Authors response to the reviewer comments

REVIEWER 1

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)

The revised manuscript of Kuyper et al. has addressed many of the issues raised in the reviews. However, there are still some points that need clarification or correction.

Response: The authors would like to thank the reviewer for their time in reviewing our paper. Their comments and suggestions have made a significant improvement in the quality and substance of the paper.

1) *General comment. Be sure to clearly identify all components of tables and figures in the associated captions.*

Response: The authors would like to thank the reviewer for this comment. We apologies for this oversight in the preparation of our figures.

Remedial action: The units in the figures have been added, where possible in the plot otherwise in the caption.

2) *Significance of Cape Point site to tropical convection….The authors make a reasonable claim that it is important to understand the sources and budget of bromoform in the global and regional atmospheres. However, if they claim that the emissions near Cape Point are entrained in tropical convection, I'd appreciate some reference that shows the significance of this transport path from the S. African MBL to the tropical UTLS.*

Response: NOAA Hysplit trajectories were run in the forward mode for 2011. These indicate that 25 % of the air masses that transition Cape Point arrive in the tropics within 96 hours. Furthermore, Tyson and Preston-Whyte (2000), show the mass transports over southern Africa. They indicate particularly in spring and autumn 25 % of the transport over southern Africa is to the Atlantic and the tropics. In summer and winter this can drop to as low as 5 %.

Remedial action: The following has been added to the text in the significance section:

"The seasonal synoptic conditions over South Africa results in varying transport patterns (Tyson and Preston-Whyte, 2000). During summer, approximately 5 % of trajectories from South Africa escape to the Atlantic (10 ºS), while 75 % of transport exits to the southeast. Ridging high pressure systems, present during spring and autumn, increase the transport to the Atlantic to 25 % (Tyson and Preston-Whyte, 2000)."

3) *Calibrations. While the authors have expanded on their discussion of analytical protocols and calibration, I still remain confused on some basic operations. First, the authors describe using sample loops for calibrating the system, as is a common practice. However, they then also describe an error associated with timing of the standard addition to the system, e.g., 30 sec instead of 1 minute for standards. If the*

> *standards are injected via single or multiple fixed volume loop injections of the output of the permeation tube, how does timing make any difference? I am confused. Second, I do not understand the relationship between the calibration curve shown in the figure and the use of intermittent standards to track drift in system response. Presumably, response factors for bromoform are calculated regularly with runs of different amounts of standard. How these different standards (a choice of from 1 – 3 standards) are used is not at all clear. How is drift calculated, and how does that relate to the calibration curve, which I have to repeat, is not correct as shown (no matter if it was used by Wevill and Carpenter). Please refer to most any textbook on analytical chemistry. Based on the calibration curve shown, I find it hard to believe that the error bars represent the 7% uncertainty as claimed in the author response.*

Response: The reviewer is correct in both their points regarding the calibration. We apologise for any confusion that has been caused. The volume of the sample loop is fixed and not related to the injection time. This has been corrected in the manuscript. Furthermore, the reviewer is correct, that we should have plotted bromoform mixing ratio (independent variable) against peak area (dependant variable).

Remedial action: The sample loop volume in the calculation has been amended to correctly reflect the 100 μl sample volume. The calibration curve has been corrected to reflect the bromoform mixing ratio as the independent variable. The calibration text has also been revised to reflect the full calculation method:

"The mixing ratios of the injected loops were calculated from the number of moles of bromoform injected, as follows. Each loop injection resulted in 0.0343 ng of bromoform being loaded on the trap, based on the calibrated rate of the permeation tube (Wevill2004, Kuyper2014). The number of moles of bromoform on the trap was calculated from this mass which resulted in 1.36 x 10^{-12} mol being loaded on the trap, per sample loop injection. The number of molecules of bromoform was calculated by multiplying the number of moles by the Avogadro constant to yield the number of bromoform molecules on the trap. The total number of molecules in a sample was calculated by multiplying the air number density (2.5 x 10^{25}) with the sample volume (1.5 l). The bromoform mixing ratio of one loop was calculated as the number of bromoform molecules of one loop as a fraction of number of molecules in a sample multiplied by 10^{12} to yield ppt."

To ensure that the reviewer can be fully confident in the calibration, a full copy of the calibration data and calculation procedure can be found in the supplementary section.

4) *Diurnal variation..p13. The authors suggest that increased photolysis of bromoform during the day is a major factor in the observed diurnal variability. However, I think that photolysis would be only a minor factor given the approximately 3 week lifetime of bromoform, which suggests that perhaps 5%/day is lost by photolysis. Thus even a constant source of bromoform would show only a minor diurnal cycle due to photolysis. Variation in source location, emission, and mixing offer much more reasonable hypotheses for the observed changes. Unfortunately, the authors seem to want to test every known factor that can influence bromoform concentrations, but they don't have sufficient data to adequately rule out or confirm any particular factor. This is, unfortunately, the weakness of the paper. Still, the data are useful and the discussion, while it could be improved, is not unreasonable.*

Response: We would like to thank the reviewer for pointing this out. We agree that the photolysis argument used here is overstated.

Remedial action: The diurnal section has been reworked as per the suggestions of both reviewers to indicate that variations in the MBL height are more locally significant on the time scale of the sampling and therefore the likely driver of the changes observed in the bromoform mixing ratios.

5) *Anthropogenic sources. It is clear from the Rn and CO measurements that the Cape Point site samples air with continental and anthropogenic influence. I think the authors still claim that anthropogenic sources can enhance the bromoform mixing ratios seen at Cape Point. I don't believe that the authors make any credible case for this influence, and perhaps the entire sections on "events" might be removed since no clear conclusions can be found to explain the variation in the data. For example, the event on the 18th of October is suggested to be influenced by emissions from the nuclear power plant cooling waters. This is due to the trajectory analysis and the observation of the highest CHBr3 level seen. However, as I look at the data, I note that: 1) The maximum on the 18th is not so different from that on the 17th or during other periods of marine biogenic influence only. 2) The trajectories on the 17th are very different from some on the 18th, with concentrations very comparable. 3) The authors suggestion implies that emissions from the Koeberg reactor would produce atmospheric CHBr3 levels much higher than the high peaks observed from marine only influence. It would be helpful to have some reasonable calculations, at least, to show that this might be possible.4) Based on the time series, it seems that the Rn/CO peak actually precedes the CHBr3 peak.*

Response: What we tried to do in response to the previous criticisms was separate the data into two groups: (i) those where anthropogenic influence could definitely be ruled out and (ii) those in which it could not be conclusively ruled out. Because a point falls into the 2nd group does not imply we have proved an anthropogenic contribution, but merely that we can conclusively exclude the possibility. Given the highly limited datasets when analysed on an event scale or case study we possibly over-interpreted the data.

Remedial action: As per the reviewer's suggestion, the case studies section as a whole has been removed from the text. This section was creating more confusion than shedding light on the measurements in this data sparse region and no clear conclusions can be found to explain the variations observed.

6) *Additional comments…1) While kelp are known sources of bromoform, there may certainly be other sources near coastlines. I say this from observations near my institution which contain very high levels of dissolved bromoform and high atmospheric levels (around 15 to 25 pptv) with no evidence of kelp in the area. We haven't yet investigated the specific sources yet. 2) If the authors continue with this work, it would be helpful to their analyses of different sources if they could measure a wider range of trace gases from their samples. The technology to do this sort of analysis is well established.*

Response: The authors would like to thank the reviewer for this comment. We agree with the points raced by the reviewer. From personal conversations with Dickon Young and Simon O'Doherty of the University of Bristol it is understood the marshes surrounding Mace Head contribute significantly to the local atmospheric loading of bromoform. This is clearly not from an oceanographic source. While there are no significant marshes surrounding Cape Point, it is possible that the local vegetation may contribute to the atmospheric loading. There is extensive, untested, vegetation surrounding Cape Point to the north of the station. The natural reserve extends for at least 15 km N of the station.

Remedial action: Further work in this region is being planned and will make use of updated equipment and include a number of related compounds, both biogenic and anthropogenic. Hence, the long gap between this data and a new campaign being initiated.

REVIEWER 2

The manuscript is much improved and I commend the authors on their hard work and perseverance. This still represents a rather limited dataset, but the authors have, in my opinion, made sensible alterations to their interpretation of the data and to the conclusions drawn. I still have some reservations, particular in the interpretation of some of the case studies, but I would be happy to recommend publication in ACP once the issues outlined below have been addressed.

Response: The authors would like to thank the reviewer for their comments and suggestions regarding our paper and for the compliment regarding our hard work! Their comments have resulted in a significant improvement of the quality of the text and content of this manuscript.

> *P1, L5: replace "an" with "a"*

Remedial action: This has been corrected.

> *P1, L12: apart from a few minor anthropogenic sources ....*

Remedial action: The sentence has been revised to remove the anthropogenic sources clause. This has been formed into a separate sentence.

> *P1, L12: are there individual references for the different anthropogenic sources or do they all come from Quack and Wallace (2003)?*

Response: The reviewer is correct, there are a number of papers relating to anthropogenic sources of bromoform.

Remedial action: Selected authors describing different anthropogenic sources have been added to the text.

> *P2, L30: higher atmospheric levels are not just seen in "tropical" regions – they are often associated with seaweeds at mid-latitudes as well (Mace Head, etc).*

Response: Agreed, it is not only in the tropics that higher atmospheric levels of bromoform are found.

Remedial action: The section has been reworked to remove the ambiguity or the focus on the tropics. That elevated levels of bromoform can be produced in kelp beds, wherever they are and not just in the tropics.

> *P3, L20: replace full stop with a comma – i.e. ".. into the UTLS, where bromine-*

initiated ...”

Remedial action: This has been done.

> *P3, L21: add “the”. i.e. “ ... contribution from the Cape Point region is ....”.*

Remedial action: This has been corrected as the reviewer suggested.

> *P3, L31: delete second use of the word “extensive”*

Remedial action: This has been removed.

> *P4, L11: typo “Perkin Elmer”, not “Perkin Elmar”.*

Remedial action: The typo has been corrected.

> *P8, L13: what does pm mean (13.2 pm 9.7 ppt)? plus/minus?*

Response: This was a typographical error in Latex. The command instruction was left out. The reviewer is correct it is meant to be plus/minus.

Remedial action: This has been corrected.

> *P8, L13: Figure number is missing*

Remedial action: This has been corrected.

> *P8, L14: I don’t particularly like this sentence “The measurements were largely consistent within a few days, however could vary by 10s of ppt between days”. What are the authors trying to say here? Please try rephrasing. Something like “Bromoform was typically in the range of 1-20 ppt but on several occasions elevated mixing ratios were encountered that could last for several hours .....”*

Response: The authors would like to thank the reviewer for this comment. Their suggestion is excellent and has been implemented as suggested.

Remedial action: The sentence has been revised as per the reviewer’s suggestion.

> *P8, L26 Should “Cape Town” read “Cape Point”?*

Response: The reviewer is correct, this should read “Cape Point”

Remedial action: This sentence has been revised and corrected.

> *P8, L28: missing parentheses around the reference.*

Remedial action: This has been corrected.

> *P9, Fig 3: Units are missing from the y-axis*

Response: The authors would like to thank the reviewer for this comment.

Remedial action: Where possible the units have been added directly to the figure, otherwise they have been included in the caption text.

> *P9, Fig.3: please make it clearer either in the Figure caption or perhaps in the text which is high tide and which is low tide. The graph (2nd panel down) varies from 0.6 to 1.4, but what does this mean?*

Response: We apologise for the confusion caused in this figure. The tide heights are given in metres above a chart datum defined by the South African Hydrographic Office. Thus, lower values denote a low tide while higher values indicate a high tide.

Remedial action: The caption of figure with tides has been amended to reflect this. Furthermore, a more complete description of the source of the tidal data and what it means has been added to the Methods and Material section.

> *P9, L4-6: You say that the tidal height is a "necessary but not sufficient factor" in the high bromoform episodes but then go on to say that "it is therefore likely that the extensive local kelp beds are an important source of the observed bromoform". These statements seem to contradict themselves a little. Please consider rephrasing these 2 sentences.*
>
> *It is interesting that the seaweeds do not become completely exposed at Cape Point. Is this true of the wider region as well? Are you able to smell the seaweeds at low tide? This might be a good indicator of very local emissions!*

Response: We thank the reviewer for observing this ambiguity in the text. The sentences have be revised to as per their suggestion to remove ambiguity and contradiction. This will greatly improve the quality of the text.

It is true of the region as a whole. The horizontal extent of the tides in South Africa is quite limited. One can definitely smell the seaweeds at low tide, especially an iodine smell. This is particularly noticeable at low wind speeds.

Remedial action: The sentences have been revised and now read:

"While the maximum tidal range in the vertical at Cape Point is comparable to that at Mace Head, the horizontal extent is much smaller, may explain the lack of correlation. Consequently, during low tide at Cape Point, only the tops of the kelp fronds become exposed to the atmosphere. This is common around the coast of South Africa. Nonetheless, the elevated bromoform events with the highest mixing ratios all appear to mostly occur shortly after low tide (Fig. 3). It is therefore likely that the extensive local kelp beds are an important source of the bromoform observed at the station."

> *P10, L3: replace "particularly" with "including"*

Remedial action: This correction has been made.

> *P11, L1: missing Table number*

Remedial action: The missing table number has been inserted.

> *P11, L2-4: I don't like this sentence very much either. "The introduction of........". How does it allow for the determination of scale of the anthropogenic contributions in this*

> *region? Do you mean anthropogenic bromoform? As I mentioned in my first review when you have seaweed beds to the north of Cape Town it is very hard to distinguish whether the CHBr3 comes from an anthropogenic source rather than a marine source further to the north.*

Response: The statement was meant to be more general about air masses rather than about bromoform in particular. We apologise for the confusion caused. The reviewer is correct that the kelp beds to the north make the attribution of sources difficult. The local measurement of radon at Cape Point has been used extensively as a marker of air mass characterisation. An air mass sample from the north could entrain bromoform from a biogenic source on its way to Cape Point. An analysis of the ratio of CH_2Br_2 to $CHBr_3$ could shed light on the source of the air mass, or whether there has been anthropogenic entrainment.

Remedial action: The sentence regarding the introduction of intermediate air has been revised to make it clear that it is anthropogenically modified in general. We feel that the description on air mass characterisation is sufficiently clear that we are able to separate clean marine air from anthropogenically modified air at Cape Point. Furthermore, that in this case we are not able to separate or identify whether there has been any anthropogenic modification to the bromoform measured at Cape Point.

> *P11, L9: strictly speaking the kelp beds were not "responsible" for the measurements. Please rephrase.*

Response: The reviewer is correct that the kelp beds were not 'responsible' for the measurements.

Remedial action: The sentence has been revised and now reads:

"It is therefore, likely that the local kelp beds were the source of the bulk of the measured bromoform, including the elevated mixing ratios observed."

> *P11, L24-25: although you say there was no correlation between bromoform and boundary layer height you cannot say that BL ht has no influence. Even in the diurnal cycle shown in Figure 4, the gradually declining concentrations after 10 am could partly be due to an expanding boundary layer as the atmosphere warms up. This would cause a dilution and therefore contribute to the decline. Similarly in the evening when the nocturnal boundary forms, might this not contribute to the higher concentrations you observe in the early evening and through to 11 pm. There could also be a link between boundary layer height and tide. Low tide and low BL could lead to higher concentrations particularly if there are emissions at night?*

Response: We thank the reviewer for these comments and suggestions.

Remedial action: The meteorological and diurnal sections have been revised to include a more complete description of the role of the MBL in the observed bromoform variations.

> P12, L5: delete "in"

Remedial action: This has been deleted.

> P12, L6: the overnight low looks more like 12-13 ppt from Figure 4

Response: The author is correct, that the wrong value had been reported.

Remedial action: This has been corrected with the revised values based on the updated calibration.

> P12, Fig 4: it would be useful to have an indication as to the number of samples in each hourly bin

Response: The reviewer is thanked for this comment.

Remedial action: The following table has been calculated, as per the reviewers suggestions. However, perhaps this represents more detail than is necessary in the final publication. We are happy to include/no include as per the editor's discretion.

Table: Calculated bromoform mixing ratios and 95% confidence intervals for sampling period to create mean diurnal pattern. Measurements of bromoform are given in ppt.

Hour of Day	Mean	Upper	Lower	Number of samples
6	21.0	27.6	16.3	3
7	17.9	25.1	11.2	8
8	18.5	22.1	14.8	8
9	20.0	24.3	13.7	8
10	24.2	39.9	12.5	5
11	29.1	44.4	12.2	5
12	20.6	28.8	12.9	11
13	26.7	38.1	17.3	12
14	20.6	31.0	13.3	10
15	25.8	36.1	17.2	9
16	18.1	28.0	11.0	9
17	12.7	18.6	6.7	8
18	19.4	27.5	10.9	6
19	17.8	26.6	8.8	9
20	19.3	26.0	11.6	7
21	19.1	26.5	11.7	8
22	16.8	26.6	5.7	7
23	26.8	NA	NA	2

> *P13, para 1: note my point about BL height (above).*

Response: The reviewer is thanked for their comments regarding the MBL.

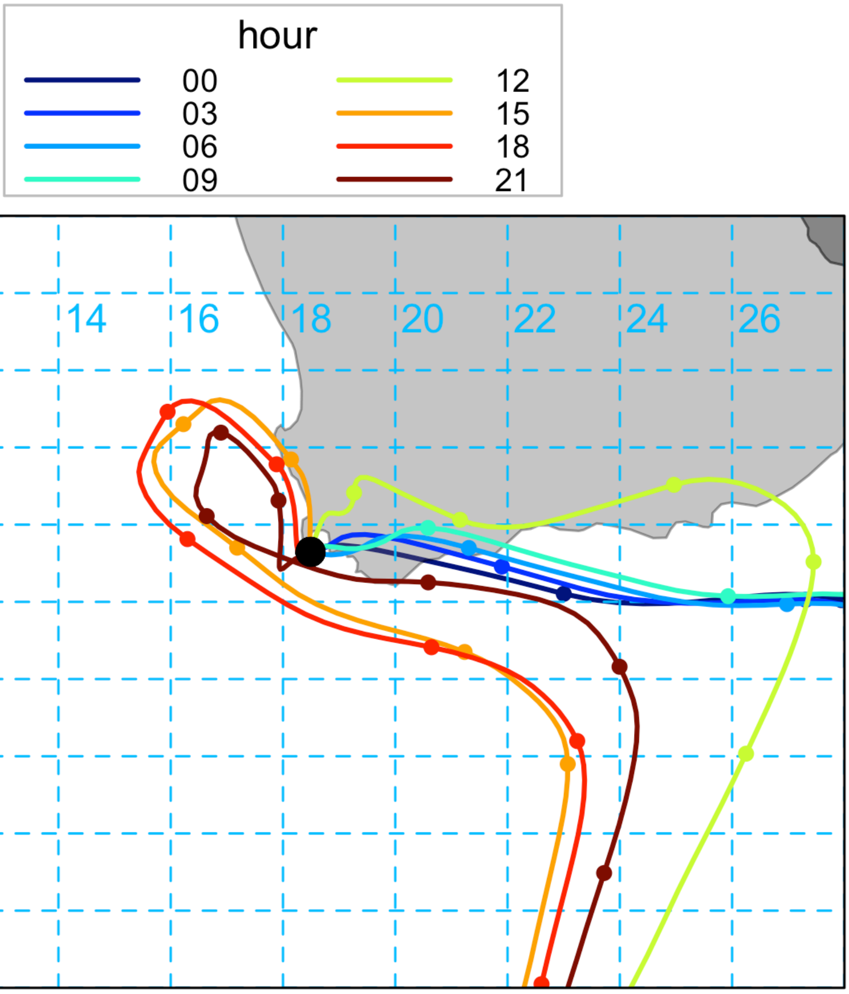
Remedial action: The meteorological and diurnal sections have been revised to include a better description of the variability of the MBL and the effect on bromoform concentrations.

> *P15, Fig 6: Does the sample with the maximum concentration of bromoform correspond to the back- trajectory that passes through Koeberg?*

Response: In short, no. It does pass, at low level, over an extensive water treatment facility though. Also, interesting to note is that later trajectories do pass over Koeberg.

Remedial action: These are calculated trajectories for 18 October 2011 for every three hours. This section has been removed from the manuscript. The elevated mixing ratio reported in Fig 6 occurred at approx. 11 am. One can see that the trajectories arriving between 9 am and 12 pm occur from an easterly direction, while later trajectories come from the north and transit over Koeberg.

Figure: Calculated back trajectories starting every three hours on 18 October 2011.



> *P15, Fig 6: why do the trajectories start at an altitude of over 200m? Is this the altitude of the sampling location (I had assumed it was lower)? Also, the trajectories look a bit odd as they seem to go to almost negative altitudes, particularly on the 18th? You do not comment on these altitude profiles in the text. What do they actually tell us?*

Response: The reviewer is correct, the South African Weather Service GAW station sits at the top of a cliff at a height of 230 m. The heights on the 18th are close to zero, but not actually negative. The size and shape of the markers might make it look like the heights transition below the zero line.

The trajectory heights, and maybe this was not made clear in the text, help to show whether surface sources might be entrained in the air mass. For example, had the trajectory height on 18 October been at 500 or 1000 m then a source at Koeberg could not have been entrained.

Remedial action: The height of the laboratory has been added into the introductory text. The case studies section has been removed entirely from the manuscript. This includes this back trajectory analysis. A revised analysis involving a concentration weighted trajectory (CWT) model analysis has been included.

> P16, Fig 7: the line for mbl looks a little odd. Was there no change in boundary layer height on the 26 October? Also, the units are missing from the y-axis (same for Figs 5 and 8).

Response: We thank the reviewer for this comment. There were occasions when the calculated MBL height did not vary between balloon runs. This has been revised.

Remedial action: The MBL heights have been checked and revised. Updated figures have been plotted for this revision of the manuscript.

> *P17, L7: "The" should read "the" (no capital required).*

Response: We thank the reviewer for this observation.

Remedial action: The word 'the' has been corrected to remove the unnecessary capital.

> *P17, L25: missing word "between 3 and 6 pm"?*

Remedial action: The missing word 'between' has been added.

> *P18, L5: delete the first "known", and, better still, replace "known" with "potential". You haven't confirmed in this work that the power and water plants in CT actually produce bromoform.*

Response: The authors thank the reviewer for this comment. Although we have not proved that nuclear power plants produce significant levels of bromoform other authors have, e.g. Quack and Suess, 1999. It is therefore reasonable to assume that Koeberg is a source, at least locally, of atmospheric bromoform.

Remedial action: The case studies have been removed as per the reviewer's suggestion. Thus, negating the need for corrections on this point.

> *P18, Fig 8: again the boundary layer height looks strange. No change between 9 am on the 7th Nov and 9 am on 8th Nov?*

Remedial action: The case studies and figures have been removed from the text.

> *P19, Fig 9: The wrong date is used in the figure caption.*

Remedial action: The figure and caption have been removed.

Comment on the case studies

I understand that the authors are trying to highlight some of the more interesting features in their data, but I worry that they do not really have enough data to come to any conclusions. For example,

in Case 1, the argument for an anthropogenic source is essentially based on one single data point, which occurs during a period of elevated CO and radon (and also at low tide). I wonder if the trajectories in Figure 6 could be coloured differently to show the gradual change of air mass origin over the period.

Response: See remedial action below.

In Case 2 it is very hard to discern anything meaningful from the various parameters discussed, particularly in regard to the tidal heights. I do however notice that the wind speed increases over the period. As the winds are coming from the west, would an open ocean source (influenced by increasing winds) not be a possibility as well? Again this would be highly speculative.

Response: The reviewer is correct that the data in this study is sparse. This makes it difficult to draw any firm conclusions. The limited data leaves little scope but to be speculative.

Remedial action: A decision has been made to remove the case studies section from the manuscript, as per both reviewers' suggestion. The paper focuses on the measurements of bromoform at Cape Point as a whole, the diurnal cycle and the likely impacts of variations in the MBL height and a back trajectory analysis which suggests that the highest concentrations might be sourced from off shore in the south Atlantic.

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 gas chromatograph-electron capture detector (GC-ECD) with a custom built front end thermal desorption trap. The measured concentrations ranged between ~~1.1 and 46.2~~ 1.3 and 59.4 (± ~~7.4~~ 24.8 %) ppt with a mean of ~~13.2~~ 20.4 ± ~~9.7~~ 13.2 ppt. The highest mixing ratios recorded here occurred at, or shortly after, low tide. The diurnal cycle exhibited ~~an~~ a 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.~~

. A concentration wighted trajectory analysis of the bromoform measurements suggests that two offshore source areas may exist. These source areas appear to be centred on the Agulhas retroflection and a transect extending from St Helena Bay to the southwest.

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~~ (Quack and Wallace, 2003). A few anthropogenic sources are known including water treatment, nuclear power plants (Quack and Suess, 1999) and rice paddies (Redeker et al., 2003), however these tend to small on a global scale (Carpenter and Liss, 2000; Quack and Wallace, 2003). It was estimated that globally between 2.2 x 10^{11} ~~-2.5~~ - 2.5 x 10^{12} g $CHBr_3$ yr^{-1} (Carpenter and Liss, 2000; Quack and Wallace, 2003) is produced of which only 3.0 x 10^{10} g $\mathrm{CHBr_3}$ yr^{-1} is anthropogenic (Gschwend et al., 1985; Allonier et al., 1999; Quack and Wallace, 2003 the rest being from natural sources, including 1.3 x 10^{11} g $\mathrm{CHBr_3}$ yr^{-1} from brown algae and 1.7 - 2.0 x 10^{11} g $\mathrm{CHBr_3}$ yr^{-1} from phytoplankton ~~(Carpenter and Liss, 2000; Quack and Wallace, 2003)~~(Manley et al., 1992; Carpenter and Liss, 2000; Quack and Wall 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; Kupper 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 ~~(Aschmann et al., 2009; Hossaini et al., 2010; Saiz-Lopez et al., 2012)~~(Aschmann et al., 2009; Hossaini et al., 2010; S Thus, bromine chemistry could play a significant role in climate change through ozone depletion in the UT (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~~ ppt of inorganic bromine is contributed directly from bromoform to the lower stratosphere ~~(Aschmann et al., 2009)~~(Aschmann 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 regions with extensive kelp beds and in areas of strong ~~upwelling and in tropical coastal regions (Quack and Wallace, 2003).~~coastal upwelling (e.g. Quack and Wallace, 2003; Quack et al., 2007a). 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 the 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~~ Similarly, no time series of measurements at a fixed point currently exists for a coastal site in southern Africa. The Cape Point GAW monitoring station provides a point from which to begin addressing this lack of southern African measurements. 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~~ . Brunke et al. (2004) classify these as follows: 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~~ , where bromine initiated catalytic ozone destruction occurs. To quantify the importance of the measurements made at Cape Point to tropical deep convection it is necessary to note how the synoptic conditions change seasonally over South Africa. During summer approximately 5 % of trajectories from South Africa escape to the Atlantic (10 °S), while 75 % of transport exits to the southeast (Tyson and Preston-Whyte, 2000). Ridging high pressure systems, present during spring and autumn, increase the transport to the tropical Atlantic to 25 % (Tyson and Preston-Whyte, 2000). Moreover, data recorded here is of

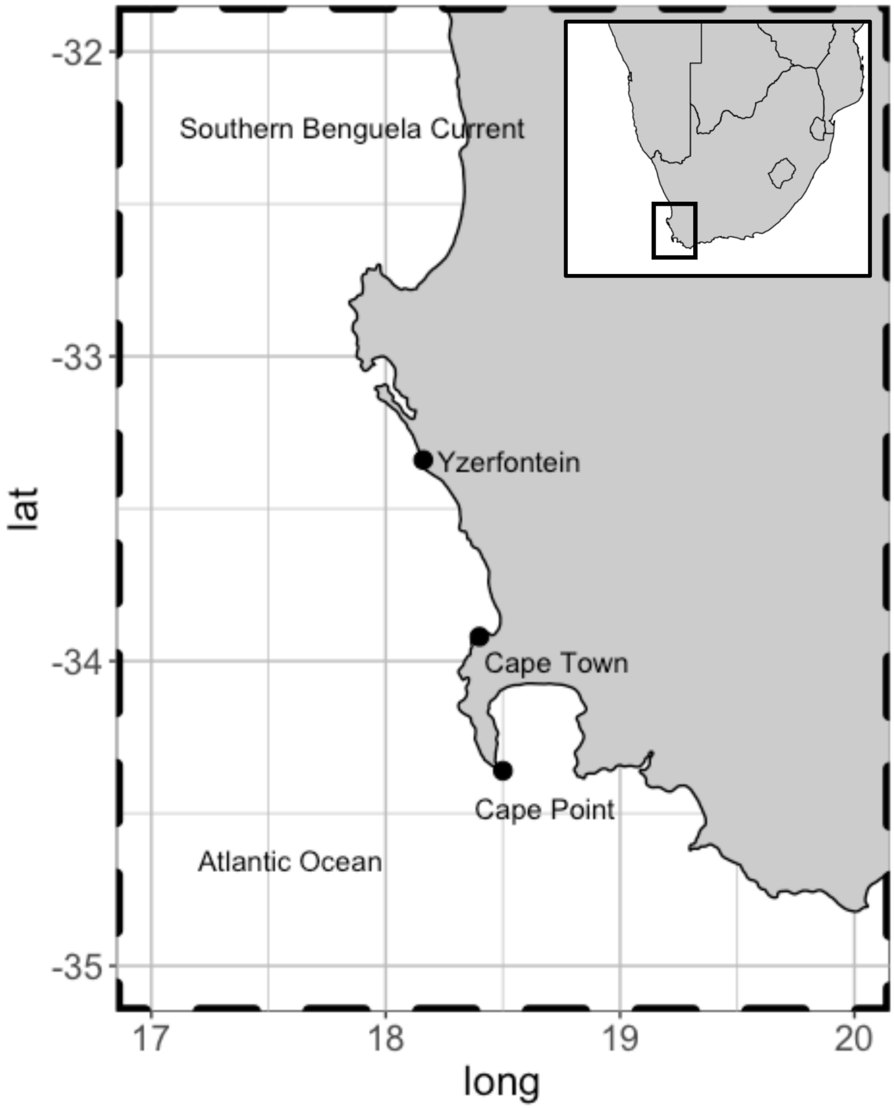


Figure 1. Location of Cape Point in relation to Cape Town. Kelp range along the entire coast. These are dominated by *Ecklonia maxima Papenfuss* south of Yzerfontein but transition to predominantly *Laminaria pallid Greville* north of Yzerfontein. Adapted from Kuyper 2014

particular value as the size of the contribution from the 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~~ 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~~ lies in close proximity to 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~~ have been 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~~ The studies have shown 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 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 GAW station sits at the top of a coastal cliff (230 m a.s.l) at the end of a peninsula south of Cape Town (Fig. 1). 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~~ Elmer 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 $\mathrm{^{\circ}C\,min^{-1}}$ and held isothermally once the new temperature was reached.

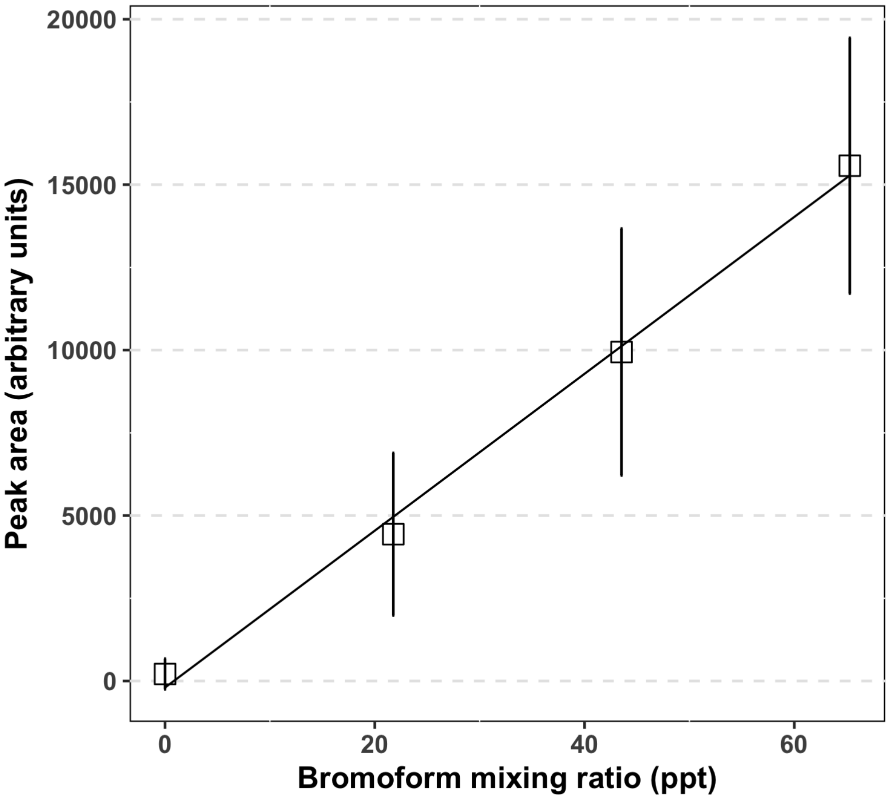
Air samples were pre-concentrated in a custom built thermal desorption unit (TDU, Kuyper et al., 2012). Adsorbents (Carbopac X and Carboxen 1016, 9 mg each) held in a glass tube were cooled to -20 °C during the trapping phase. The cooling of the system was achieved by a recirculating chiller filled with 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 $^{\circ}\mathrm{C}$ 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 $^{\circ}\mathrm{C}$ (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 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~~ 0.343 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~~ which resulted in 1.36 x10^{-12} mol being loaded on the trap, ~~the number of moles (bromoform) was converted to a mixing ratio.~~ per sample loop injection. The number of molecules of bromoform was calculated by multiplying the number of moles by the Avogadro constant to yield the number of bromoform molecules on the trap. The total number of molecules in a sample was calculated by multiplying the air number density (2.5 x10^{25} $\mathrm{molecules\,m^{-3}}$) with the sample volume (1.5 l). The bromoform mixing ratio of one loop was calculated as the number of bromoform molecules of one loop as a fraction of number of molecules in a sample multiplied by 10^{12} to yield ppt.



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

Figure 2. Calibration of the GC-ECD system for bromoform, based on multiple loop injections. Peak area calculated using the trapezoid method.

~~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~~ performed at the start of the sampling at Cape Point. Thereafter, a calibration point of 1-3 loops was ~~run~~ measured every 5 air samples to account for system drift. Comparison of the same number of loop injections of different days was used to see if any change was present, resulting in drift. Based on a linear regression between the introduced sample and peak area response a ~~99.7~~ 99.6 % accuracy was achieved on this system (Fig. 2). An analysis of repeated ~~2~~ three loop injections indicated a system precision of ~~7.4 %~~ 24.8 % based on the RSD of repeated standard peak areas. 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: CO_2, CH_4, CO, radon (^{222}Rn) and 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 $^{\circ}\mathrm{C}$ 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.

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 min with a calibration occurring every 2 hours. Radon (^{222}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~~ reanalysis data as the meteorological data in *R*. The back trajectories were ~~run for 72~~ calculated for 96 hours prior to bromoform measurement. The trajectories were merged with the bromoform data set to allow for integrated analysis using the *openair* package (Carslaw and Ropkins, 2012). This package comprises a range of statistical tools to examine back trajectories, in order to identify source regions or contributions.

The potential source contribution function (PSCF) in *R openair* calculates the probability that a source exists at a specific location (Fleming et al., 2012; Pekney et al., 2006). The PSCF is calculated by the ratio of trajectories with elevated concentrations to the number of times those trajectories pass through a specific point, defined as grid cells. A value for each grid cell is calculated. These grid cell values can be the same when the sample concentrations are either marginally above or greatly elevated from a defined criterion, e.g. the mean (Hsu et al., 2003; Carslaw and Ropkins, 2012). Consequently, the difference between strong and moderate sources can be difficult to distinguish. The concentration weighted trajectory (CWT) method can be used to potentially identify source areas through the calculation of concentration fields. The mean of the concentration for each grid cell was calculated as follows:

$$ln(\bar{C}_{ij}) = \frac{1}{\sum\limits_{k=1}^{N} \tau_{ijk}} \sum_{k=1}^{N} ln(c_k)\tau_{ijk} \qquad (1)$$

where i and j are the grid indices, k is the index of the trajectory, N is the total number of trajectories used, c_k is the pollution concentration of trajectory k upon arrival and τ_{ijk} is the residence time of trajectory k in grid (i, j) (Carslaw and Ropkins, 2012). High concentrations at the measurement site would, on averaged, be caused by grid cells with elevated values of $\bar{C}_{ij}$. Thus, indicating possible source regions. The CWT back trajectory calculation was performed on the entire data set of bromoform measurements at Cape Point. As a first approximation of the offshore sources of bromoform to Cape Point a concentration weighted trajectory (CWT) model analysis of the back trajectories was performed.

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.

Tidal height

The tidal height for Cape Town was obtained from the South African Hydrographic Office (SAHO). Tidal gauges are used to measure the height in the harbours around South Africa. Due to peridoic instrument failures of some of the gauges around Cape Town during the bromoform sampling period, tidal hight estimates were used to interpolate over any gaps. The height is given in metres above a SAHO locally defined chart datum and therefore the lower the value the lower the tide.

Diurnal cycle

A mean diurnal cycle was calculated from the full range of Cape Point measurements using the *timeVariation* function of *openair* (Carslaw and Ropkins, 2012). 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~~ mean in each bin 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~~ 1.34-59.4 ppt with a mean of 20.4 ± 13.2 ~~9.7~~ ppt (Fig.~~time-series). The measurements were largely consistent within a few days, however could vary by 10s~~

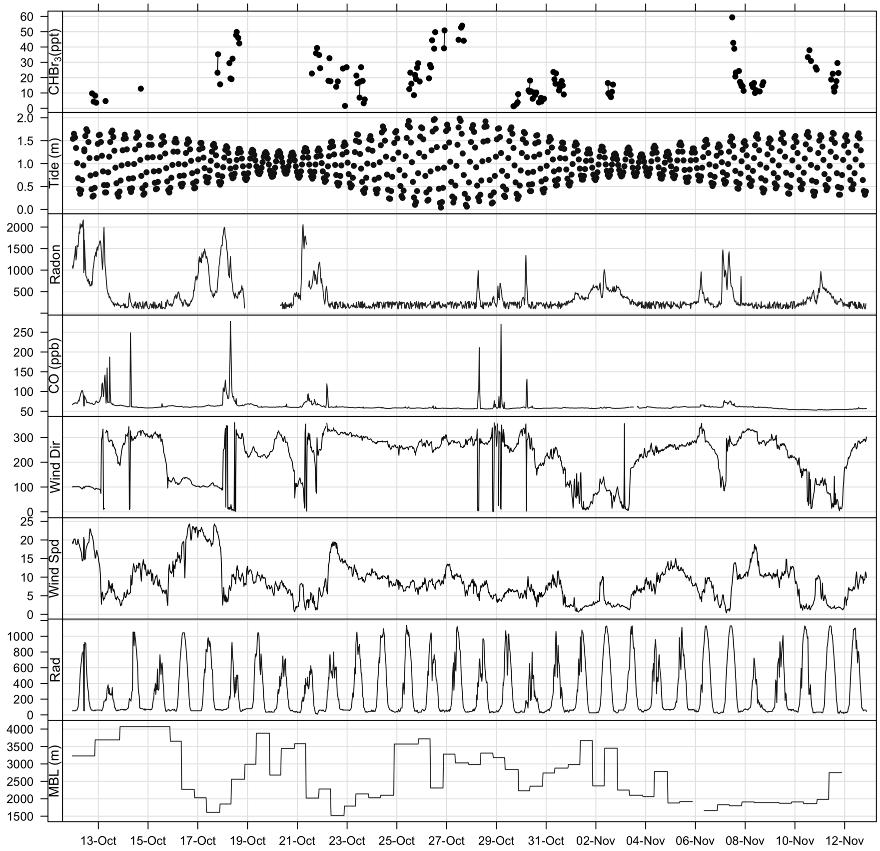


Figure 3. Time series plot of bromoform and meteorological measurements at Cape Point during October/November 2011. ~~Events are highlighted by the coloured lines: E1 = red~~Tide height given in m above SAHO datum, ~~E2 = green~~Radon mBqm^{-3}, ~~E3 = violet~~Wind direction in degrees, Wind speed ms^{-1}, Radiation Wm^{-2}.

~~of~~ 3). Bromoform was typically in the range of 1-20 ppt ~~between days~~ but on several occasions elevated mixing ratios were encountered that could last for several hours (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~~ 57 % 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 measured 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.~~

Table 1. Selected comparison measurements of bromoform in air samples above coastal, upwelling, open ocean and lower marine boundary layer regions. Tidal height is given in m above the standard datum.

				$CHBr_3$ (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., 2007b	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., 2016a	Open ocean
R/A Falcon	July 2014	2-16 °N	0.99	3.78	1.90	Fuhlbrügge et al., 2016a	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., 2016b	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~~1.34**	**~~84.7~~59.4**	**~~24.7~~20.4**	**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

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~~Point) 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~~(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 reported here do not correlate well with the tidal pattern~~, with higher mixing ratios being recorded regardless of the tidal range. This lack of correlation may be explained as, while~~. While the maximum tidal range in the vertical at Cape Point is comparable to that at Mace Head, the horizontal extent is much smaller.

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

	Clean Marine	**Intermediate**	**Continental**
$^{222}\mathrm{Rn}\ \mathrm{mBq\,m^{-3}}$ (number)	< 350 (~~881~~1028)	800-1500 (115)	>1500 (45)
Mean $CHBr_3$ ppt (number of samples)	~~12.8 (75~~18.7 (92)	~~16.0 (12~~19.4 (13)	~~2.93 (1)~~NA
Range $CHBr_3$ (~~ppt~~ppt)	~~1.10-42.3~~ 1.34-53.9	~~2.35-46.2~~ 3.64-35.9	~~–~~NA

~~Consequently~~ This may explain the lack of local correlation. Consequently, during low tide at Cape Point, only the tops of the kelp fronds become exposed to the atmosphere. This is common around the coast of South Africa. 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.

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~~ including 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~~ , 68 % were of clean marine origin. The bromoform mixing ratios in this clean air displayed a mean ~~12.8~~ 18.7 ppt and ranged between ~~1.10 and 42.3~~ 1.34 and 53.9 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~~ , which suggests a continental ~~and anthropogenic source~~origin and therefore anthropogenic contributions to the chemical composition of the air masses. The continental contaminated air made up ~~3~~ 9 % of the total measurements, with intermediate air masses accounting for 7.5 % of the measurements.

The bromoform mixing ratios in intermediate air samples showed a similar mean to that of clean marine air ~~(Table. ??~~with a mean of 19.3 ppt (Table 2). The introduction of ~~this~~ intermediate or continental air at Cape Point ~~allows for a determination of~~ potentially allows for the determination of the scale of the anthropogenic contributions in general for this region. Since ~~this~~ the intrusion of intermediate air occurs predominantly in winter, a longer time series could test the relative contributions more extensively.

In the case presented here, we are not able to conclusively separate anthropogenic and biogenic sources, due to the limited, single species data set. However, given the small difference in means, the data suggests that an anthropogenic contribution is not significant. The extensive kelp beds present to the north of Cape Town further complicate the matter. An expanded suite of sampled compounds would assist in the separation of sources through the examination of related compounds such as the ratio to CH_2Br_2. 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~~While, on a local scale anthropogenic source can dominate (Quack and Suess, 1999) ~~. During~~ during this sampling period the dominant contribution of bromoform was from the clean marine air masses and therefore, from biogenic sources (Table 2). ~~It is therefore, likely that the local kelp beds were responsible for the bulk of the measurements , including the~~

Atmospheric bromoform measurements from Mace Head, Ireland show periods of elevated mixing ratios ~~observed. Occasional intrusions of anthropogenically modified air may have contributed to the observed variability in~~ (D. Young, pers. comm. 2017). Analysis of these elevated mixing ratios at ~~Cape Point, as is discussed in the case studies below~~Mace Head suggests that the local marshes may be the most likely source. However, the reason why the marshes should be a source of bromoform remains unclear at this time. Although not surrounded by marshes, Cape Point is enclosed by natural vegetation called fynbos. It is possible that the fynbos releases bromoform into the local atmosphere. This would be particularly pertinent with air masses arriving from the north. A small study has previously examined the bromoform emissions from fynbos when burnt (Kuyper et al., 2012). The measured mixing ratios in this study showed a high degree of variability with a mean of 33.9 ppt and standard deviation of 40 ppt. The limited scope and high variability meant that no firm conclusions could be drawn regarding the release of bromoform from the fynbos (Kuyper et al., 2012).

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 a given location. 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 at this site 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~~ Although a direct relationship between bromoform mixing ratios and MBL height was ~~found in this study. This~~ observed at Cape Point, it is possible that MBL height played a role in the measurements observed. As the MBL height is elevated the rate of atmospheric dilution increases. This would result in lower measured bromoform mixing ratios. Conversely as the MBL decreases, so the volume of atmosphere into which gases are diluted decreases, resulting in a concentrating effect and increase in measured concentration. The lack of a direct observed relationship 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~~were released. However, the affect of changes in the MBL height may be reflected in the variability of the bromoform measurements.

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~~ 21 ppt, based on the first measurements of the day, to a mean maximum of ~~25.2 ppt~~ 26.7 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~~ 26.8 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~~ . As discussed above, changes in the height MBL act to concentrate or dilute the mixing ratio of samples in the lower atmosphere. The atmosphere into which gases can mix increases through the morning as the the MBL height rises, thus causing a dilution of trace gas in the atmosphere (Fuhlbrügge et al., 2013). This is most likely reflected in the decrease in bromoform mixing ratios at about noon and the stabalisation through the afternoon. A small contribution from the photolysis of bromoform ~~. Thus at high photolysis rates during the midday sun lower mixing ratios are observed. The literature also~~ may be present, however this would be neither detectable nor significant. A decrease in the rate of production in the afternoon or the arrival of air masses from alternate sources might explain the decrease in the late afternoon. A decreasing MBL height in the late afternoon or early evening would act to concentrate any locally released bromoform. The literature 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~~ (Ekdahl et al., 1998; Carpenter and Liss, 2000). During respiration, it is theorised that ~~the through~~ through the 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.~~ Therefore, production into the evening is possible and with a lowered MBL height the measured bromoform might be large. The evening maximum in mixing ratios is, therefore, expected

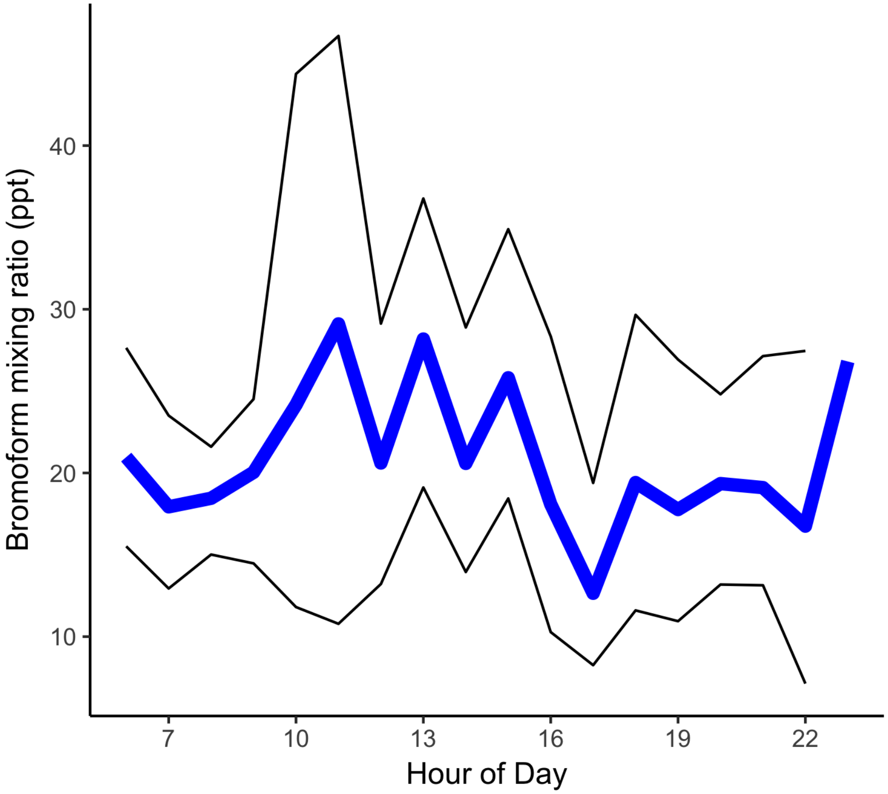


Figure 4. Mean diurnal cycle, calculated from all measurements binned by hour. The black lines above and below signify the 95 % confidence interval.

and consistent with previously studies in Gran Canaria and the Southern Ocean (Ekdahl et al., 1998; Abrahamsson et al., 2004).

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~~

3.2 Back Trajectory Analysis

Given the relatively long atmospheric life time of bromoform (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. **??**). Only a few bromoform measurements were captured on 17 October, which showed an increase from 13.0 . After reaching a maximum of 41.9 , the following bromoform mixing ratio measurement was 8.9 . These measurements were made in the early evening concurrently with an ebb tide. A series of measurements (10.7-16.4)surrounding the mean were observed on the morning of 18 October, just prior to the elevated measurements . The maximum concentration of 46.2 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) until sampling was stopped at 4 pm.~~

~~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.~~

~~The radon concentrations were elevated above 1000 for both mornings in this event window. However, CO concentrations were at baseline levels over 17 October, but showed a sharp increase to 250 on the morning of 18 October. The maximum in CO on 18 October is mirrored in the 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, 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 - the highest 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. **??**). This combination hypotheses would explain why we saw the highest mixing ratiosin 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.~~

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

~~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. **??**). A number of varying factors influencing the bromoform mixing ratios~~ weeks), there could be sources offshore that contribute to the observed measurements at Cape Point (Carpenter and Liss, 2000). While not excluding the local source, the contribution of offshore sources was investigated using the *openair* concentration weighted trajectory (CWT) calculations of back trajectories associated with bromoform mixing ratios. The CWT model suggests a large fetch and variability of source region for air masses arriving at Cape Point ~~were highlighted during this event. It is notable that the mixing~~

~~ratios remained below 300 over the entire event window~~ (Fig. ~~??~~5a). This ~~was coupled with CO concentrations that displayed typically baseline values (Brunke et al., 2004).~~

~~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) and remained below 20 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 to 24.6 at 10 am. These occurred during the flood tide and just before the local solar maximum. Bromoform mixing ratios increased to 27.5 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). The mixing ratios increased to a maximum of 38.9 at the end of sampling on 26 October.~~

~~Bromoform mixing ratios started out at a similar 38.8 at 5:00 am on 27 October. Thereafter the mixing ratios increased rapidly to 42.3 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 , which was comparable to the tides on either side (1.81 and 1.92 , respectively). The wind speed remained at approximately 10 for much of the event window, increasing late on 26 October to a maximum of 12 at 3 am. Thereafter the wind speed decreased back to 10 on the morning of 27 October.~~ large fetch typically included large areas of low bromoform entrainment, as would be expected from most of the open ocean. The model output suggests two main possible source regions of bromoform away from Cape Point: a transect line to the southwest of South Africa with three areas of increased mixing ratios sources and an area directly south of Cape Town. The area directly to the south of Cape Point exhibits the highest $\bar{C}_{ij}$ values and appears to be centred over the Agulhas retroflection region (Beal et al., 2011).

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~~ Agulhas retroflection region is an area in which the highly productive cold waters of the southern Benguela meet the warmer water from the Agulhas current. This combination of productive waters (with potentially high $CHBr_3$) and warmer sea surface temperatures driving higher rates of sea-air fluxes, could represent ideal conditions for observing higher atmospheric bromoform mixing ratios.

~~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) and increased slightly with edd tide to peak at 16.3 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 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) . The mixing ratios peaked just after the low tide but before the solar maximum. The 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 ratiosdecreased 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~~ transect line extends SW from South Africa to 45 °S and appears to contain three smaller areas of increased bromoform mixing ratios~~were captured during the event window (Fig. ??). Bromoform mixing ratios showed a decrease from 32.7 at 12:~~. It is possible that, certainly the two outer areas are warm core rings that have been shed off the Agulhas current. The elevated area at the coast of South Africa extends from Cape Columbine (33 °S) to 30 ~~on 7 November to a minimum of 6.6 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 . The decreasing bromoform mixing ratios occurred during a flow tide and followed into the next low tide.~~ °S (Fig. 5b). This area appears to be centred over St Helena Bay, an area known for strong coastal upwelling (Jennings et al., 2001; Kudela et al., 2005). Given the limited nature of this data set we can not draw any firm conclusions regarding the offshore source of bromoform to Cape Point. However, this is still an interesting aspect of the region that will be monitored carefully in future work.

~~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.~~

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~~ 135 discrete measurements made over the course of October/November 2011 exhibited a mean bromoform ~~concentration of 13.2~~ mixing ratio of 20.4 ± ~~9.2~~ 13.2 ppt. The maximum ~~reported value here (46.2~~ bromoform mixing ratio reported here (59.4 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~~ 68 %) 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

~~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. Radon mixing ratios were elevated (1500) in the morning of 7 November but decreased to below 500 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)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 , 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 , except for one measurement at 1 pm (24.4). This 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 .~~

~~The 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. **??**). By midnight on 7 November the and CO mixing ratios recorded were at baseline concentrations, strongly suggesting a clean marine air mass was sampled on 8 November.~~

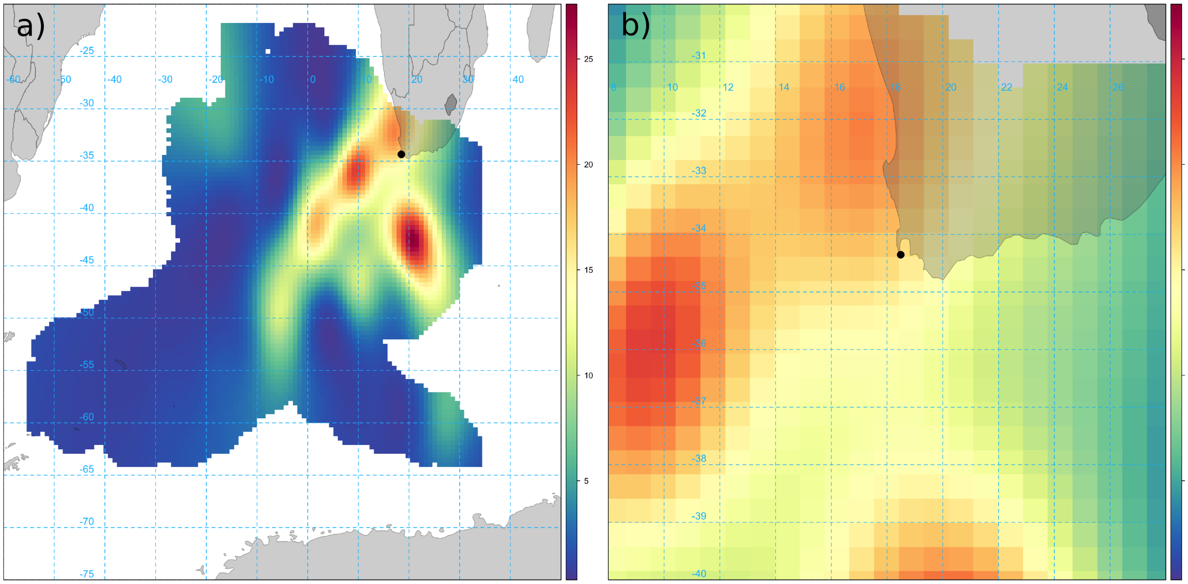


Figure 5. ~~Back trajectories~~ Smoothed CWT calculation of ~~17 and 18 October 2011~~bromoform based on Hysplit back trajectories, ~~highlighting the transit over Koeberg and~~ a) Zoomed to show full extent of 96 hour back trajectories. b) Zoomed to focus on Cape ~~Town~~Point. Units in colour bar reflect bromoform mixing ratios measured at Cape Point.

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.

In a similar manner to the marshes surrounding Mace Head, it is possible that the fynbos vegetation at Cape Point may be a local source of bromoform to the north. The fynbos as a local source remains speculative at this stage, but will be examined going forward.

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. Changes in the MBL height through the day is the most likely source of variation in bromoform mixing ratios in the diurnal cycle at Cape Point.

Back trajectory analysis using the CWT model from the *openair* package provides compelling evidence to suggest an offshore biogenic source. The main region of the source appears to be centred on the Agulhas current retroflection area. A second region of elevated bromoform mixing ratios appears to exist as a transect line extending from St Helena Bay southwest off South Africa. These will be monitored carefully going forward.

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. Work is currently underway to develop a more extensive halocarbon data set at Cape Point using updated equipment and calibration protocols.

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.

Disclaimer. TEXT

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