Atmospheric bromoform at Cape Point, South Africa: a first time series on the African continent

Brett Kuyper[1,*], Carl J. Palmer[1,2], Casper Labuschagne[3], and Chris J. C. Reason[1]

[1]Department of Oceanography, University of Cape Town, Cape Town
[2]Applied Centre for Climate and Earth System Science, CSIR, Rosebank
[3]South African Weather Service, Stellenbosch
[*]Now at: Department of Chemistry, University of the Western Cape, Cape Town

Correspondence to: Brett Kuyper (3479857@myuwc.ac.za)

Abstract. Bromoform mixing ratios in marine air were measured at Cape Point Global Atmospheric Watch Station, South Africa. This represents the first ever bromoform data set recorded at this unique 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 2.3 ± 0.4 and 84.7 ± 10.8 ppt with a mean of 24.7 ± 3.1 ppt. Our analysis shows the concentration of bromform varies significantly according to wind direction and the trajectory of the air mass sampled. Air masses which had come into contact with multiple potential source of bromoform showed the highest average mixing ratios. The measurements reported here represent some of the highest recorded coastal bromoform concentrations globally. These high concentrations may be explained by the multiple local sources of bromoform around Cape Point.

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, with a sweet odour similar to that of chloroform. Bromoform, apart from its anthropogenic sources, is naturally produced by kelp and phytoplankton in the upper layers of the ocean and, as a result, appears to be a ubiquitous competent of the global marine boundary layer (Quack and Wallace, 2003; Carpenter and Liss, 2000). Atmospheric outgassing 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 (Jones and Carpenter, 2005; Carpenter and Liss, 2000; Quack and Wallace, 2003). 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 (Küpper et al., 2008; Palmer et al., 2005; Quack and Wallace, 2003) and a peak in 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 bro-

5 moform source to the marine environment (Carpenter and Liss, 2000). Laboratory studies have measured significantly higher mixing ratios from kelp, per weight, when compared to phytoplankton (Carpenter and Liss, 2000; Tokarczyk and Moore, 1994; Moore et al., 1996). However, kelp species are coastally constrained, while phytoplankton are able to cover hundreds of square kilometers (Jennings et al., 2001; Kudela et al., 2005). A question remains regarding the dominant contribution to the global bromoform budget.

10 ## 1.2 Implications for atmospheric chemistry

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, this 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

15 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).

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

20 reaching the UT-LS region (Hossaini et al., 2010; Saiz-Lopez et al., 2012). Understanding the sources within this region is therefore of great specific scientific interest (Palmer and Reason, 2009). However, there exists a paucity of measurements of bromoform in this region (Palmer and Reason, 2009). Existing data tend to be from discrete shipboard measurements. By definition, these data are discrete snapshots and only measure a given location at a single point in a transient manner. No time series of measurements at a fixed point currently exist for a coastal site like Cape Point. The usefulness of atmospheric chemistry

25 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. These gases could play a significant role in climate change (Saiz-Lopez et al., 2012; Hossaini et al., 2010).

1.3 Significance of Cape Point location

30 Here we present the first ever bromoform dataset recorded at the Cape Point Global Atmospheric Watch (GAW) station (34.36° S 18.50° E, Fig. 1). This station offers a unique location to 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. The dominant wind direction results in a mixture of air sources ranging from marine sources (baseline) to intermediate air samples (Brunke et al., 2004). The
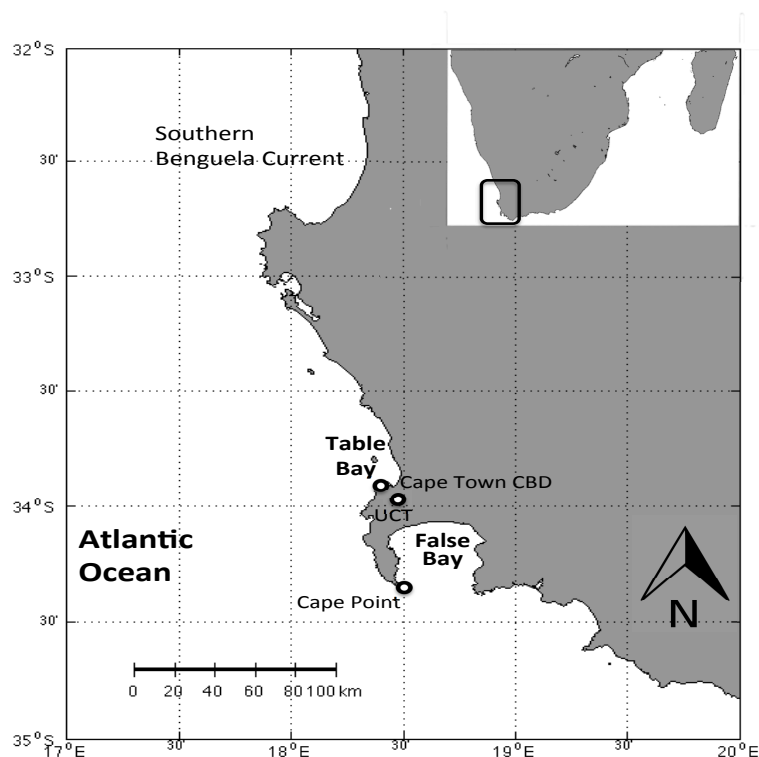
Figure 1. Location of Cape Point in relation to Cape Town CBD and southern Africa. Adapted from Kuyper 2014

subtropical location of Cape Point may make this region an important source of bromoform to the atmosphere. Elsewhere in the Southern Hemisphere, a time series measurements of bromoform has been made at Cape Grim, Tasmania but this location is much further south (~41° S) and in the Indian sector whereas the Cape Point data presented here represent the first of their kind in Africa, or for the South Atlantic region (Cox et al., 2003).

5   The Southern Ocean is largely regarded as a highly productive 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 largely 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 medium timescale measurements of bromoform in Southern Ocean air.

10   In addition to receiving baseline air from the south Atlantic and Southern Ocean Cape Point also sits above extensive kelp beds. 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 because of the 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

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

2.1   Sampling

10   The measurements of bromoform were made at 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-discrete sampling pattern with a measurement frequency of approximately 45 min to 1 hour. A total of 131 discrete bromoform measurements were made in air samples during this period.

2.2   Gas chromatography system

15   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. A constant helium flow of $5 \, \mathrm{ml \, min^{-1}}$ (Grade 5.0, Air Liquide) was maintained through the column at the start of the each analysis. The limited nature of the GC system meant that no adjustment was possible for the change in gas viscosity with the temperature ramp. The oven was maintained at 35 °C for 5 min following the injection of a sample. Thereafter the oven
20   temperature was ramped at $65 \, \mathrm{^\circ C \, min^{-1}}$ to 60, 90, 150 and 200 °C every 5 min.

2.3   Pre-concentration of samples

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. Air was passed through the trap at $100 \, \mathrm{ml \, min^{-1}}$ for 15 min, resulting in a 1.5 l sample size. The cooling of the system was achieved by a recirculating
25   chiller filled with glycol. An oil free piston pump was used to draw air through the trap. The pump was operated at 400 $\mathrm{ml \, min^{-1}}$ with the excess gas vented to the atmosphere.

After trapping air samples were rapidly heated for desorption. A built in resistance wire heated the glass tube to 400 °C. 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
30   the samples trapped at the head of the column.
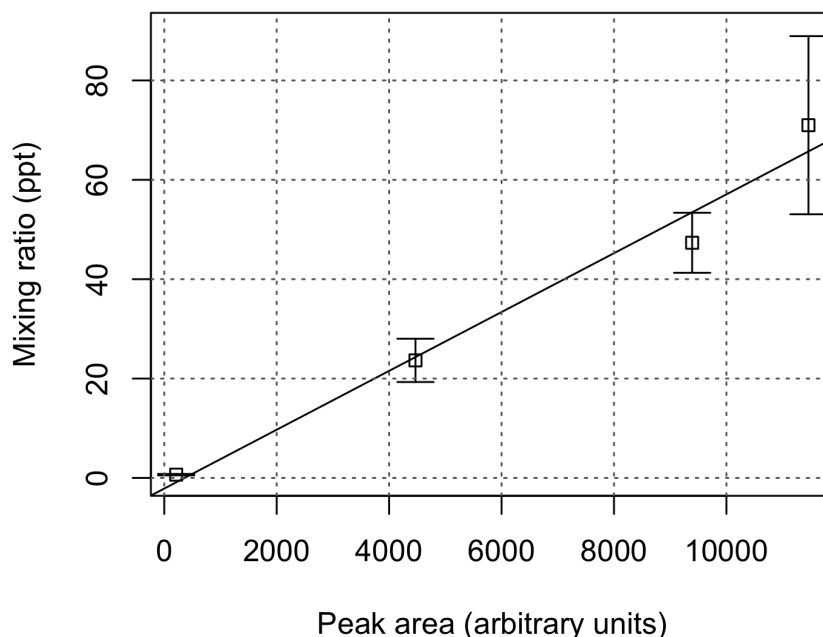
Figure 2. Calibration of the GC-ECD system for bromoform, based on multiple loop injections. Peak area calculated on the trapezoid method. (Adapted from Kuyper 2014)

2.4 Calibration

An external calibration method was used to verify the system performance. Bromoform at varying concentrations was introduced to the trap by means of a custom built permeation oven (Wevill and Carpenter, 2004; Kuyper, 2014). Aliquots of 100-300 µl of pure bromoform were introduced to the thermal desorption unit from the permeation oven. 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. Thereafter, a calibration point of 1-3 loops was run every 5 air samples to account for system drift. A 99 % accuracy was achieved with a 12 % precision utilising this system as described. The peak areas were calculated through the trapezoid method (Poole, 2003).

2.5 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 (Brunke et al., 2004; Whittlestone and Zahorowski, 1998; 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 an accumulation of contamination. Sequential cold trapping at -5 and -40 °C along the flow pass 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 a ANSTO-build, two-stage α-decay system which detects the collected radon daughter products (Whittlestone and Zahorowski, 1998; Whittlestone et al., 2009).

2.6 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.

3 Results

3.1 Chemical climatology

A variable wind speed and direction pattern was observed at Cape Point during the bromoform sampling period (October/November 2011). The wind was predominantly from the WSW to NW, drawing air from the mid Atlantic to southern Benguela. The highest wind speeds were also coincident upon this direction. A second mode of high wind speeds were observed from the E to ESE (Fig. 3a). Small contributions were added to from the north and south. Wind direction and radon concentration (^{222}Rn) at Cape Point were used to classify the arriving air masses (Whittlestone et al., 2009), (i) clean marine, (ii) continental, and (iii) intermediate (a mixture of marine and continental, as per Brunke et al., 2004). The bulk of the measurements were clean marine where ^{222}Rn concentrations were less than $350 \, mBq \, m^{-3}$ (Brunke et al., 2004; Fig. 3b).

The wind speed and direction time series shows the progress of different air masses influencing Cape Point (Fig. 4). The wind speed and direction shift from southeasterly through westerly to northwesterly as subtropical anticyclones pass and cold fronts approach from the southwest. Periods of stability were seen particularly between 15, 16 and 23-28 October. The transit of weaker cold fronts caused the occasional rapid shifts on the 19th, 29th and 30th. The wind speed was highest between the 14
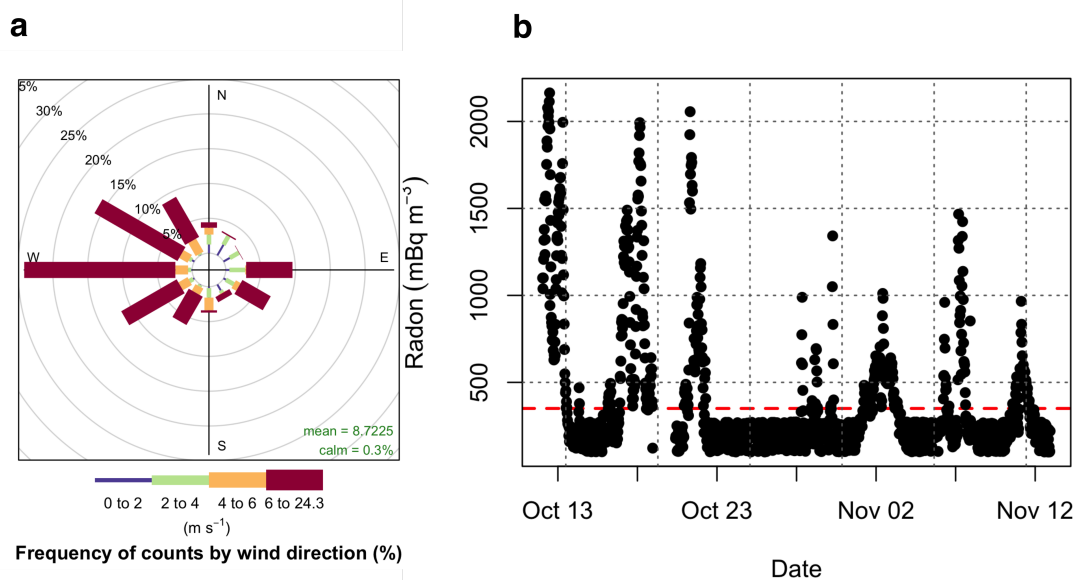
Figure 3. (a) Wind rose of wind speed and direction at Cape Point during the sampling period. **(b)** Radon time series at Cape Point. The grey dashed line indicates the 350 mBq m-3 separating clean marine air from intermediate air samples.
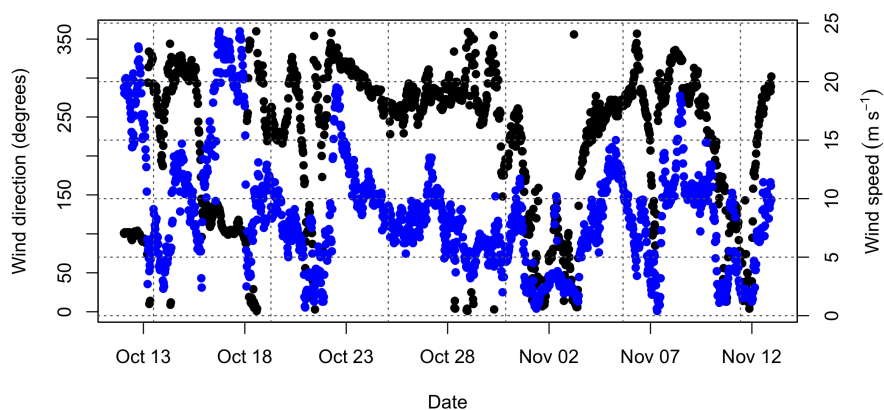
Figure 4. Wind speed and direction time series at Cape Point. Wind direction indicated in black and wind speed in blue.

and 16 October reaching above $20\,\mathrm{m\,s^{-1}}$. High wind speeds were recorded on the 5 and 9 November (~$15\,\mathrm{m\,s^{-1}}$). Otherwise the observed wind speeds were typically below $10\,\mathrm{m\,s^{-1}}$ (Fig. 4).
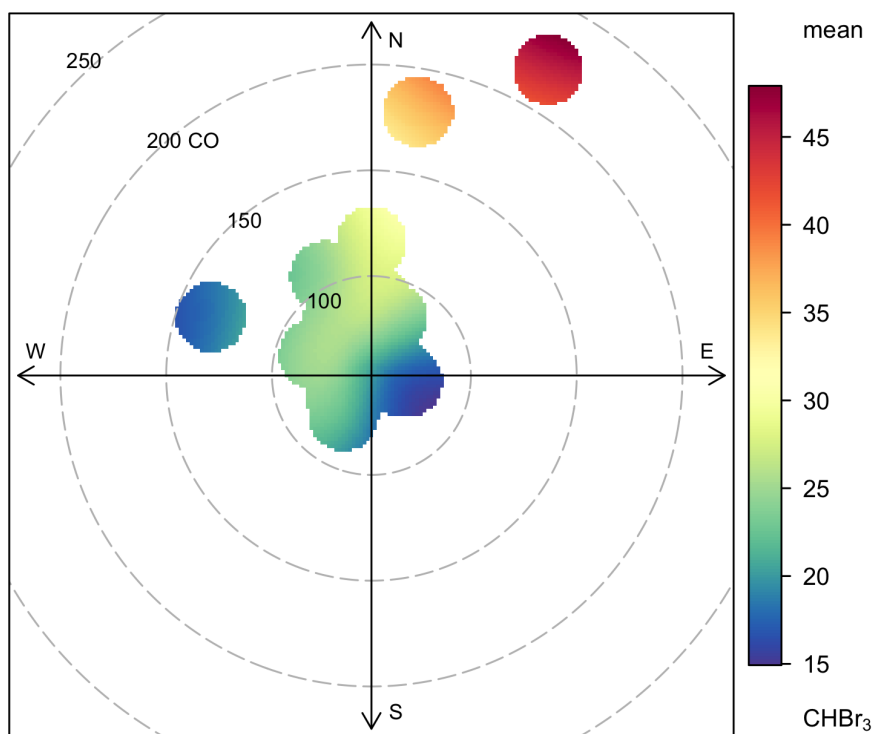
Figure 5. Polar plot of bromoform around Cape Point as a function of wind direction and CO mixing ratio. The colours denote bromoform concentration. The distance from the centre indicates increased CO concentration while direction is given by wind direction.

3.1.1 Carbon monoxide climatology

Concurrent measurements of carbon monoxide (CO) were used as an anthropogenic marker in the air samples. This further augmented the separation of the samples by air mass. Elevated CO concentrations (250 ppb) were observed to the northeast of Cape Point (Fig. 5). These elevated CO concentrations are coincident with a mean bromoform mixing ratio of 45 ppt (overall mean of 25 ppt). There were however, few bromoform measurements at these CO levels (9 discrete samples). Lower CO concentrations (<100 ppb) are associated with lower bromoform mixing ratios, especially those immediately surrounding Cape Point (Fig. 5). Measurements of bromoform at all ranges were recorded at CO levels below 100 ppb. The overall relationship between CO and bromoform in this data set is weak (r = 0.13).

3.1.2 Ozone climatology

The ozone mixing ratios measured at Cape Point were largely stable ranging between 20 and 35 ppb with a mean of 27.6 ppb (Fig. 6, 7). There were two periods of elevated O_3: 18-23 October and 7-10 November (Fig. 7). During these periods the ozone
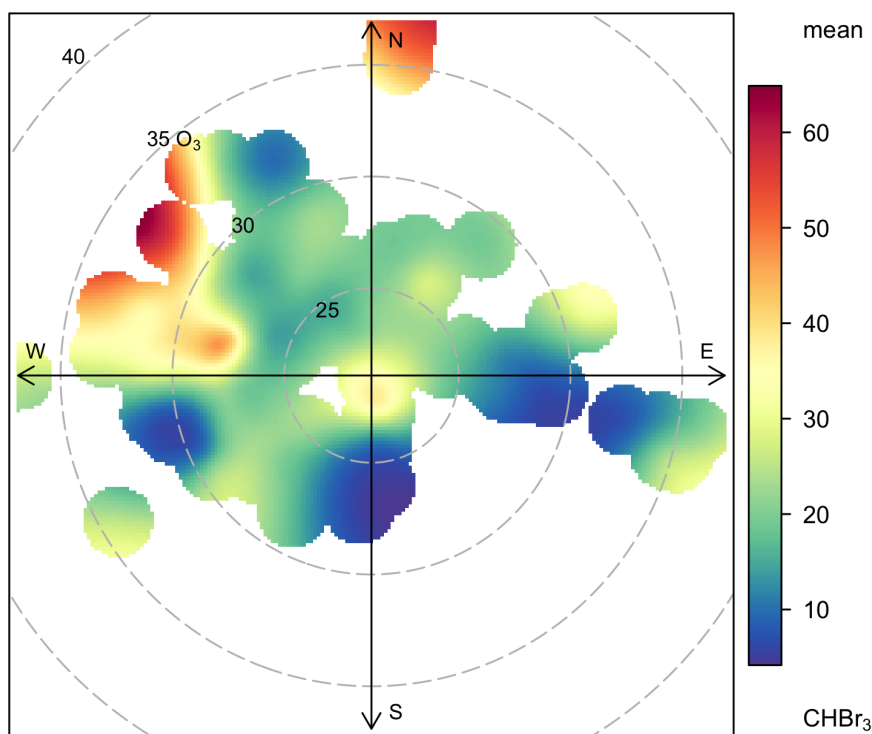
Figure 6. Mean bromoform concentration displayed as a function of ozone and wind direction.

mixing ratios were elevated above 35 ppb, otherwise the mixing ratios were below 30 ppb. Two regions of elevated bromoform mixing ratio were discovered when measured against ozone concentration and wind direction (Fig. 6). The occurrence to the north was co-incident with the highest ozone concentrations. The elevated bromoform event to the northwest exhibited lower ozone concentrations. This elevated event sits in stark contrast with the observations from the southeast. These observations have similar ozone concentrations as those to the northeast, however the bromoform mixing ratios were significantly lower at between 10-30 ppt (Fig. 6).

3.2 Bromoform time series

The time series measurements of bromoform at Cape Point displayed three periods of elevated mixing ratios above 40 ppt (Fig. 7). A maximum of 84.7 ± 10.8 ppt and a minimum of 2.3 ± 0.4 ppt was observed at Cape Point, having a mean of 24.7 ± 3.1 ppt during the sampling period. Over this time series 63 % of the measurements recorded were below the mean (Fig. 7). Periods of elevated mixing ratios occurred between 18-23 October, 26-30 October and 7-11 November: hereafter called events
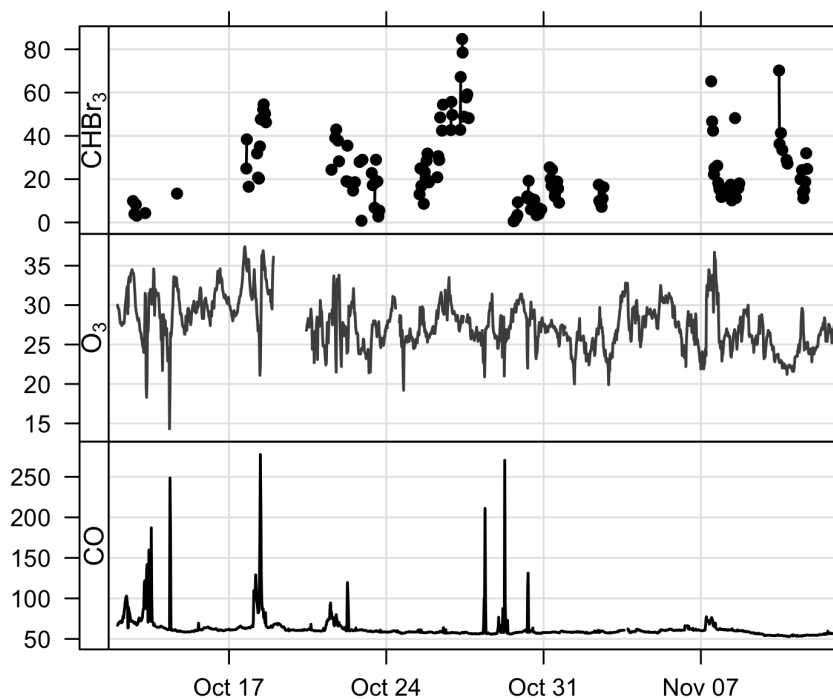
Figure 7. Time series of selected measured compounds observed at Cape Point between October and November 2011

1, 2, and 3, respectively. The second and third events were larger than the first. A maximum of 58 ppt was reached in event 1, while events 2 and 3 reached 85 and 70 ppt, respectively (Fig. 7).

An analysis of wind speed and direction indicates that three wind regimes were responsible for the observed elevated bromoform events. The largest of these is from the northeast and occurred at high wind speeds (~10 m s^{-1}). A second source, more to the west was identified at intermediate to low wind speeds (between 5 and 10 m s^{-1}). The third source, located to the east, has the highest wind speeds. A low-level source surrounding Cape Point with a mean of 30 ppt also exists at low wind speeds (Fig. 8).

Measurements of bromoform were obtained from all wind directions, with the bulk of measurements arriving from the westerly to northwesterly air sectors (Fig. 9). The highest bromoform mixing ratios arrived from the northeast. Elevated bromoform mixing ratios were also observed to the west and east of Cape Point (Fig. 8, 9). In contrast, fewer measurements containing high mixing ratios were observed to the south and a few from due north. A background of low mixing ratios (< 10 ppt) were observed from all wind directions (Fig. 9).
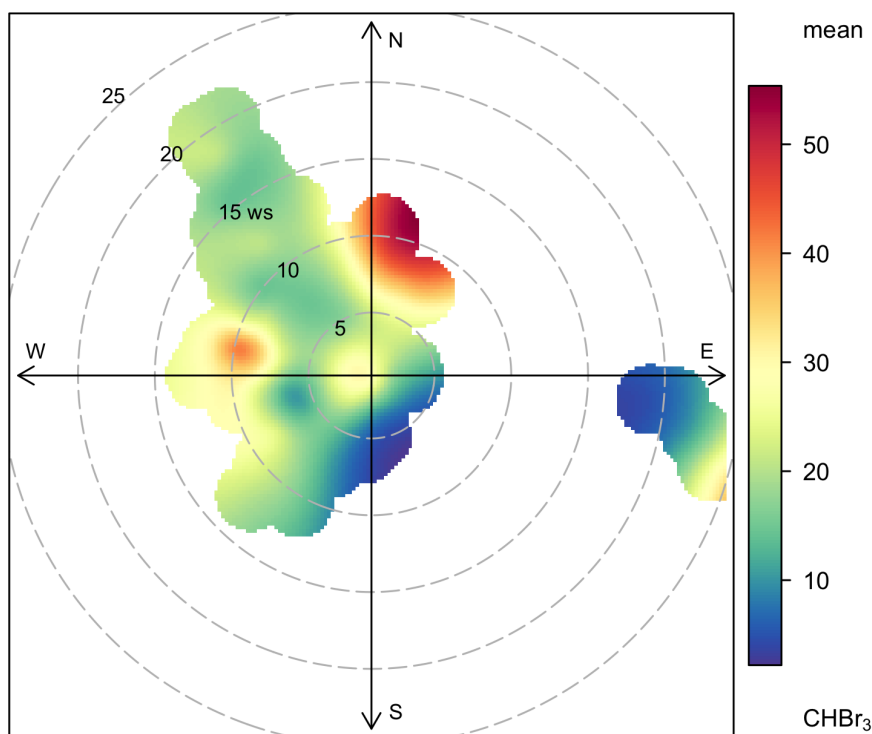
Figure 8. Polar plot displaying mean of bromoform mixing ratios as a function of wind speed and direction. Three peaks in the mixing ratio can be observed at varying wind speeds. A generally elevated mixing ratio was observed surrounding Cape Point.

3.3   Episodic events

The highest concentrations of bromoform all occurred within three narrowly defined time windows, suggesting that these episodes were a result of specific environmental conditions, allowing for the sampling of varying source regions. These three episodes and the conditions that precipitated them are described below.

Event 1: 18-23 October 2011

The ^{222}Rn concentrations over this period were significantly elevated above baseline levels: between 500 and 2000 $\mathrm{mBq\,m^{-3}}$ (Fig. 3b). The CO mixing ratios displayed a mean of 67.1 ppb with an elevated event on 18 October. Mixing ratios of CO rose to 250 ppb during event 1, concurrently with the elevated radon. Ozone mixing ratios varied between 21.1 and 37.4 ppb. The values rose late on the 17th and showed a significant drop to 21.1 ppb on the 18th. This rapidly increased into the high 30s ppt by the 19th. Bromoform mixing ratios were elevated above a baseline of 20 ppt during this event (Fig. 7). These mixing ratios rose rapidly from 16.5 ppt to a maximum of 54.5 ppt on 18 October. The mixing ratios decreased slowly from the maximum

Frequency of counts by wind direction (%)
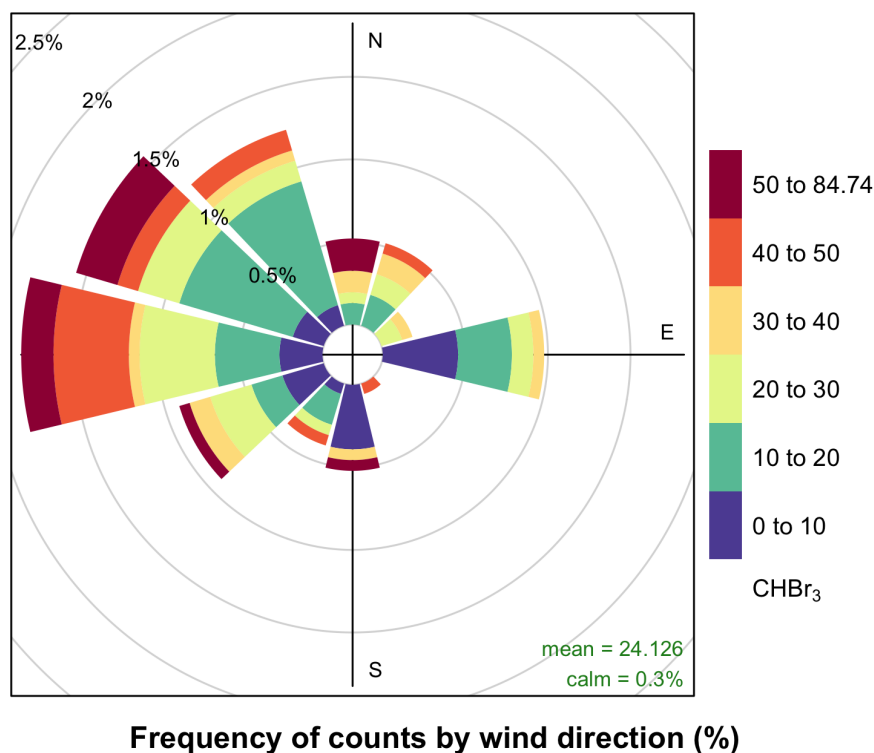
Figure 9. Distribution rose of bromoform mixing ratios observed at Cape Point. The mean mixing ratio of bromoform is displayed as a function of wind direction. The size of the paddles indicates the number of measurements made from that direction.

arriving back at 20 ppt on 23 October (Fig. 8). The wind speed varied between near 0 and $20 \, \mathrm{m\,s^{-1}}$ with a mean of $8.8 \, \mathrm{m\,s^{-1}}$ (Fig. 4). The wind direction was dominantly from the west to northwest. Two cold fronts transitioned Cape Point during this period. The first cold front passed through on the 19th while the second impacted Cape Point from 21 October. While the back trajectories all source from the Southern Ocean, the air parcels transition over the terrestrial biosphere prior to their arrival at

5   Cape Point (Fig. 10). This is particularly noticeable on the 18th when the trajectories pass over Cape Town.

Event 2: 25-28th October 2011

This event represents the highest recorded mixing ratios (85 ppt) of the three episodes examined here. In contrast to event 1, during event 2 the radon concentrations remained below $350 \, \mathrm{mBq\,m^{-3}}$. The wind direction was consistently from the west-northwest and the wind speed showed a small peak of $12 \, \mathrm{m\,s^{-1}}$ on 25 October. Thereafter the wind speed decreased to < 5

10    $\mathrm{m\,s^{-1}}$ by 28 October. While the CO values remained < 100 ppb and O_3 mixing ratios exhibited only a modest increase towards the middle of the period considered. The ozone mixing ratios rose from 24.6 ppb to a maximum of 33.5 ppb. Bromoform mixing ratios rose steadily from a minimum of 8.8 ppt on 25 October to a peak of 85 ppt on 27 October (Fig. 8). The
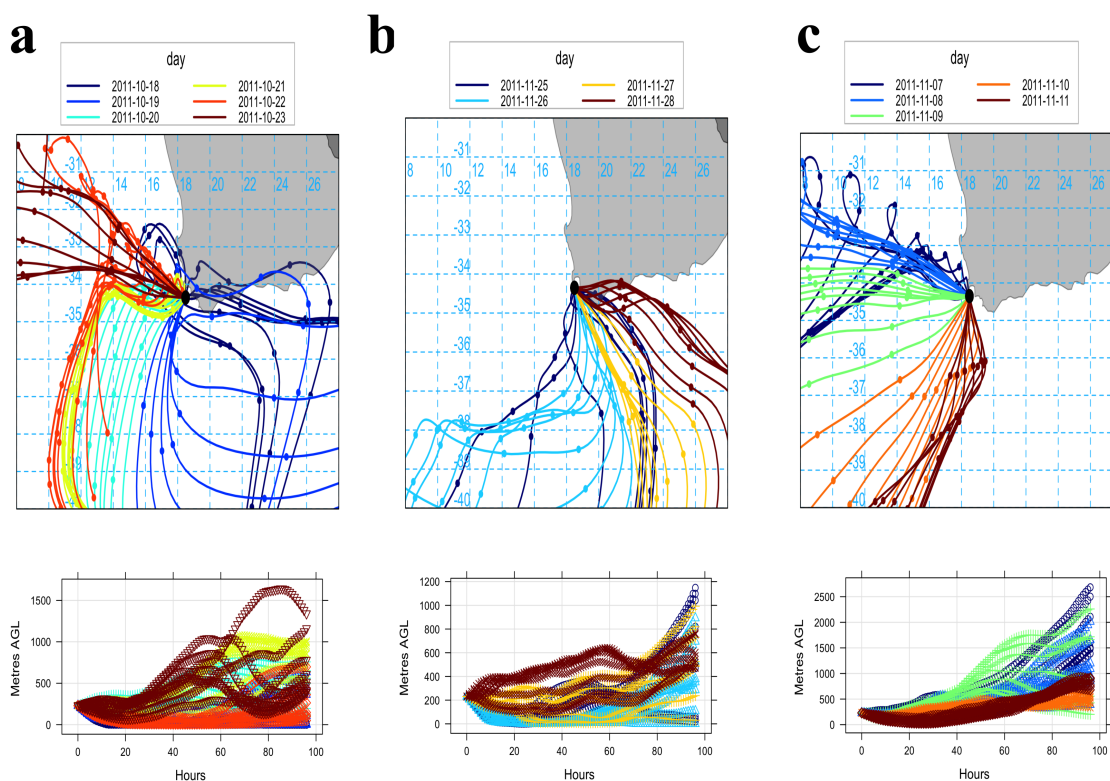
Figure 10. Composite daily back trajectories for Events **(a)** 1: 18-23 October 2011, **(b)** 2: 25-28 October 2011 and **(c)** 3: 7-11 November 2011. Trajectory heights for the events are shown below. The colours and dates correspond respectively for each event.

bromoform measurements largely remained above the background during this event. The back trajectories during this event all source from deep in the Southern Ocean to the east of Bouvet Island (54.43° S 3.38° E, Fig. 10b). The air masses uniformly transition directly from the Southern Ocean to Cape Point during this event.

Event 3: 7-11 November 2011

Bromoform mixing ratios showed two elevated events of similar magnitude within this period. Following the first peak the bromoform mixing ratios decreased from 65.2 ppt to a low of 10.2 ppt. Thereafter the mixing ratios rose to a maximum of 70.2 ppt. The radon concentrations followed a similar pattern decreasing initially from 1470 mBq m^{-3} on 7 November to < 350 mBq m^{-3} on the 8th. A second event began on 10 November with radon rising to 1000 mBq m^{-3}. The wind direction backed from northwesterly on 7 November, through the south to the north by the 11th. A decrease in CO mixing ratios occurred over this period. The mixing ratios decreased from 75.0 ppb on 7 November to < 55 ppt on the 11th. A second event was not observed in the CO mixing ratios. Ozone mixing ratios showed a similar pattern to bromoform and radon, with 2 events. An

initial decrease between 7 and 8 November with a minimum on the morning of 10 November. This is followed by a rapid rise from 21.1 ppb to 30.0 ppb. The back trajectories showed that the air masses arriving at Cape Point moved from north to south. Air masses on 7 and 8 November arrived from the north, transitioning over the Benguela Current. On 9 and 10 November the air masses arrived directly at Cape Point from the west and south west, respectively. The final trajectories arrived from the south (Fig. 10).

4 Discussion

4.1 Chemical climatology

The shifts between winds with a westerly component to those with an easterly component observed during this period is typical of the Cape Point region which is subjected to the passage of migratory anticyclones and cold fronts during the austral spring (Tyson and Preston-Whyte, 2000; Risien et al., 2004). Cape Point is dominated by southeasterly winds during austral summer, driven by the pressure gradient between the South Atlantic High Pressure (SAHP) system, whose average position moves southeastward toward western South Africa in summer and away to the northwest during winter, and heat lows over the interior. This seasonal migration allows midlatitude depressions and their associated cold fronts to influence Cape Point during spring. As these systems can advect clean marine air from the Southern Ocean over the city of Cape Town in a northwesterly direction, it is possible for this modified anthropogenic air to reach Cape Point. This process is the likely source of the occasionally elevated ^{222}Rn mixing ratios observed in this study. The CO and radon measurements show that the majority of the bromoform measurements were made in marine air and therefore of biogenic origin. However, all the measurements of bromoform made in continental air displayed elevated mixing rations above the mean (Fig. 7). This finding provides strong, if circumstantial, evidence to suggest that anthropogenic sources can play a significant role in the variability of bromoform concentrations at the Cape Point site.

The two events of elevated ozone concentrations observed at Cape Point (18 October and 7 November) were coincident with elevated CO and ^{222}Rn measurements, strongly suggesting an anthropogenic source. The exposure of kelp to ozone (a strong oxidant) has been shown to result in the production of bromoform (Palmer et al., 2005) and thus the elevated ozone on these occasions would be anticipated to have elicited a response from the local kelp beds lying to the north and northwest of Cape Point. The data presented here tentatively appear to confirm this hypothesis with high concentrations of $CHBr_3$ being reported during periods of high ozone concentrations, specifically and uniquely from air masses coming from north and northwest (Fig. 8).

The elevated bromoform mixing ratios to the north coincide with elevated ozone and may be a function of anthropogenic sources. However, when we cross reference these data against a tide table (data not shown), we obtain an unexpected result. Interestingly the bromoform mixing ratios appeared to show a peak at high tide and not low, as would have been anticipated (Jones and Carpenter, 2005). One possible explanation for the coincidence of high bromoform at high tide is that the source of the bromoform lies ca. 350 km up the west coast (the coast is populated with kelp from Cape Point all the way to Angola, some 4000 km up the coast). Using the HYSPLIT model it appears that some of the source air parcels being sampled had

passed over the coast 6 hours prior to arriving at Cape Point, giving further weight to the hypothesis that local tidal height is not a driving factor (Fig. 10). It is however, also possible that another mechanism not investigated could have influenced the bromoform mixing ratios. Possible mechanisms include anthropogenic sources from Cape Town or phytoplankton and kelp from the Benguela region. These sources are clearly independent of the local tides at Cape Point. The extensive kelp beds

5 surrounding Cape Point may contribute bromoform to both the consistent baseline and the extreme events observed.

While, other typical meteorological conditions were recorded during the bromoform sampling period they do not appear to have played a role in the variability of the measurements. These conditions might have played a smaller role in the variability and been dwarfed by factors such as the changing wind direction and the alternating sources. The quasi-discrete nature of the bromoform measurements may also mean that only the factors that have a large impact show an impact on the variability, while

10 smaller process although important are lost due to the nature of the sampling.

4.2 Bromoform time series

The observed bromoform mixing ratios presented here were approximately 2-5 times larger than most of the previously published work, specifically at coastal sites (Table 1). The highest concentration reported here (85 ppt) is second only to those reported in Gran Canaria (300 ppt) and around 25 % higher than those reported in Borneo (60 ppt) (Ekdahl et al., 1998; Pyle

15 et al., 2011). However, focusing merely on the maximum value does not tell the whole story. Looking at the reported minimum or mean values, those reported here are more similar to past studies (Table 1). The minimum value reported here (2.29 ppt) is remarkably similar to that reported in Borneo or Cape Verde (2 ppt), moreover the average is less than 2 times higher than many other studies. What these statistics show is that the Cape Point bromoform concentrations are actually similar to previous studies, but the maximum and the mean have been skewed by a small number of extremely high values. This pattern is com-

20 parable (although somewhat more extreme) to that observed in Borneo, but stands in contrast to Gran Canria, where all of the values were elevated. It is likely that the strongly elevated events observed here are the cause of the anomalously high mean values reported.

4.3 Episodic events

Event 1: 18-23 October 2011

25 The data presented here allows us to characterise this event as being a result of air passing over the City of Cape Town and entraining $CHBr_3$ from terrestrial anthropogenic sources. Throughout event 1, the ^{222}Rn, CO and O_3 mixing ratios were all elevated which suggests a strong anthropogenic influence. This was a result of typical spring weather patterns which see the arrival of episodic cold fronts and migratory anticyclones drawing air from the interior and specifically from Cape Town to Cape Point. Two dominant periods of westerly to northwesterly wind direction were observed during event 1, driven by these

30 synoptic systems. That this airmass was strongly influenced by anthropogenic sources is confirmed by back trajectory analysis (Fig. 10). The air masses pass over Cape Town on 18 October and then move off shore before swinging back to the northwest on 22 October, drawing air masses from Cape Town and then marine sources. These circulation patterns confirm that an important

Table 1. Selected previous atmospheric measurements of bromoform. Adapted from Kuyper (2014).

| | | | CHBr$_3$ (ppt) | | |
Location	Date	Latitude	min	max	mean	Reference	Region
New Hampshire TF	Jun.-Aug. 2002-4	43.1° N	0.2	37.9	5.3-6.3	3	Coastal
New Hampshire AI	Jul.-Aug. 2004	42.9° N	0.9	47.4	14.3	3	Coastal
Gran Canaria	Aug. 1993	30° N	25	300	100	8	Coastal
Mauritanian Upwelling	Mar.-Apr. 2005	16-21° N	0.1	0.6	0.2	7	Upwelling
Cape Verde	May-Jun. 2007	16.8° N	2.0	43.7	4.3-13.5	5	Coastal
Atlantic Ocean	Oct.-Nov. 2002	10° N	0.5	27.2	-	6	Open ocean
Borneo	Apr.-Jul. 2008	4.70° N	2-5	~60	-	2	Coastal
Christmas Island	Jan. 2003	1.98° N	1.1	31.4	5.6-23.8	4	Coastal
San Cristobal Island	Feb.-Mar. 2002, 2003	0.92° S	4.2	43.6	14.1	4	Coastal
Cape Point*	**Oct.-Nov. 2011**	**34.5° S**	**2.29**	**84.7**	**24.7**	**1**	**Coastal**
Cape Grim	Jan.-Dec. 2003	40.7° S	1.3	6.4	2.9	4	Coastal

References: *This study 1 Kuyper et al. (2012); 2 Pyle et al. (2010); 3 Zhou et al. (2008); 4 Yokouchi et al. (2005); 5 O'Brien et al. (2009); 6 Quack et al., 2004; 7 Quack et al., 2007; 8 Ekdahl et al., 1998.

contributing factor to the elevated bromoform concentrations observed during this period, may be from anthropogenic sources. The City of Cape Town metropolitan area encompasses both multiple water treatment works and a nuclear power station; both of which are demonstrated sources of bromoform to the environment (Quack and Wallace, 2003). However, given the fact that Cape Town is situated on the coast and in proximity to extensive kelp beds, the contribution from marine biogenic sources may
5 be equally important. Thus, the data presented here imply that the high concentrations observed resulted from a combination of anthropogenic sources augmented with marine biogenic sources, but do not necessarily reveal the extent of the contribution from each.

Episode 2: 25-28 October 2011

This episode, which exhibited the highest bromoform concentrations, appears to be one driven purely by biogenic factors. In
10 contrast to the first event, the CO and radon values strongly suggest that the air mass was not anthropologically influenced. An event of moderately elevated ozone was observed during this period. However, given that this event was not associated with a concurrent increase in the other anthropogenic traces, it is safe to conclude that this ozone was biogenic in origin. The westerly wind direction indicates wind coming directly from the south Atlantic arriving over the local kelp beds. The HYSPLIT back trajectories show that over these three days the air masses came consistently from the Southern Ocean and arrived directly
15 at Cape Point from the west. Therefore, the extensive kelp beds appear to be the most likely source of bromoform measured during this event. Most likely elicited from the kelp through increased oxidative reactions under elevated ozone conditions. If it is accepted that the high bromoform concentrations are purely biogenic in origin, then this raises the question as to

why the concentrations were significantly higher than measured in other studies. One potential hypothesis is that is that this higher concentration may be due to the specific kelp species (*Ecklonia maxima* (Sea Bamboo), *Ecklonia radiata* (Spined kelp), *Macrocycstis angustifolia* (Bladder kelp), *Laminaria palilida* (Split-fan kelp), *Bifurcaria brassicaeformis* (Hanging wrack) and *Bifurcariopsis capenis* (Upright wrack)) found in this region (Peschak, 2005; Branch et al., 2010). However no work to date

5   has been done to quantify the rate of release from these species of algae. Another hypothesis could be that the arriving air masses entrain bromoform from both the local kelp beds and the Benguela Current upwelling system or the highly productive Southern Ocean. However, in this particular instance the back trajectories suggest that this is not the case.

Event 3: 7-11 November 2011

The data suggests that the third event in early November (7-11) presents a mixture of sources. The atmospheric radon concen-

10   trations suggest an intermediate air-mass. This constitutes air that is mostly clean marine, but has recently come into contact with the terrestrial biosphere. The CO mixing ratios suggest that anthropogenically modified air influenced Cape Point on 7-8 November. The decrease in CO and the absence of any other elevated period suggest that the increase in radon is due to the wind direction changing from easterly through to a westerly and then back through to a northeasterly as a cold front was followed by a migratory anticyclone passing through the region. The northeasterly winds, locally known as 'berg winds', draw

15   air from the interior to the coastal region and often precede frontal passage particularly in the winter and spring (Reason and Jury, 1990). This flow would introduce anthropogenic air to Cape Point. The westerly winds, and to a lesser extent easterlies, advect clean marine air to Cape Point. These conditions would thus introduce a mix of anthropogenic and clean marine air to the Cape Point and this conjecture is supported by the moderate ozone and ^{222}Rn concentrations throughout.

    From events one and two, it has been shown that, while the anthropogenic source of bromoform at Cape Point was strong,

20   the biogenic source appeared to be stronger. During event 3, it is proposed that the mix of anthropogenic and biogenic sources resulted in an elevated mixing ratio midway between those of events 1 and 2. Thus the mix of biogenic and anthropogenic sources at Cape Point likely lead to the elevated background mixing ratios. The episodic events of elevated bromoform mixing ratio were driven by different sources, anthropogenic to the north and biogenic to the west.

5   Conclusions

25   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 dataset of its kind in southern Africa. The approximately 130 discrete measurements made over the course of October/November 2011 exhibited a mean bromoform concentration of 24.7 ± 3.1 ppt. This mean concentration was marginally elevated compared to past studies in similar regions, although the average was skewed by a small number of extremely high bromoform mixing ratios. The maximum reported value here (84.7 ppt) was

30   still less than that reported previously in Gran Canaria at a similar latitude (300 ppt; Ekdahl 1998), but twice that reported in Cape Verde (43.7 ppt; O'Brain et al., 2009) or New Hampshire (47.4 ppt; Zhou et al., 2008). Thus, these data indicate that this under-sampled region may be particularly significant in terms of bromoform sources to the atmosphere.

Why bromoform should exhibit such high concentrations around Cape Point warrants careful analysis. Candidate sources include (a) production from macroalgae in the extensive kelp beds to the west and north of the Cape, (b) production from microalgae in the Benguela upwelling system to the north west of Cape Point and anthropogenic sources and (c) anthropogenic sources (including water treatment and a power station), (d) production from micro algae in the south Atlantic and Southern

5 Ocean. Case studies of three events where bromoform concentrations were significantly elevated were presented. By using a combination of chemical tracers, wind direction and back trajectory analysis we were able to show that, although there is evidence of an anthropogenic source in the region, the highest bromoform concentrations were only reported when the air mass sampled was influenced by marine and coastal air with no evidence of anthropogenic influence. This implies that the high concentrations were a result of either the local kelp beds or the Benguela upwelling system.

10 Further work needs to be done to categorise these biological sources. The production rate of the kelp species around Cape Point is currently unknown. These kelp beds could be a significant global source of bromoform and thus, Cape Point could be an important site to begin untangling the question of whether phytoplankton or kelp dominate in the global budget of bromoform.

It is interesting to note that the only other study to report higher concentrations of bromoform than observed at Cape Point also occurred in a subtropical west coast upwelling system (Gran Canaira). Although one would need to obtain more

15 measurements form other sites and for longer periods, it is tempting to infer that these subtropical upwelling systems could be a significant source of bromoform to the marine boundary layer atmosphere which, if true, would have important implications for global atmospheric bromoform and halocarbon budgets. Nevertheless, it is clear that ongoing measurements at Cape Point are highly desirable. An important next step is to fully characterise the seasonal and diurnal cycles of bromoform at this site which will help in assessing any changes in bromoform mixing ratio in the long term.

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.

5   C. J. Palmer, C. Labuschagne and B. Kuyper performed the analysis. All authors contributed to review and improve the text.

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