. Since this occurs predominantly in winter a longer time series could test the relative contributions more extensively.

It has been well documented that the contribution of anthropogenically produced bromoform is generally smaller than from natural processes on a global scale (Quack and Suess, 1999; Quack and Wallace, 2003). However, on a local scale anthropogenic source can dominate (Quack and Suess, 1999). During this sampling period the dominant contribution of bromoform was from the clean marine air masses and therefore, biogenic sources (Table 2). It is therefore, likely that the local kelp beds were responsible for the bulk of the measurements, including the elevated mixing ratios observed. Occasional intrusions of anthropogenically modified air may have contributed to the observed variability in mixing ratios at Cape Point, as is discussed in the case studies below.

Meteorology

Wind speed has a complicated relationship with observed bromoform mixing ratios in marine air. The processes of bromoform sea-air flux and atmospheric dilution, both proportional to wind speed, oppose each other in their effect on the atmospheric concentration of bromoform. At low wind speeds there is a low dilution and bromoform flux into the atmosphere. As the wind speed increases so do the rates of dilution and gas flux. The wind speed observed at Cape Point over this sampling period was dominated by lower wind speeds (<10 $\mathrm{m\,s^{-1}}$). The full range extended from calm (<5 $\mathrm{m\,s^{-1}}$) to occasionally reach gale force (> 20 $\mathrm{m\,s^{-1}}$). The elevated wind speeds were associated with transient cold fronts that influence the Cape in winter and spring (Tyson and Preston-Whyte, 2000). The bromoform mixing ratios at Cape Point show a varied response to the observed wind speed; on some occasions at high wind speeds the mixing ratio was also elevated whereas at other times it was not. The lack of direct correlation may be evidence of the complexity and interaction of these processes as described above.

In a coastal upwelling environment it has been shown that the height of the marine boundary layer (MBL) can play a significant role in the observed bromoform mixing ratio. For example Fuhlbrügge et al., 2013 found that a lower marine boundary layer height acted to concentrate bromoform mixing ratios recently released from the ocean surface. No correlation between bromoform and MBL height was found in this study. This could be a result of Cape Point sitting approximately 60 km from Cape Town international airport, where the radiosondes, used to characterise the MBL height, were released.

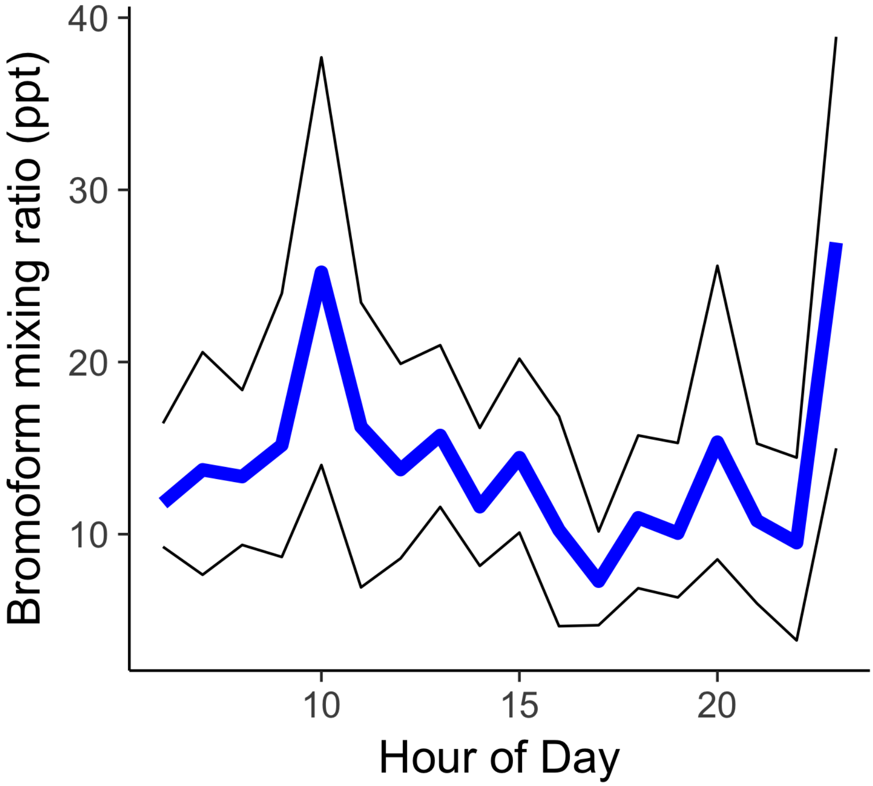

Figure 4. Mean diurnal cycle, calculated from all measurements binned by hour. The black lines above and below signify the 95 % confidence interval.

3.1 Solar radiation and Diurnal cycle

During the sampling period the solar radiation at Cape Point daily reached a level of 600-1000 $\mathrm{W\,m^{-2}}$ (Fig. 3). While there was no direct correlation between solar radiation and bromoform observed, the highest mixing ratios occurred when the the solar radiation was typically above 800 $\mathrm{W\,m^{-2}}$.

The mean Cape Point diurnal cycle of bromoform mixing ratios displayed an increase in through the morning from an estimated overnight low of 20 ppt to a mean maximum of 25.2 ppt (Fig. 4). Thereafter the mixing ratios decreased through the afternoon. A second maximum in the mean mixing ratios was observed in the early evening. This secondary maximum reached a mean mixing ratio of 26.9 ppt. There were no measurements taken between midnight and 5 am and the first morning measurements were taken prior to local sunrise. It is assumed that these measurements, taken before sunrise, were representative of the night time conditions.

This pattern in the diurnal mean bromoform mixing ratio measurements at Cape Point is similar to that observed in previously published literature (Ekdahl et al., 1998; Carpenter and Liss, 2000; Abrahamsson et al., 2004). It has been hypothesised that the increase in concentrations observed in the morning are as a result of sunrise. The onset of solar radiation stimulates photochemistry leading to oxidative stress in the kelp cells and the release of bromoform (Collén et al., 1994; Pedersén et al., 1996; Ekdahl et al., 1998). Whereas it would appear that, through this mechanism, the maxima of bromoform mixing ratios and solar radiation should coincide (Abrahamsson et al., 2004), the increased solar radiation throughout the day also increases the rate of photolysis of bromoform. Thus at high photolysis rates during the midday sun lower mixing ratios are observed. The literature also suggests that bromoform production may also be related to respiration ((Ekdahl et al., 1998; Carpenter and Liss, 2000). The evening maximum in mixing ratios is, therefore, expected and consistent with previously studies in Gran Canaria and the Southern Ocean (Ekdahl et al., 1998; Abrahamsson et al., 2004). It is theorised that the through haloperoxidase enzyme reactions excess intracellular hydrogen peroxide ($\mathrm{H_2O_2}$) is removed and bromoform formed (Collén et al., 1994). A decreased photolysis rate and continued production, through respiration, is the likely explanation for the observed evening maximum.

3.2 Case Studies

Three case studies were selected to further examine the relationships between bromoform mixing ratios and the meteorological conditions at Cape Point. These case studies examine bromoform mixing ratios above the mean and include the maximum mixing ratios. Factors that have been shown in the literature to influence bromoform mixing ratios were examined. These three case study events were defined as: 17-18 October 2011, 25-27 October 2011 and 7-8 November 2011; hereafter called events 1, 2 and 3, respectively (Fig. 3).

Event 1 (17-18 October 2011)

During this event window two periods of bromoform mixing ratios elevated above the mean were observed, one on each day (Fig. 5). Only a few bromoform measurements were captured on 17 October, which showed an increase from 13.0 ppt. After reaching a maximum of 41.9 ppt, the following bromoform mixing ratio measurement was 8.9 ppt. These measurements were made in the early evening concurrently with an ebb tide. A series of measurements (10.7-16.4 ppt) surrounding the mean were observed on the morning of 18 October, just prior to the elevated measurements. The maximum concentration of 46.2 ppt on 18 October occurred in correlation with the solar maximum. The tidal height had been falling through the morning of 18 October and began the flood phase at noon. Following the maximum at 11 am the bromoform mixing ratios remained elevated (20-30 ppt) until sampling was stopped at 4 pm.

The radon concentrations were elevated above 1000 $\mathrm{mBq\,m^{-3}}$ for both mornings in this event window. However, CO concentrations were at baseline levels over 17 October, but showed a sharp increase to 250 ppb on the morning of 18 October. The maximum in CO on 18 October is mirrored in the $^{222}\mathrm{Rn}$ mixing ratios. This indicates that the air masses sampled were intermediate and that on the 18 October contained anthropogenic modification.

Conditions on 18 October were conducive for biogenic production to occur. The bromoform maximum occurred just before low tide and high solar radiation, both conditions which should favour local biogenic production of bromoform. However, the correlation of the CO, $^{222}\mathrm{Rn}$ and bromoform maxima on 18 October implies there may be anthropogenic element to the observed bromoform. We therefore postulate that the high bromoform concentration observed here (46.2 ppt - the highest

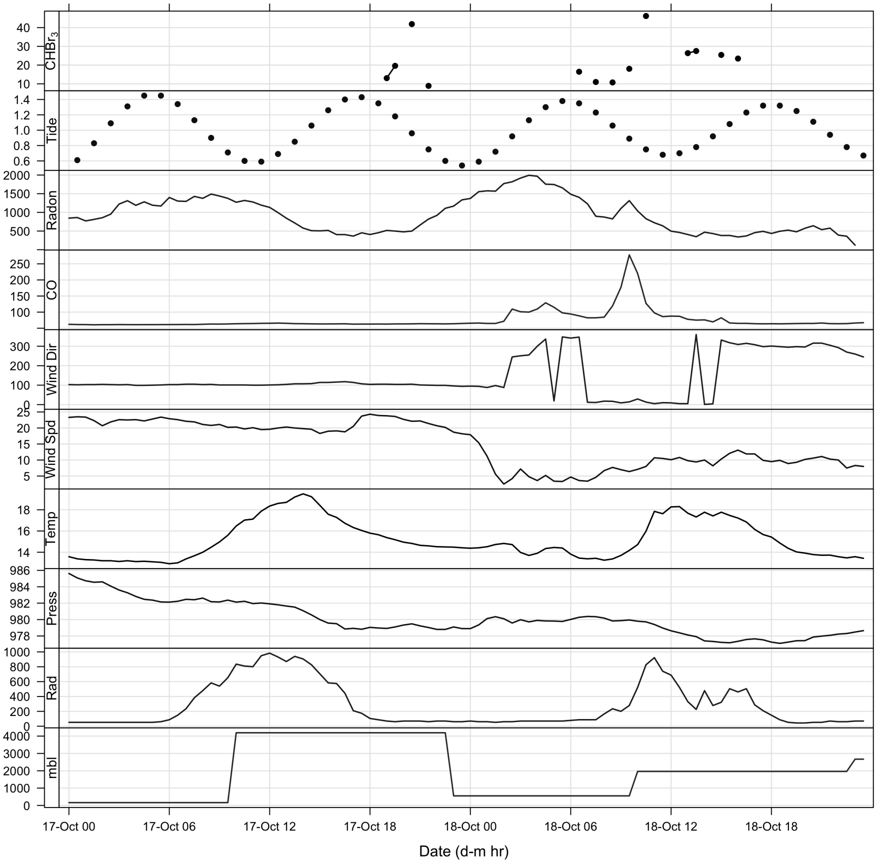

Figure 5. Time series plot of measurements at Cape Point during Event 1: 17-19 October 2011. Dates are given as day-month with the hour separately.

reported in this study) may be as a result of high local production augmented with anthropogenic bromoform which had been entrained downstream. Moreover, the trajectory over which the air passes passes over known anthropogenic sources of bromoform such as a water treatment works and Koeberg nuclear power station (Fig. 6). This combination hypotheses would explain why we saw the highest mixing ratios in this period. No other available evidence from the suite of measurements taken here appears to be able to offer an adequate alternative explanation for this.

Event 2 (25-27 October 2011)

This event window captured sequences of bromoform mixing ratios over three days. The bromoform mixing ratios were around the mean in the first sequence, a little above the mean and well elevated of the mean, during the second and third sequences respectively (Fig. 7). A number of varying factors influencing the bromoform mixing ratios at Cape Point were highlighted

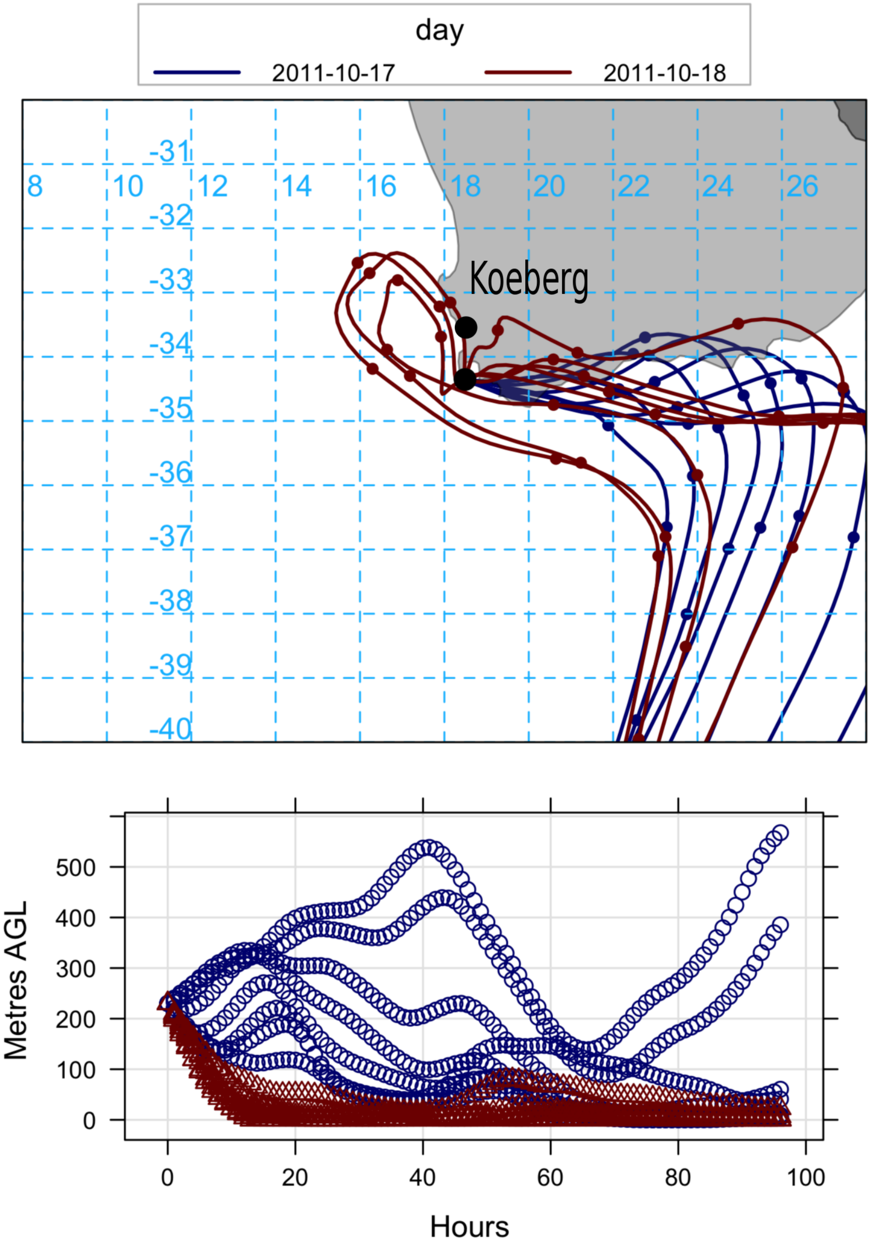

Figure 6. Back trajectories on 17 and 18 October 2011, highlighting the transit over Koeberg and Cape Town

during this event. It is notable that the $^{222}\mathrm{Rn}$ mixing ratios remained below $300\ \mathrm{mBq\,m^{-3}}$ over the entire event window (Fig. 7). This was coupled with CO concentrations that displayed typically baseline values (Brunke et al., 2004).

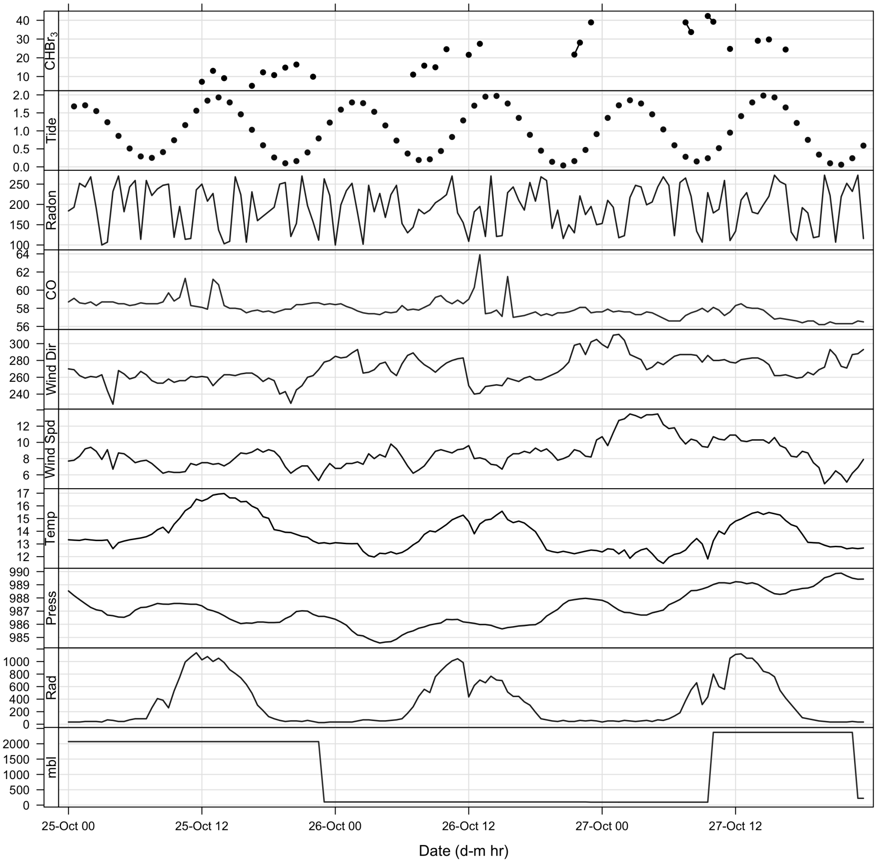

Figure 7. Time series plot of measurements at Cape Point during Event 2: 25-28 October 2011. Dates are given as day-month with the hour separately.

At noon on 25 October bromoform measurements were taken around the tidal maximum and into the afternoon, concurrently with an ebb tide. These measurements were also taken after the solar maximum. The bromoform mixing ratios observed here surrounded the mean (13.2 ppt) and remained below 20 ppt through the afternoon and evening. Sampling recommenced with the trough of the low tide on the morning of 26 October. Bromoform mixing ratios increased from 11.3 ppt to 24.6 ppt at 10 am. These occurred during the flood tide and just before the local solar maximum. Bromoform mixing ratios increased to 27.5 ppt just before the high tide. The subsequent low tide in the evening of 26 October saw bromoform mixing ratios similar to those at the end of the morning low tide (± 20-30 ppt). The mixing ratios increased to a maximum of 38.9 ppt at the end of sampling on 26 October.

Bromoform mixing ratios started out at a similar 38.8 ppt at 5:00 am on 27 October. Thereafter the mixing ratios increased rapidly to 42.3 ppt at 9:30 am, consistent with the diurnal cycle (detailed in Sec. 3.1). This coincided with low tide, but before the solar maximum, which occurred at 11:30 am. The bromoform mixing ratios remained elevated through the remainder of the afternoon. The tidal range in the morning of 27 October was 1.83 m, which was comparable to the tides on either side (1.81 and 1.92 m, respectively). The wind speed remained at approximately 10 $\mathrm{m\,s^{-1}}$ for much of the event window, increasing late on 26 October to a maximum of 12 $\mathrm{m\,s^{-1}}$ at 3 am. Thereafter the wind speed decreased back to 10 $\mathrm{m\,s^{-1}}$ on the morning of 27 October.

The tracer measurements coupled with the constant westerly wind, strongly suggests that only clean marine air was sampled during this event. Therefore, the bromoform observed here was of biogenic origin. The amount of bromoform released varied between the different low tides. This variation is likely attributable to The tidal height is therefore a necessary but not sufficient factor in explaining the variability of the bromoform mixing ratios observed at Cape Point.

On the afternoon of 25 October the bromoform mixing ratios coincided with the end of an ebb tide. The mixing ratios in the early afternoon were around the mean (13.2 ppt) and increased slightly with edd tide to peak at 16.3 ppt in the early evening. Since these measurements were made after the solar maximum and into the evening this release of bromoform may be attributable to the respiration of kelp. The solar maximum reached 1079 $\mathrm{W\,m^{-2}}$ during the morning. The high solar radiation may have stimulated a large photosynthetic response in the local kelp beds. Furthermore, exposure of the kelp fronds with the ebb tide suggests that the direct air transmission was possible. Although on a smaller scale, the bromoform mixing ratios in this sequence showed a small decrease with the onset of the flood tide.

The bromoform mixing ratios on the morning of 27 October were elevated above the mean and comparable to the final measurements on 26 October (38.8 ppt). The mixing ratios peaked just after the low tide but before the solar maximum. The $^{222}\mathrm{Rn}$ and CO remained at baseline conditions for the duration of the day. Therefore, the bromoform observed on 27 October was of biogenic origin. After the maximum was reached the mixing ratios decreased with the flood tide. The MBL was also estimated to have increased through the morning on 27 October. We can therefore hypothesise that the flood tide and the increasing MBL acted to diminish the bromoform mixing ratios observed.

Event 3 (7-9 November 2011)

Two sequences of bromoform mixing ratios were captured during the event window (Fig. 8). Bromoform mixing ratios showed a decrease from 32.7 ppt at 12:30 on 7 November to a minimum of 6.6 ppt at 10:30 pm. Although a small gap exists in the measurements 3 and 6 pm, the measurements either side were nearly identical at 13.1 and 13.6 ppt. The decreasing bromoform mixing ratios occurred during a flow tide and followed into the next low tide.

Radon mixing ratios were elevated (1500 $\mathrm{mBq\,m^{-3}}$) in the morning of 7 November but decreased to below 500 $\mathrm{mBq\,m^{-3}}$ by noon. The radon remained low for the remainder of the event window. The CO mixing ratio showed a similar trend, being marginally elevated in the morning and decreasing to baseline concentrations by noon. Compared to the CO intrusion in event 1, the CO mixing ratio here was low (< 75 ppb) and therefore considered a local event. This suggest that air mass had been modified by continental influences, but likely not anthropogenic.

Evident in this event window were two low tides where the bromoform mixing ratios remained below 15 and 10 ppt, respectively. The former occurred in the early evening and that latter in morning, under low solar radiation conditions. The bromoform mixing ratios on 8 November largely remained below 10 ppt, except for one measurement at 1 pm (24.4 ppt). This

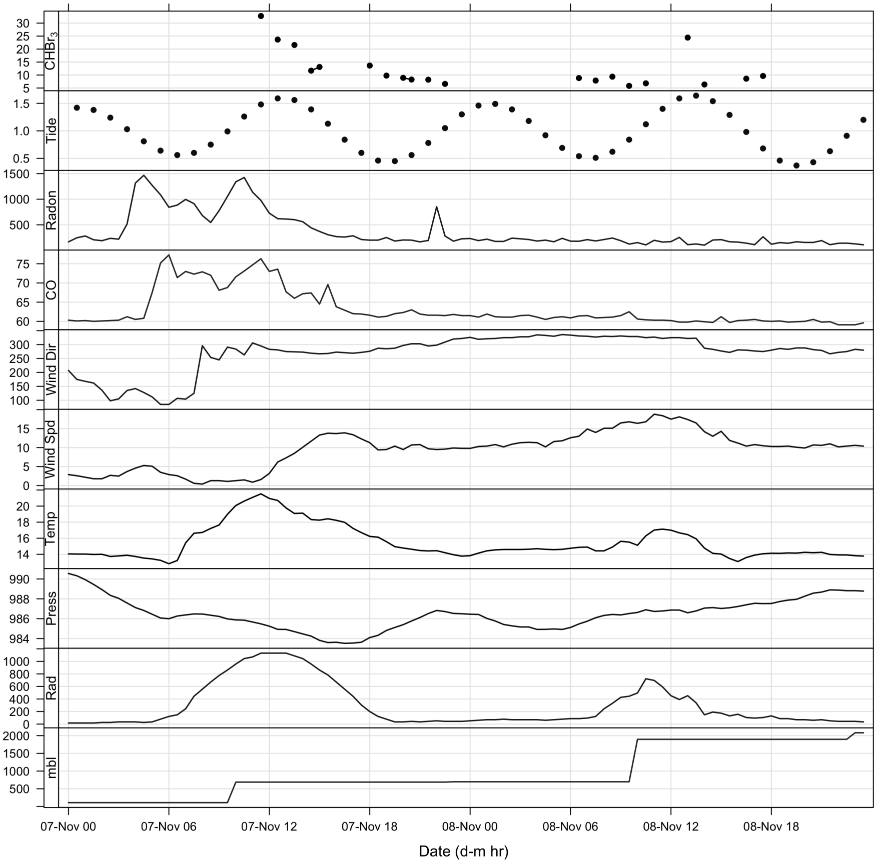

Figure 8. Time series plot of measurements at Cape Point during Event 3: 7-9 November 2011. Dates are given as day-month with the hour separately.

occurred just before the peak of high tide and about 2 hrs after the solar maximum on that day. The solar maximum was low on 8 November reaching a maximum of 722.4 W m^{-2}.

The $^{222}\mathrm{Rn}$ and CO mixing ratios were marginally elevated at the start of the event window. This implies that measurements on 7 November were taken in continentally modified air. This could have augmented the mixing ratios recorded. The back trajectories on 7 November confirm that the air masses had passed over known a known anthropogenic source of bromoform (Fig. 9). By midnight on 7 November the $^{222}\mathrm{Rn}$ and CO mixing ratios recorded were at baseline concentrations, strongly suggesting a clean marine air mass was sampled on 8 November.

The mixing ratios on 7 November may have been augmented by anthropogenic sources, resulting in the elevated mixing ratios observed. As the afternoon progressed the radon concentration decreased and the wind speed increased. Thus suggesting that clean marine air was influencing Cape Point and the bromoform present was being diluted. Since the measurements were in the afternoon it is expected that mixing ratios would decrease, as per the diurnal cycle.

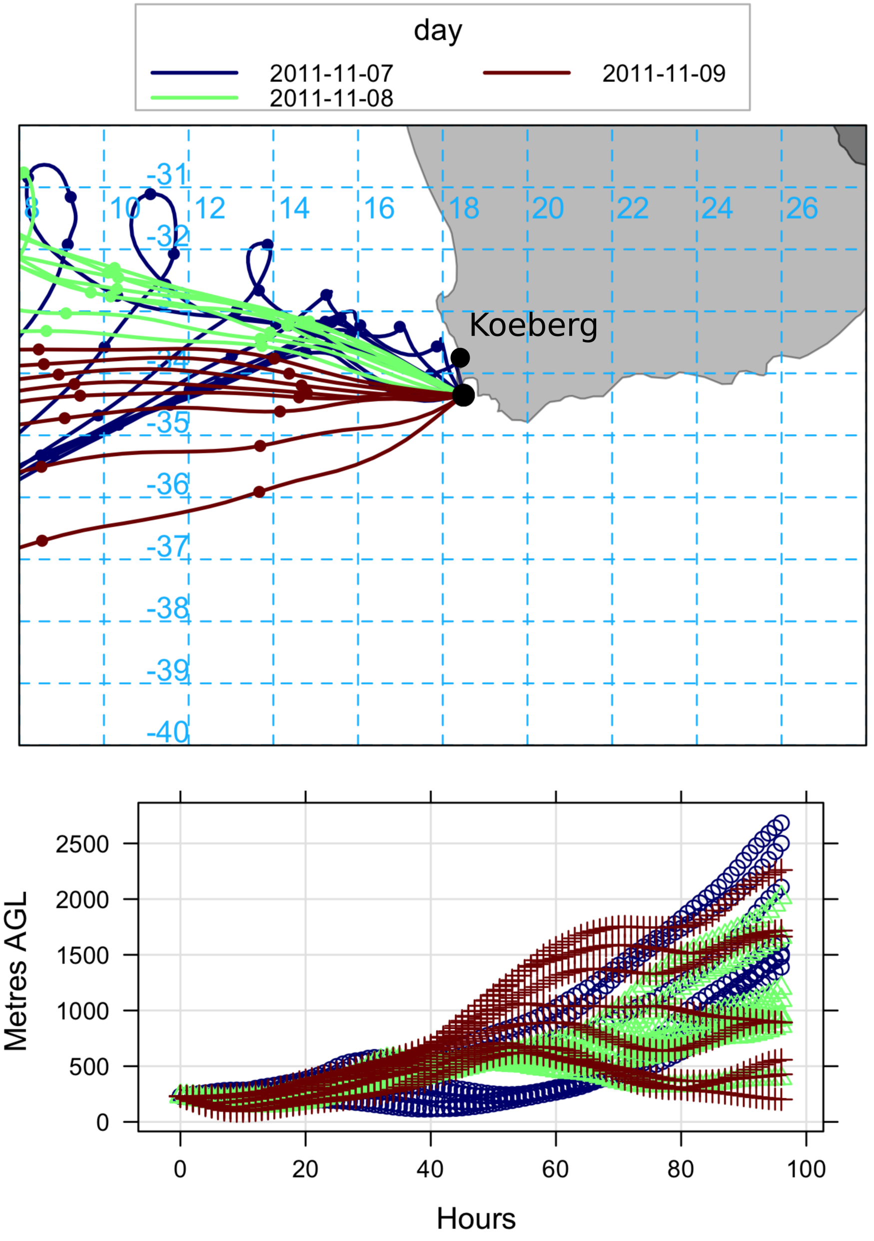

Figure 9. Back trajectories of 17 and 18 October 2011, highlighting the transit over Koeberg and Cape Town

4 Conclusions

The data presented here represents the first fixed point medium term quantitative atmospheric bromoform measurements at the Cape Point Global Atmospheric Watch Station, but also the first such dataset in southern Africa. The approximately 130 discrete measurements made over the course of October/November 2011 exhibited a mean bromoform concentration of 13.2 ± 9.2 ppt. The maximum reported value here (46.2 ppt) was consistent with past studies, for example: that reported in Cape Verde (43.7 ppt, O'Brien et al., 2009) or New Hampshire (47.4 ppt, Zhou et al., 2008).

The majority of measurements (57 %) were made in clean marine air, implying that for these measurements the bromoform being sampled was entirely biogenic. From the data presented here it appears that the most likely source of the this bromoform is production from local kelp. Most of the periods in which bromoform concentrations were elevated for a prolonged time occurred around low tide, where kelp are exposed and most likely to produce bromoform as a response to oxidative stress. However, occasional intrusions of anthropogenically modified air may have contributed to the bromoform loading at Cape Point.

The mean diurnal pattern appears to exhibit a similar pattern to, and fall within the range of, previously published reports. An increase in the mixing ratio was observed through the morning, returning to low concentrations throughout the rest of the day. A second maximum in the mean mixing ratios was observed in the early evening.

Given the relatively high concentrations reported, these data indicate that this under-sampled region, may be particularly significant in terms of bromoform sources to the atmosphere. Further work needs to be done to categorise the source strength and halocarbon release from the local kelp sources. Additional measurements, both in time, space and halocarbon species, will be required to attain a greater understanding of specific local processes governing the variability in bromoform in this region. It is thus clear that future measurements of bromoform mixing ratios at Cape Point would make an important contribution to the field.

Code availability. TEXT

Data availability. TEXT

Code and data availability. TEXT

Appendix A

A1

Author contributions. B. Kuyper, C. J. Palmer and C. J. C. Reason designed the experiments. B. Kuyper measured the samples of bromoform, performed analysis, wrote most of the manuscript, created all the figures. C. Labuschagne measured the meteorological and ancillary data. C. J. Palmer, C. Labuschagne and B. Kuyper performed the analysis. All authors contributed to review and improve the text.

Competing interests. The authors declare that they have no conflict of interest.

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