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

1 Introduction

1.1 Bromoform in the marine environment

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

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

1.2 Implications for atmospheric chemistry

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

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

Quantifying inventories of bromoform emissions is thus critical in better characterising the oxidative capacity of the atmosphere. This is particularly pertinent in the tropics, where deep convection results in a greater percentage of bromine radicals reaching the UT/LS region (Hossaini et al., 2010; Saiz-Lopez et al., 2012). Understanding the sources in the tropics is therefore of great specific scientific interest (Palmer and Reason, 2009). However, there exists a paucity of measurements of bromoform in the tropics (Palmer and Reason, 2009). Existing data in this region tend to be from transient ship cruises, which only provide a discrete snapshot at the point in space/time that the cruise transects the area of interest. No time series of measurements at a fixed point currently exists for a coastal site in southern Africa. Furthermore, the Cape Point monitoring station fills a critical Southern Hemisphere latitudinal gap between Cape Matatula, American Samoa (14 $^{\circ}\mathrm{S}$) and Cape Grim, Tasmania (41 $^{\circ}\mathrm{S}$) (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 $^{\circ}\mathrm{S}$ 18.5 $^{\circ}\mathrm{E}$, Fig. 1). This station offers a unique location from which to measure bromoform mixing ratios in a subtropical region, but is also suitable to sample air from the south Atlantic and Southern Ocean. Wind direction and radon concentration ($^{222}\mathrm{Rn}$) at Cape Point have been extensively used to classify the arriving air masses (Brunke et al., 2004; Whittlestone et al., 2009). A mixture of air sources have been recorded at Cape Point; ranging from 100 % clean marine (baseline, $^{222}\mathrm{Rn}$ <350 $\mathrm{mBq\,m^{-3}}$) to 100 % continental (with/without anthropogenic influence, $^{222}\mathrm{Rn}$ >1500 $\mathrm{mBq\,m^{-3}}$) and intermediate (mixture of baseline and continental, 800 < $^{222}\mathrm{Rn}$ < 1500 $\mathrm{mBq\,m^{-3}}$) adapted from Brunke et al. (2004). The subtropical location of Cape Point may make this region a particularly significant source of bromoform to the atmosphere, specifically when considering the potential impact on global ozone budgets. The region lies in close proximity to the tropics where deep convection is able to rapidly transport the outgassed bromoform into the UT/LS. Where bromine initiated catalytic ozone destruction occurs. Moreover, data recorded here is of particular value as the size of the contribution from Cape Point region is to date largely untested. The Cape Point data presented here represent the first of their kind in Africa, or for the South Atlantic region (Cox et al., 2003).

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

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

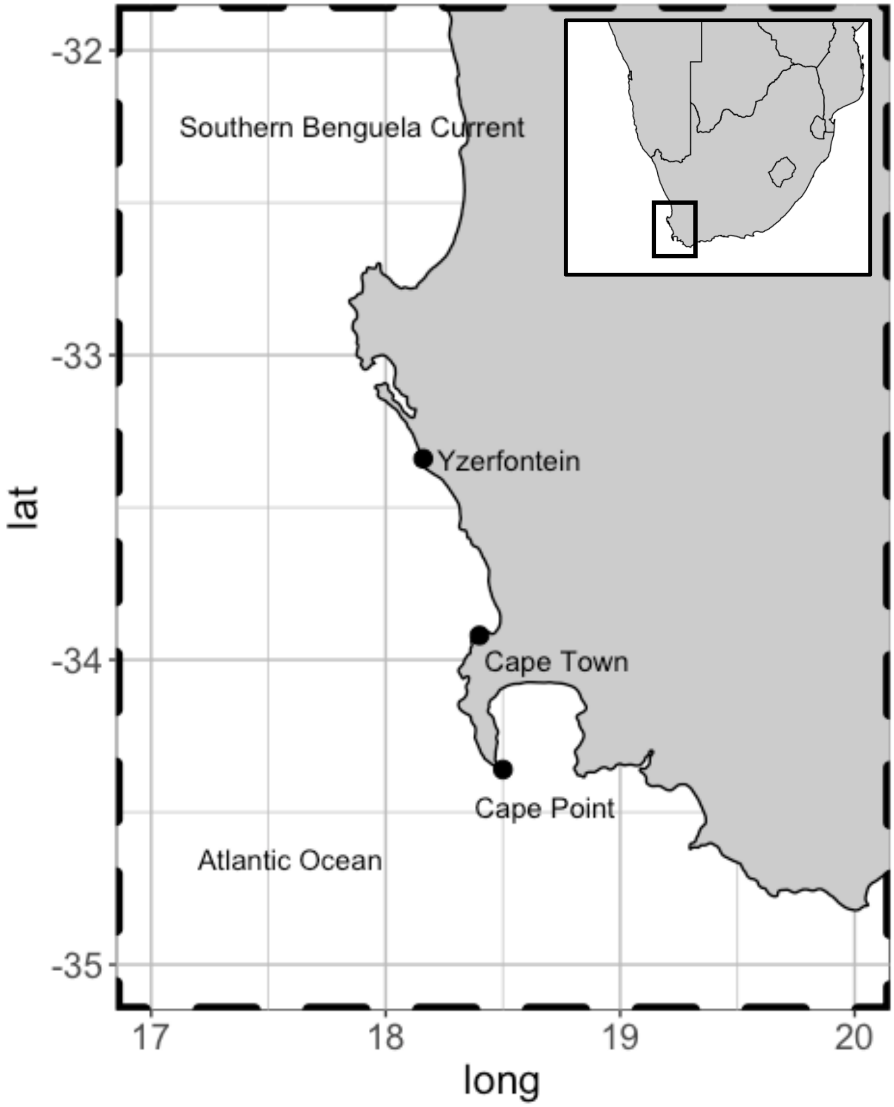

Figure 1. Location of Cape Point in relation to Cape Town. Kelp range along the entire coast. These are dominated by *Ecklonia maxima Papenfuss* south of Yzerfontein but transition to predominantly *Laminaria pallid Greville* north of Yzerfontein. Adapted from Kuyper 2014

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

2 Methods

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

2.1 Sampling

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

A Shimadzu GC-8A with a Perkin Elmar F-22 ECD was used to record the bromoform concentrations. A J & W Scientific DB-624 (30 m x 320 x 1.8 $\mathrm{\mu m}$, 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 $^{\circ}\mathrm{C}$ for 5 min following the injection of a sample. Thereafter, the temperature was increased to 60, 90, 150, and 200 $^{\circ}\mathrm{C}$ every 5 min. The temperature in the oven was increased at 65 $^{\circ}\mathrm{C\,min^{-1}}$ and held isothermally once the new temperature was reached.

Air samples were pre-concentrated in a custom built thermal desorption unit (TDU, Kuyper et al., 2012). Adsorbents (Carbopac X and Carboxen 1016, 9 mg each) held in a glass tube were cooled to -20 $^{\circ}\mathrm{C}$ 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 s to ensure complete transport of the calibrant onto the adsorbent trap. Calibration samples were passed through the drying trap as for air samples, thus any loss would be consistent for air and calibration methods. The calibration points were analysed using the same temperature programme as air samples to ensure identical retention times. These were also used for the identification of bromoform.

A complete calibration curve (Fig. 2) was measured prior to the start of the experimental period. The peak area was determined from the injection of 1-3 loops of diluted bromoform in nitrogen gas. Peak areas were calculated through the trapezoid integration method and were computed in MATLAB (Poole, 2003). The mixing ratios of the injected loops were calculated from the number of moles of bromoform injected, as follows. Each loop injection resulted in 0.1865 ng of bromoform being loaded on the trap, based on the calibrated rate of the permeation tube (Wevill and Carpenter, 2004; Kuyper, 2014). The number of moles of bromoform on the trap was calculated from this mass. Then through the air number density and the number of molecules loaded on the trap, the number of moles (bromoform) was converted to a mixing ratio.

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

A complete system calibration was run at the start of the sampling at Cape Point. Thereafter, a calibration point of 1-3 loops was run every 5 air samples to account for system drift. Based on a linear regression between the introduced sample and peak area response a 99.7 $\%$ accuracy was achieved on this system (Fig. 2). An analysis of repeated 2 loop injections indicated a system precision of 7.4 $\%$. Following an analysis of the calibration curve a limit of detection of 0.21 ppt was determined for this system.

2.3 Ancillary measurements: Cape Point, Global Atmospheric Watch

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

Air samples were drawn in at the top of a 30 m high sampling mast. A continuous flow system was used in the laboratory to exclude the accumulation of any contamination. Sequential cold trapping at -5 and -40 $^{\circ}\mathrm{C}$ 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.

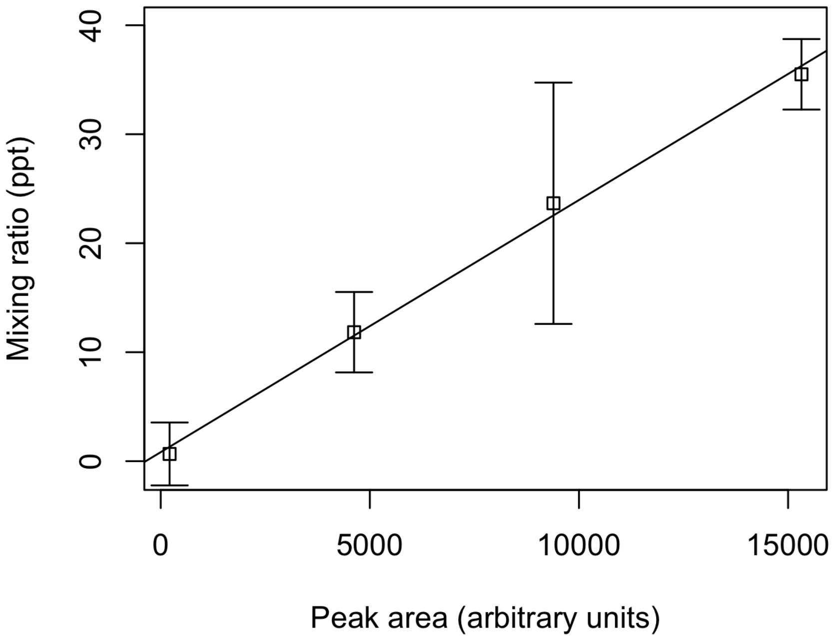

Figure 2. Calibration of the GC-ECD system for bromoform, based on multiple loop injections. Peak area calculated on the trapezoid method. (Adapted from Kuyper 2014)

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

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

NOAA Hysplit model

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

Marine boundary layer (MBL) height

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

Diurnal cycle

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

3 Results and Discussion

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

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

Link to tidal cycle

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

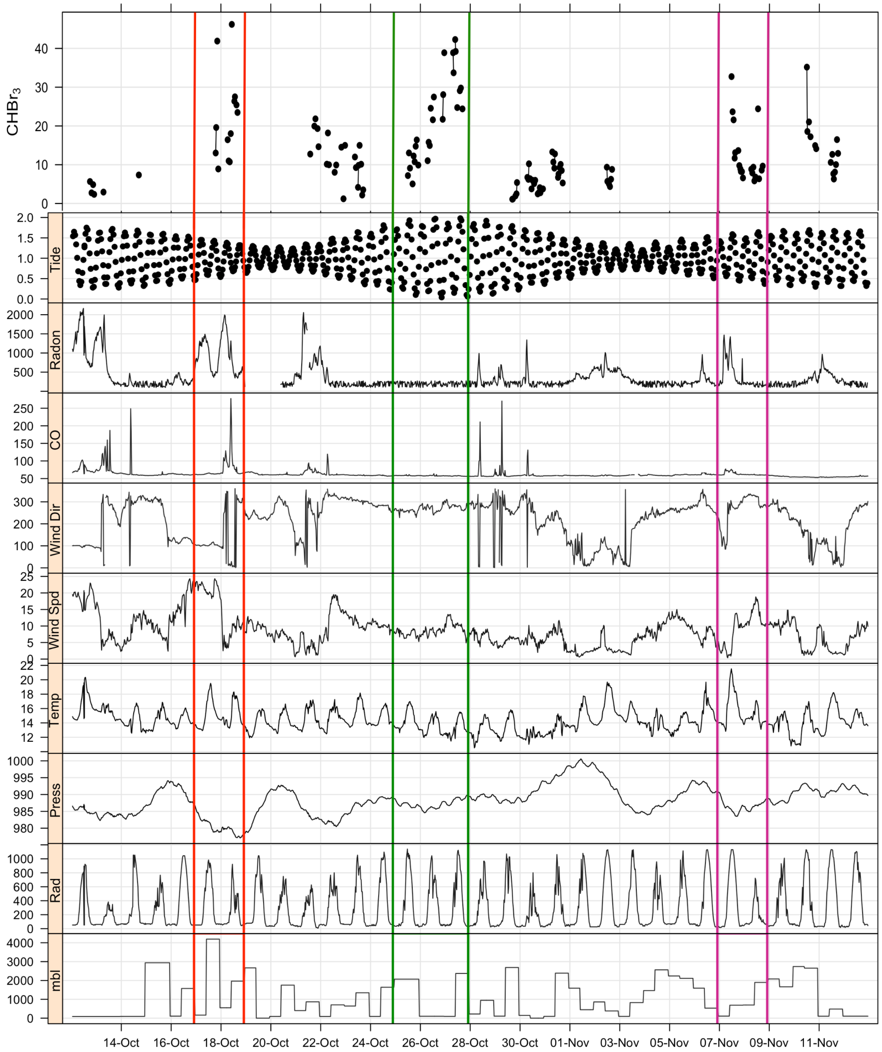

Figure 3. Time series plot of bromoform and meteorological measurements at Cape Point during October/November 2011. Events are highlighted by the coloured lines: E1 = red, E2 = green, E3 = violet.

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

Table 1. Selected comparison measurements of bromoform in air samples above coastal, upwelling, open ocean and lower marine boundary layer regions.

			$\mathbf{CHBr_3}$ **(ppt)**				
Location	**Date**	**Latitude**	**min**	**max**	**mean**	**Reference**	**Region**
New Hampshire TF	Jun-Aug 2002-2004	43.1 °N	0.2	37.9	5.3-6.3	Zhou et al., 2008	Coastal
Hateruma Island, Island	Dec 2007-Nov 2008	24 °N	0.5	7	0.91-1.28	Yokouchi et al., 2017	Coastal
Mauritanian upwelling	Mar-Apr 2005	16-21 °N	0.1	0.6	0.2	Quack et al., 2007	Upwelling
Cape Verde	May-Jun 2007	16.8 °N	2.0	43.7	4.3-13.5	O'Brien et al., 2009	Coastal
R/V Sonne	July 2014	2-16 °N	0.79	5.07	2.08	Fuhlbrügge et al., 2016b	Open ocean
R/A Falcon	July 2014	2-16 °N	0.99	3.78	1.90	Fuhlbrügge et al., 2016b	MABL WASP
Atlantic Ocean	Oct-Nov 2002	10 °N	0.5	27.2	-	Quack et al., 2004	Open ocean
SHIVA	Nov-Dec 2011	0-8 °N	1.23	3.35	1.81	Sala et al., 2014	MABL WASP
Borneo	Apr-Jul 2008	4.70 °N	2-5	60	-	Pyle et al., 2011	Coastal
Strait of Malacca	Jun-Jul 2013	2-6 °N	1.85	5.25	3.69	Mohd Nadzir et al., 2014	Coastal
Sulu-Sulawesi	Jun-Jul 2013	2-6 °N	1.07	2.61	1.60	Mohd Nadzir et al., 2014	Coastal
Christmas Island	Jan 2003	1.98 °N	1.1	31.4	5.6-23.8	Yokouchi et al., 2005	Coastal
San Cristobol Island	Feb-Mar 2002, 2003	0.92 °S	4.2	43.6	14.2	Yokouchi et al., 2005	Coastal
Peruvian upwelling	Dec 2012	5-16 °S	1.5	5.9	2.9	Fuhlbrügge et al., 2016a	Upwelling
Indian ocean	Jul-Aug 2014	2-30 °S	0.68	2.97	1.2	Fiehn et al., 2017	Open ocean
Cape Point	**Oct-Nov 2011**	**34.5 °S**	**2.29**	**84.7**	**24.7**	**This study**	**Coastal**
Cape Grim	2003	40.7 °S	1.3	6.4	2.9	Yokouchi et al., 2005	Coastal
Coastal South America	Dec 2007-Jan 2008	55 °S	1.8	11	7.4	Mattsson et al., 2013	Coastal
Antarctic coast	Dec 2007-Jan 2008	65 °S	2.1	4.9	3.2	Mattsson et al., 2013	Coastal
Antarctic Ocean	Dec 2007-Jan 2008	65-67 °S	1.9	3.9	2.3	Mattsson et al., 2013	Open ocean

Air mass characterisation

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

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

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

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

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

Meteorology

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

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

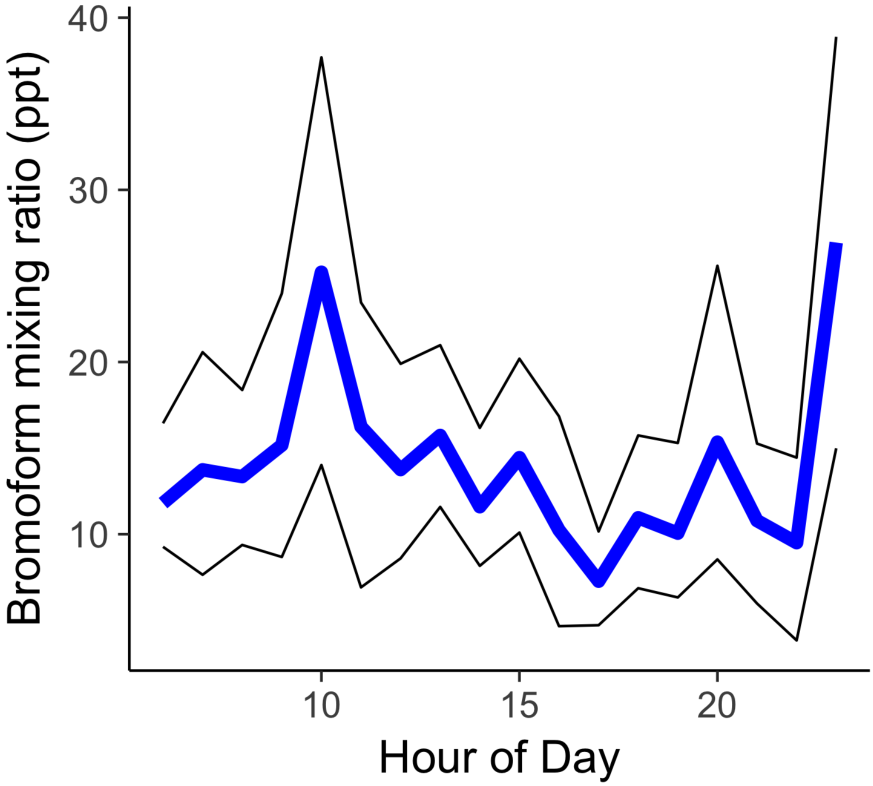

Figure 4. Mean diurnal cycle, calculated from all measurements binned by hour. The black lines above and below signify the 95 % confidence interval.

3.1 Solar radiation and Diurnal cycle

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

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

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

3.2 Case Studies

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

Event 1 (17-18 October 2011)

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

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

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

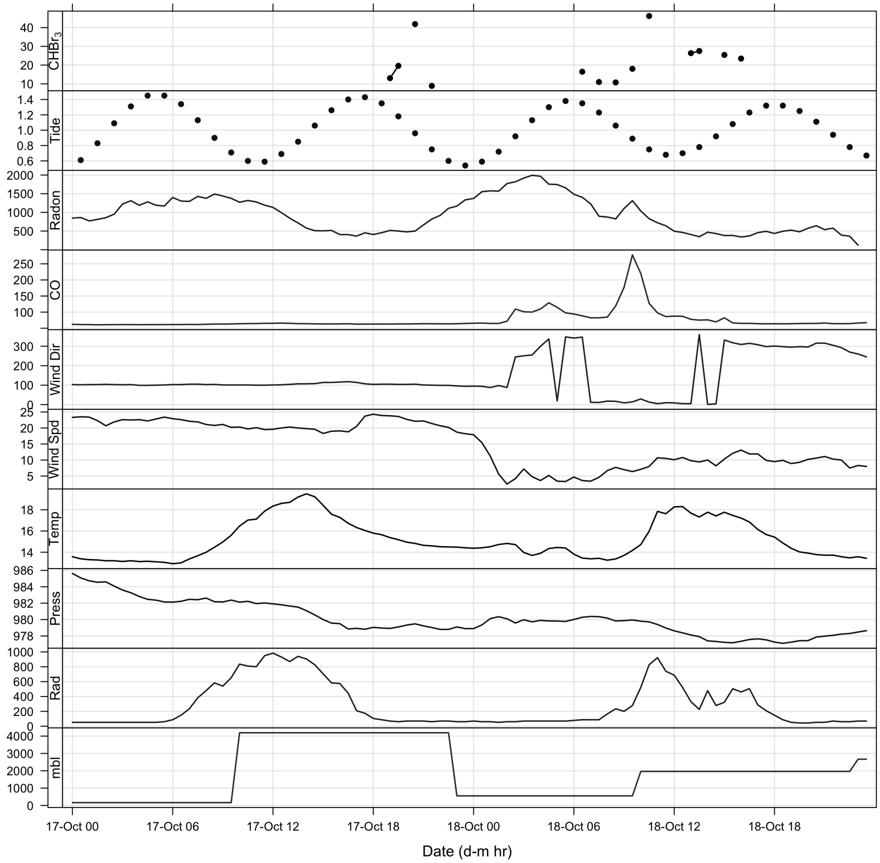

Figure 5. Time series plot of measurements at Cape Point during Event 1: 17-19 October 2011. Dates are given as day-month with the hour separately.

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

Event 2 (25-27 October 2011)

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

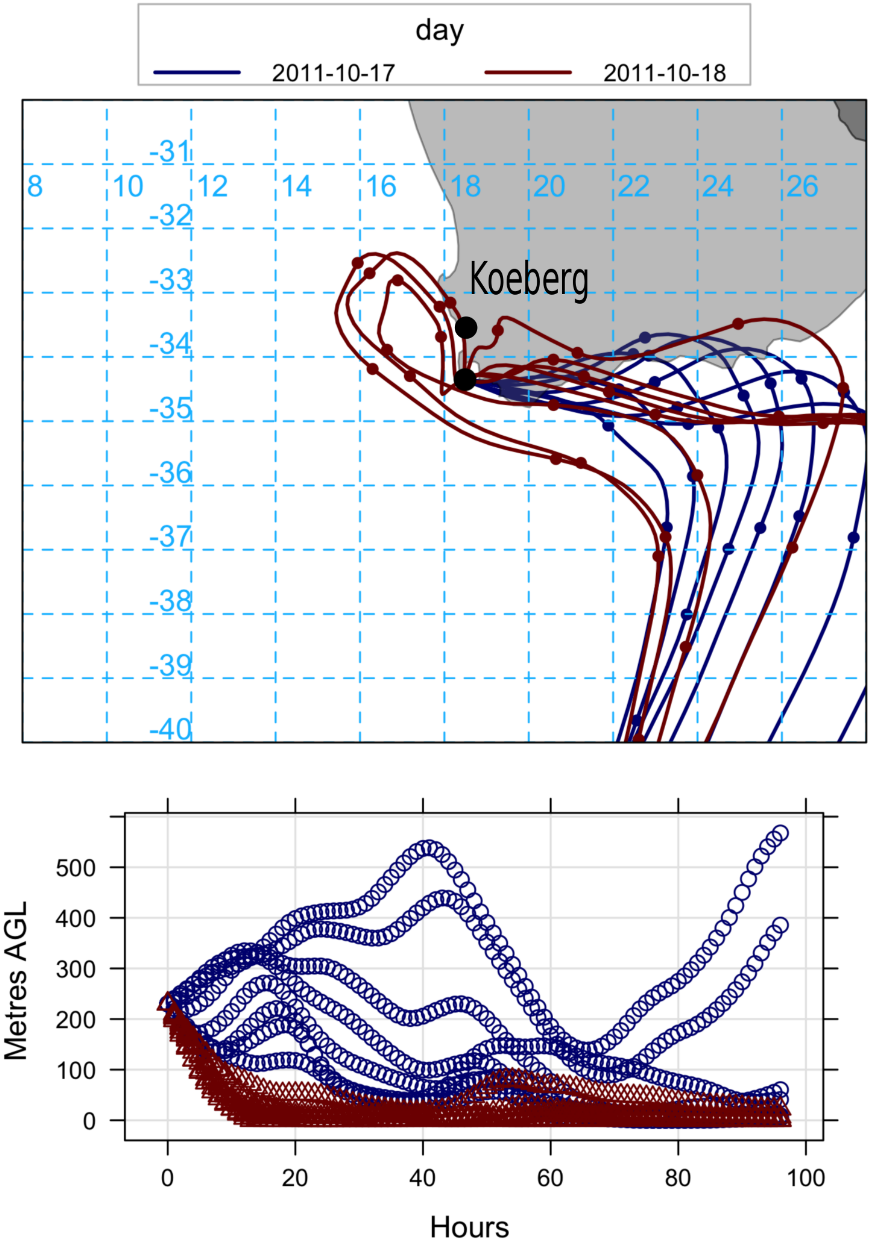

Figure 6. Back trajectories on 17 and 18 October 2011, highlighting the transit over Koeberg and Cape Town

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

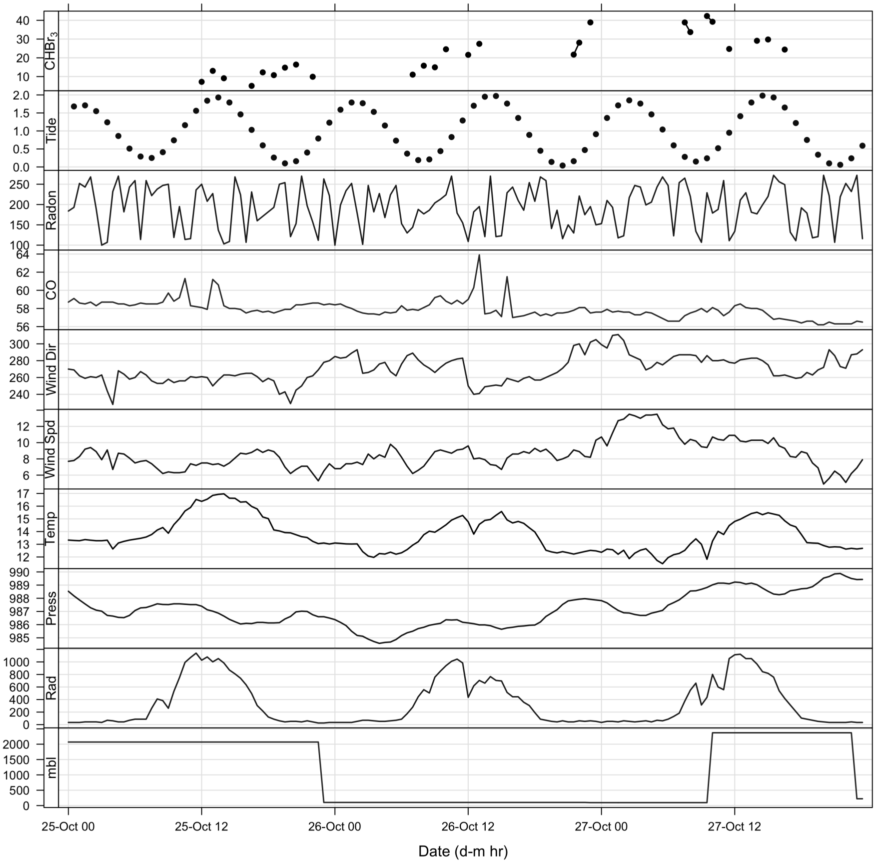

Figure 7. Time series plot of measurements at Cape Point during Event 2: 25-28 October 2011. Dates are given as day-month with the hour separately.

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

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

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

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

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

Event 3 (7-9 November 2011)

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

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

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

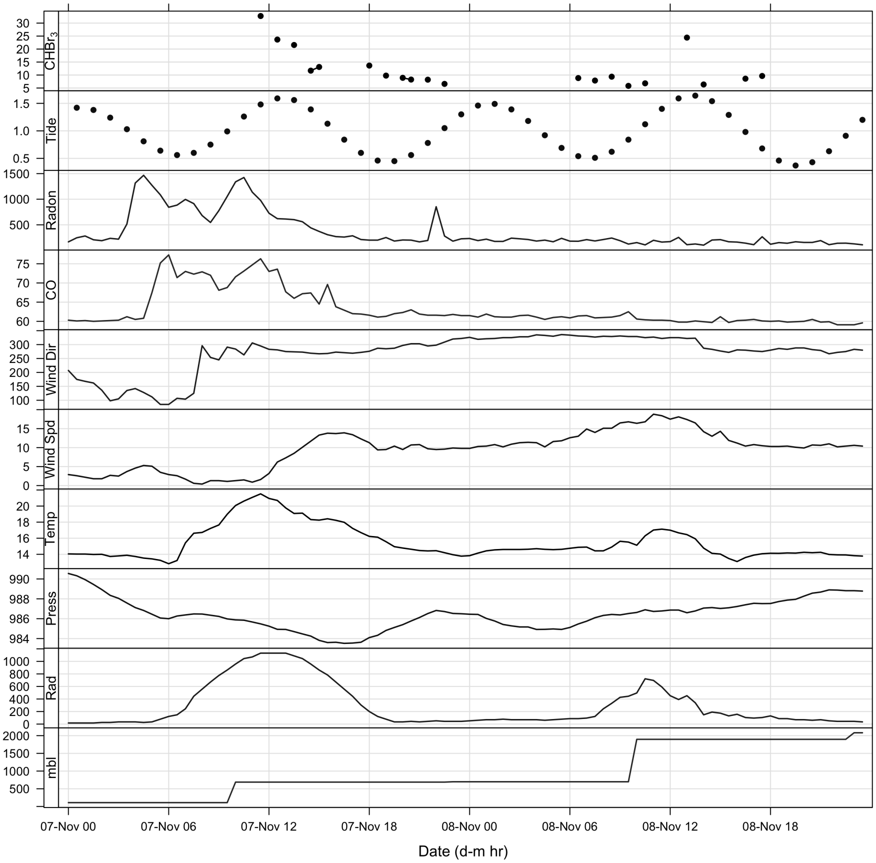

Figure 8. Time series plot of measurements at Cape Point during Event 3: 7-9 November 2011. Dates are given as day-month with the hour separately.

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

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

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

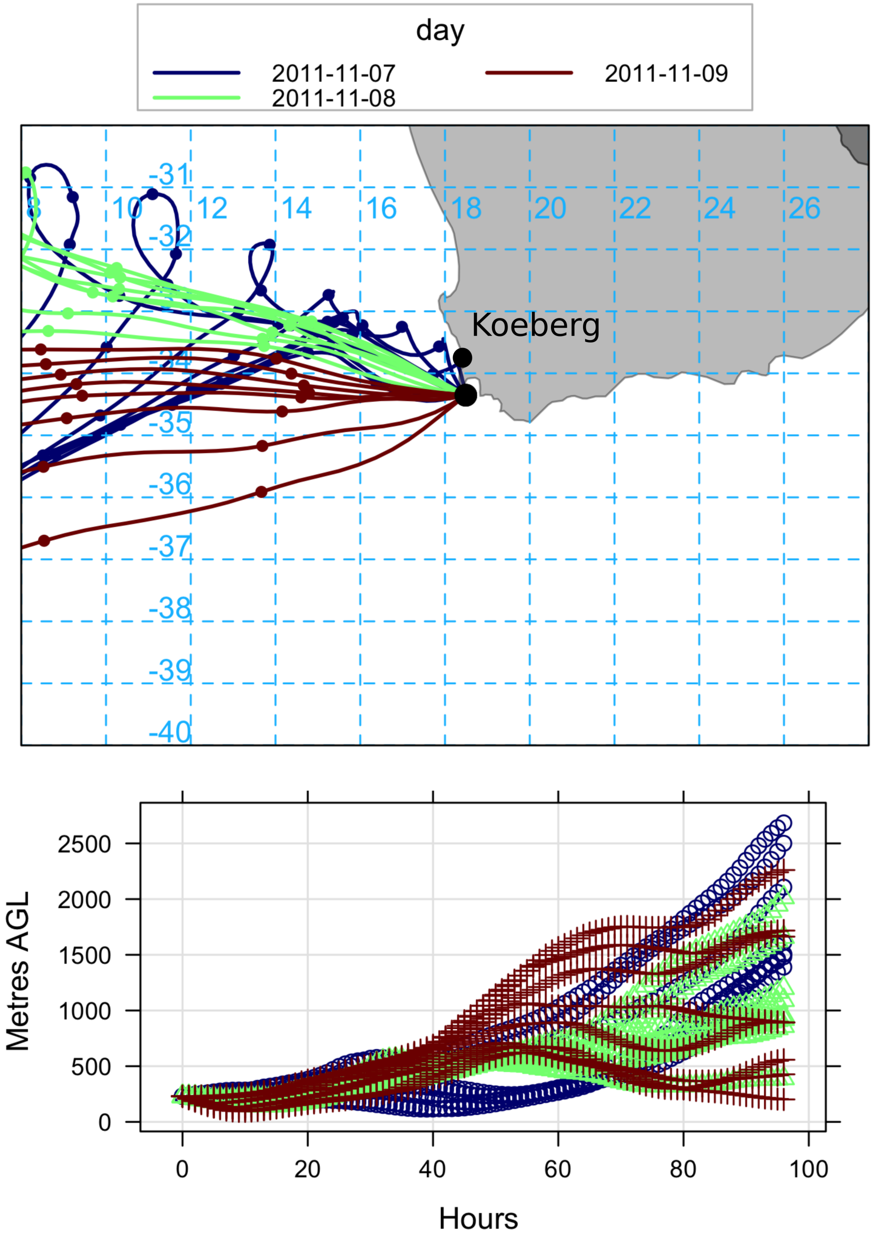

Figure 9. Back trajectories of 17 and 18 October 2011, highlighting the transit over Koeberg and Cape Town

4 Conclusions

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

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

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

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

Code availability. TEXT

Data availability. TEXT

Code and data availability. TEXT

Appendix A

A1

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

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

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