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A review of four decades of atmospheric trace gas measurements at Cape Point, South Africa

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Abstract

South Africa's Cape Point (CPT) trace gas observatory, operated by the South African Weather Service (SAWS), has been monitoring mole fractions (mol/vol) of ambient greenhouse gases (GHG), e.g. carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and selected chlorofluorocarbons (CFCs) since the late 1970s. In addition, the Cape Point trace gas observatory boasts the longest atmospheric carbon monoxide (CO) dataset continuously from 1977 in the Southern Hemisphere (SH). Instruments for the measurement of radiation and other selected gases, such as ozone (O_3), have gradually been added since the inception of measurements. The year 1995 heralded a milestone when the Cape Point observatory became part of the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. Besides supplying data to the World Data Centres, it also supports the local database, South African Air Quality Information System (SAAQIS). These affiliations, which require strict measurement protocols, make the Cape Point data records available within the global data centres. Due to its location in a mostly pristine marine environment and its proximity to the Southern Ocean, Cape Point measurements are highly valued in the United Nations Environment Programme (UNEP)/WMO Ozone and IPCC Climate Assessments and serves as a bellwether for regional changes in southern African atmospheric composition. A review of selected climate change relevant trace gas measurements acquired at Cape Point is presented here.

1. INTRODUCTION

1.1 An historical perspective

In the late 1970's, it became apparent that due to the growing evidence of anthropo-

genic driven climate change an atmospheric trace gas monitoring station was needed in 1

South Africa. In order to assess the chemical composition of the atmosphere and its 2

temporal changes, information was required from a baseline of undisturbed atmosphere 3

- typically referred to as background (BG) - on a global or hemispheric scale. Conse- 4

quently, a collaboration was initiated between the Atmospheric Sciences Division of the 5

South African Council for Scientific and Industrial Research (CSIR) and the Max 6

Plank Institute (MPI), Germany (later Fraunhofer Institute for Atmospheric Environ- 7

mental Research) which resulted in the establishment of a baseline monitoring station at 8

Cape Point (34° 21' S, 18° 29' E; Figure 1) on the southern tip of the Cape Peninsula 9

within the Table Mountain National Park approximately 60 km south east of Cape 10

Town (Brunke and Halliday, 1983; Scheel et al., 1990; Nyeki et al., 2015). The monitor- 11

ing station was initially confined to two small, lighthouse keepers' cottages, originally built 12

in the 1860s below the Cape Point lighthouse. Surrounded on three sides by the open ocean, 13

and sited on top of a steep sided cliff (approximately 230 m above sea level; Figure 2) the 14

station is ideally situated for monitoring the chemistry of the marine boundary layer; a **well-** 15

mixed layer that typically extends from the surface ocean to an altitude of **700 m, and can** 16

reach a maximum of approximately 2 km (Seidel et al. 2010, Fuhlbrügge, 2011). 17
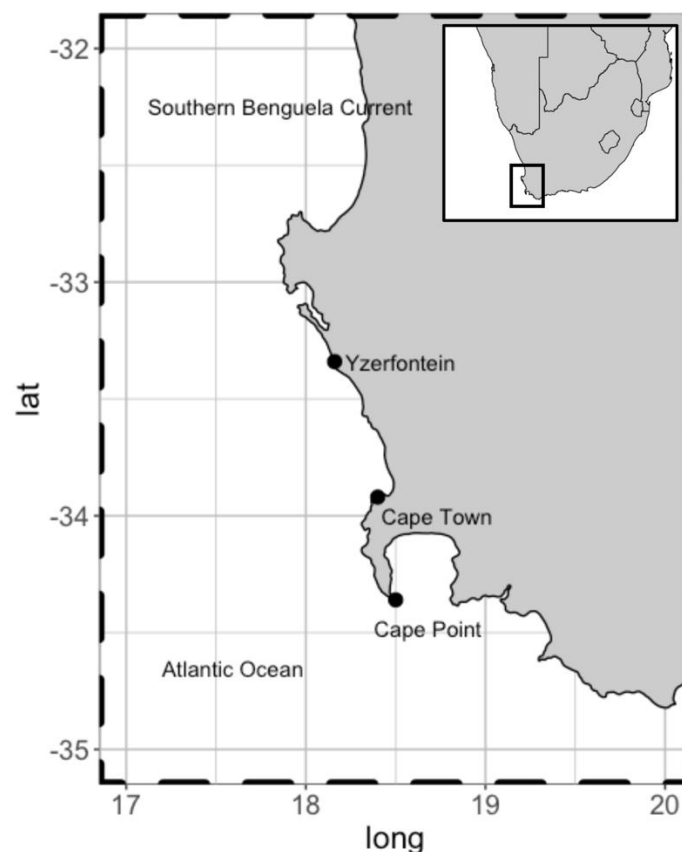
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Figure 1. Map of Cape Point indicating proximity to Cape Town. (Adapted from Kuyper 2014). 20

Figure 2. View of SAWS GAW monitoring station in relation to coastal cliffs surrounding the sampling site. Note the 30m sampling tower on the flat roof of the station that supports the air intake to the station.

The position of the Cape Point monitoring station fills a crucial latitudinal gap in atmospheric trace gas monitoring in the Southern Hemisphere (SH) in the region Cape Matatula (14 ºS, 171 ºW) in American Samoa and Cape Grim (41 ºS, 145 ºE) in Australia (Brunke and Halliday, 1983). Most importantly the Cape Point station is also the only monitoring station for the south Atlantic sector of the SH. The long-term time series trace gas measurements currently made at Cape Point, and reviewed here, highlight the importance of this monitoring station to our global understanding of the atmosphere. The local meteorological conditions typically draw clean marine air from the southern Atlantic Ocean (Martin et al., 2017) which makes Cape Point an ideal baseline station to monitor key indicators of changes and trends in the atmosphere of the SH. The atmosphere in the SH is generally considered to be cleaner than its northern hemisphere (NH) counterpart because the SH is mostly comprised of oceans, whereas the NH includes the large continents of Asia, Europe and North America with the increased pollution levels typically associated with high levels of industrialization (e.g. Sillman, 1999; Jaeglé et al., 2005).

The clean marine air predominates during the austral spring to autumn (November to April) when the Cape Peninsular is buffeted by strong south easterly to south westerly winds

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(Brunke et al., 2004; Figure 3). During this period, the South Atlantic High Pressure system is situated to the SW of the sub-continent (Preston-White and Tyson, 1993; Garstang et al., 1996) and is responsible for the advection of air towards Cape Point from a SE direction. Southerly wind episodes, which constitute 75% and 55% of the summer and winter totals, respectively, are characteristic of the south Atlantic (Brunke and Halliday, 1983). Throughout the winter months of June-August, the South Atlantic High Pressure system retreats towards the equator relative to its summer position (Preston-White and Tyson, 1993; Garstang et al., 1996) resulting in the intensification and advancement of the westerly winds across the southern tip of the African sub-continent. From autumn to spring (May to October) the prevailing wind speed therefore increases from a north to north westerly direction (Brunke et al., 2016). During the austral winter, the weather at Cape Point is also largely dominated by passing cold fronts, often with accompanying rainfall, moving from west to east. (Preston-White and Tyson, 1993; Garstang et al., 1996). The north westerly winds in winter (Figure 3) drive polluted air from the city of Cape Town southwards, and this anthropogenic derived pollution is occasionally detected at the Cape Point monitoring station (Brunke et al., 2016).

The primary focus of the Cape Point GAW programme has been to measure the most important long-lived greenhouse gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and short-lived greenhouse gases e.g. surface ozone (O_3), on a sustainable, long-term basis (WMO, 2017). Initially, the monitoring station focused on the measurements of CO and four halocarbon species (e.g. $CFCl_3$, CF_2Cl_2, CH_3CCl_3 and CCl_4) in the atmosphere with measurements of these gases conducted in collaboration with **the Max Plank Institute and the University of Reading, UK (Brunke and Halliday, 1983; Scheel et al., 1990)**. A progressive expansion of the monitoring programme saw the range of atmospheric trace gases measured increase to 19 by 1998. Some of this expansion included the measurement for the first time of surface O_3 and CH_4 from 1983. Other important greenhouse gases such as N_2O and CO_2 were added in 1989 and 1993, respectively. Because of this programme expansion, space in the small lighthouse keepers' cottages came at a premium. As a result of the growing international interest in atmospheric measurements at Cape Point, a new monitoring station was commissioned in 1994 and completed in 1995. The new monitoring station, built into the cliff face (Figure 2), was connected to one of the lighthouse keepers' cottages housing the original monitoring station. Two years after the opening of the new laboratory, on the 20th anniversary of the founding of the monitoring station, ownership was transferred from the CSIR to the South African Weather Service (SAWS) to ensure continued monitoring of the atmosphere in this strategically important part of the world in terms of global atmospheric research. The former Portnet radio mast (30 m high) was taken over by CSIR after it became

technically dysfunctional. Several air intake lines were attached to the mast (for example to measure aerosols and radon concentrations). The mast also accommodated, and continues to house, two wind anemometers: one at the top (30 m) and one at a height of 10 m. The station's flat roof has also been used to house a number of meteorological instruments and additional air-intake masts.
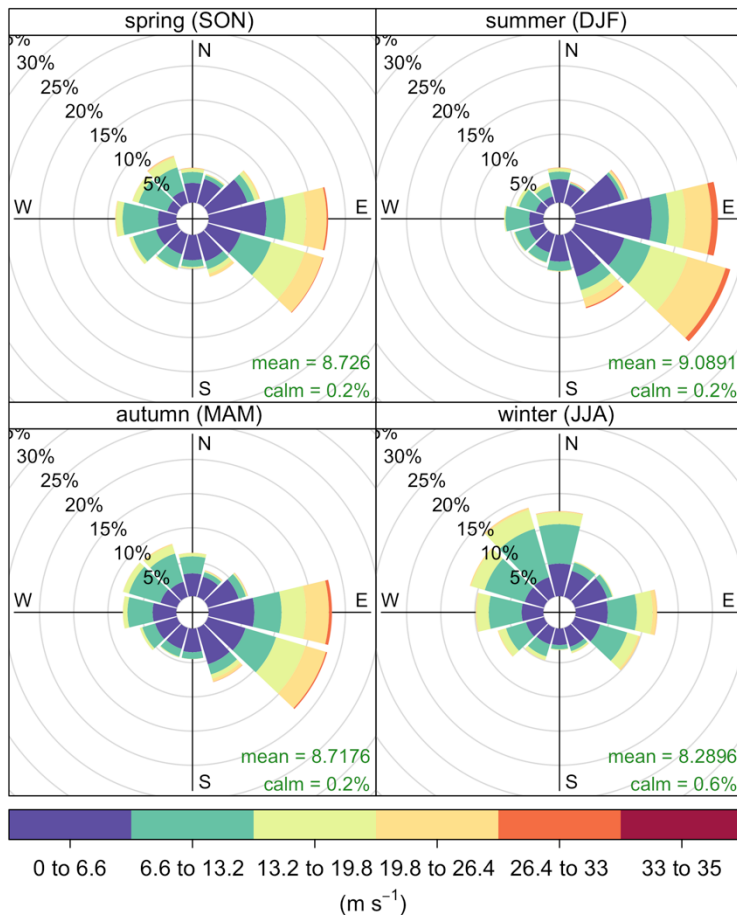
Figure 3. Cape Point wind roses averaged over the period 1995-2015 per season (months of the year).

The monitoring station was officially accepted into the World Meteorological Organisation (WMO)'s Global Atmospheric Watch Program in early 1995. In agreement with the broader goals set by the WMO/GAW programme, the Cape Point measurements target air chemical species, which are either known to enhance the anthropogenic greenhouse effect, e.g. CO_2, various nitrogen oxides represented as NO_x, and CH_4; or induce cooling, e.g. aerosols (Solomon et al., 2007).

This review focuses on greenhouse gases and selected reactive gases measured at Cape Point, which each exhibit independent atmospheric lifetimes. The lifetime is based on the

chemistry and **uncertainties** in our understanding of the processes involved **which can** results 1

in a range of estimated lifetimes (Table. 1). As noted previously, the measurement of the var- 2

ious compounds began in stages since the inception of the laboratory in 1977 (Table 1). Over 3

the last four decades a number of local and international collaborators have worked at Cape 4

Point, delivering high quality data and further developed the infrastructure. 5

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Table 1. A detailed list of the current suite of atmospheric species measured at Cape Point, their underlying ana- 7
lytical technique, commencement of program and where applicable, their atmospheric residence times (GAW 8
EMPA http://gaw.empa.ch/gawsis, Jacob, 1999; Prather et al., 2012; **IPCC, 2001**). 9

Class of Species	Parameter	Analytical Method	Start of program	Atmospheric residence times
Reactive gases	CO	Gas Chromatography coupled to Atomic absorption spectroscopy	1977	30-90 days
	CO	Cavity ring down spectroscopy (CRDS)	2012	
Halocarbons	CFC-11, CFC-12, CCl_4, CFC-113 and Trichloroethylene (TCE)	Gas Chromatography-Electron capture detector (GC-ECD)	1978	45-260 years
Ozone	Surface O_3	UV Photometry	1983	**3 - 18 days**
	Surface O_3	Passive Sampling	2000	
Greenhouse gases	CH_4	Gas Chromatography-Flame Ionization Detector (GC-FID)	1983	9.1 ± 0.9 years
	CH_4	Whole air sampling (NOAA-ESRL-GMD)	2010	
	CO_2	Non-dispersive Infra-Red (NDIR)	1993	5-200 years
	CO_2	Whole air sampling (flasks): analysis by NOAA-ESRL-GMD)	2010	
	CO_2	Cavity ring down spectroscopy	2012	
	N_2O	Gas Chromatography-Electron capture detector (GC-ECD)	1983	131 ± 10 years
Radio Nuclide	Radon [^{222}Rn]	Alpha Counting	1999	3.8 days (half-life)
Halocarbons	CFCs, HCFC, HFC, biogenic	Gas Chromatography-Mass Spectrometry (GC-MS)	2016	0.02-146 years

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The primary aims of the Cape Point GAW station are to fulfil a mandate from the scientific 11

and policy communities to provide regional trace gas BG data for future climate change sce- 12

narios. Moreover, it also honours environmental treaties such as the United Nations Frame- 13

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work Convention on Climate Change (UNFCCC; http://unfccc.int/2860.php) and through the World Data Centres (WDCs). In addition, it provides information to policy makers and to the Intergovernmental Panel for Climate Change (IPCC; http://www.ipcc.ch/). These data, once quality assured, is also readily available to the scientific community via the local South African Air Quality Information System (SAAQIS: http://www.saaqis.org.za/) and the WDC for GHG (http://ds.data.jma.go.jp/gmd/wdcgg/).

Most notably this information is also of vital importance to South Africa itself. Such measurements assist with meaningful predictions on how elevated GHGs will impact South Africa's biosphere systems e.g. the natural shrub land of the Western Cape with its endemic plant species of heath, protea and lily families (known as Fynbos), agricultural regions and rainfall patterns. This can best be done, if information, specific to the SH mid-latitudes is available. As such, the SAWS is making an important international and national contribution by providing high quality long-term data for this part of the globe. In addition to meeting its international obligations, the Cape Point data also offers a benchmark against which local South African urban GHG levels and trends can be compared. This opportunity avails itself when measurements at Cape Point are made under non-BG conditions with the advection of air from the northern sector. Such air masses carry a strong urban-continental signature-mainly from Cape Town, and to some extent also from the industrialized Vaal triangle (Whittlestone et al., 2009; Brunke et al., 2011b).

The purpose of this review is to contextualise the contribution of forty years of baseline measurements of selected greenhouse and reactive gases in the air at Cape Point to our understanding of the chemistry of the atmosphere. The methods of data collection and air mass characterisation of samples arriving at Cape Point are outlined in section 2. The time series of selected gas measurements, CO_2, CH_4, N_2O, O_3, CO, and halocarbons (CFCs: 11, 12, 113, CH_3CCl_3 and CCl_4), made at the Cape Point GAW observatory are discussed in section 3. Through different chemical pathways and processes these compounds each play an important role in climate change. Understanding how the baseline measurements may be changing provide early warning of future atmospheric change and insights into possible consequences for the climate of southern Africa, and the globe. Understanding how the non-BG conditions are changing could have a significant impact on our knowledge of the natural system. Local changes in non-BG measurements for three species is discussed in section 4. These could influence the natural processes.

2 METHODS AND DATA

2.1 Measuring Programme

The measurement programme at Cape Point is designed to meet and maintain GAW standards. Samples, drawn from the top of the sampling mast, are dried through a 2-stage moisture (drying; -10 ℃ and -40 ℃) trapping system prior to measurement, except for ozone which is sampled directly from the atmosphere. The frequency of measurements is determined by the instrument and measurement technique employed. These range from 1 to 15 min sampling rates. These data are averaged to 30 min windows to ensure data conformity. In keeping with the GAW mandate, gas measurements are audited on a regular basis as described in the next section.

2.2 Calibration Scales and Quality Assurance

The data quality objectives set out for the individual parameters measured within the WMO/GAW programme are detailed in a number of WMO/GAW documents (see for example WMO, 2017 and references therein). To achieve these goals, various centralized GAW calibration facilities have been established. A summary of the Cape Point reproducibility and repeatability is presented in Table 2.

Analytical details for the greenhouse gas species (CO_2, CH_4, N_2O, O_3, and CO), are provided here. For measurements of CO_2, CH_4 and N_2O, the instrument reproducibility is determined from several repeated injections of a gas mixture of constant composition once per day, while repeatability of instrumental performance is determined by the injection of the same type of sample in a sequence during one day (typically 6 times per day). Both the reproducibility and repeatability are expressed in terms of relative standard deviation [%]). For O_3 measurements, a Thermo Electron instrument is used with the internal ozonator set at 150 ppb. The ozonator is activated once daily for about 20 min. These data provide information on reproducibility, whilst repeatability is determined via an external calibrator (duration of a single level: 30 min) connected to the O_3 analyser. For the CO_2, CH_4 and CO, historic GC measurement techniques were replaced with the more modern cavity ring down spectrometer (CRDS, Picarro) technique. The reproducibility and repeatability of the CRDS is determined using a daily flow of a target gas mixture containing a constant concentration. The precision and repeatability of the measurements of standards are outlined in Table 2.

Instrument calibrations are performed through analysis of gas cylinders with known trace gas mole fractions which are obtained from the Central Calibration Laboratory (CCL) maintained by NOAA ESRL in Boulder, USA (GAW, 2009). Given the long-term stability of CRDS, these instruments are calibrated bi-annually. By following these analytical protocols, the Cape Point greenhouse gas measurements can be directly related to the GAW calibration

scales as well as the inter-network comparability.   1

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Table 2. Statistical details (reproducibility and repeatability) of the analytical techniques in use at Cape Point to   4
measure CO_2, CH_4, N_2O, CO and O_3.   5

Trace Gas	Measuring period	Typical Reproducibility[β]	Typical Repeatability[β]	GAW compatibility goal[*][$]
CO	1978 – present (2017)	2.68% (76.99 ± 2.06 ppb, N = 31)	0.74% (49.8 ± 0.37 ppb, N= 24)	± 2 ppb
CH_4	1983-present (2017)	0.03% (1830.6 ± 0.5 ppb, N=24)	0.06% (1830.6 ± 1.1 ppb, N=18)	± 2 ppb
O_3	1983-present (2017)	2.07% (101.6 ± 2.1 ppb, N=58)	0.34% (116.4 ± 0.4 ppb, N=22)	± 1 ppb
N_2O	1989-present (2017)	0.07% (318.57 ± 0.21 ppb, N=8)	0.14% (339.03 ± 0.46 ppb, N=9)	± 0.1 ppb
CO_2	1993-present (2017)	0.03% (381.89 ± 0.10 ppm, N=75)	0.01% (396.32 ± 0.02 ppm, N=15)	± 0.05 ppm (in SH)

Note: N represents the number of measurements.   6
[β] **WCC-EMPA** *Report* **15/4;**   ***WMO/GAW** *Report* **No. 229;**   [$] **WMO/GAW** *Report* **No. 209**   7

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In order to ensure that the required data quality goals are achieved, periodic station audits   9
are performed by the Swiss Federal Laboratories for Material Science (EMPA; **WCC-EMPA**   10
Report **15/4;** www.empa.ch). In addition, the station participates in the international InterCom-   11
Parison (ICP) experiments organized under the auspices of the GAW programme (e.g. WMO,   12
2013). Recently efforts to implement continuous quality control have been supplemented by   13
joining ICP experiments, based on regular whole air (flask) samples being analysed-as men-   14
tioned above-by laboratories in France, the UK and the USA. The ICP serves as an independ-   15
ent   validation   of   the   measurements   and   identification   of   systematic   errors   16
(http://www.wmo.int/pages/prog/www/IMOP/intercomparisons.html). After internal quality   17
checks have been assured, Cape Point greenhouse gas data are submitted annually to the   18

World Data Centre for Greenhouse Gases (WDCGG, http://ds.data.jma.go.jp/gmd/wdcgg/) in   1
Tokyo, Japan, in order to make them available to the wider scientific community. **Recently,**   2
the archiving responsibility for reactive gases (other than CO) has been moved to the   3
newly established GAW World Data Centre for Reactive Gases (WDCRG) hosted by   4
the Norwegian Institute for Air Research (NILU).   5

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2.3 Air Mass Characterisation and Related Data Processing   7

GAW stations around the globe are influenced by site-specific atmospheric circulation pat-   8
terns, and each require a different approach for the selection and definition of BG conditions   9
that influence the measurement of individual gas species. Suitable BG conditions require   10
clean air samples that have not been influenced by anthropogenic processes and thus provide   11
insights into the natural processes and the contribution of anthropogenic sources to climate   12
change. The most important criterion in establishing BG conditions is wind direction. Analy-   13
sis of back trajectories derived from the NOAA on-line trajectory service   14
(http://www.ready.noaa.gov/HYSPLIT.php) has shown that Cape Point predominantly expe-   15
riences BG air (> 70% in summer), which has its primary origin in the south-western Atlantic   16
Ocean (Figure 4) and thus has not been in direct contact with anthropogenic emission sources   17
for at least several days. These conditions, that provide clean marine air from the south-   18
western Atlantic Ocean, were a Cape Point GAW pre-requisite for making meaningful, long-   19
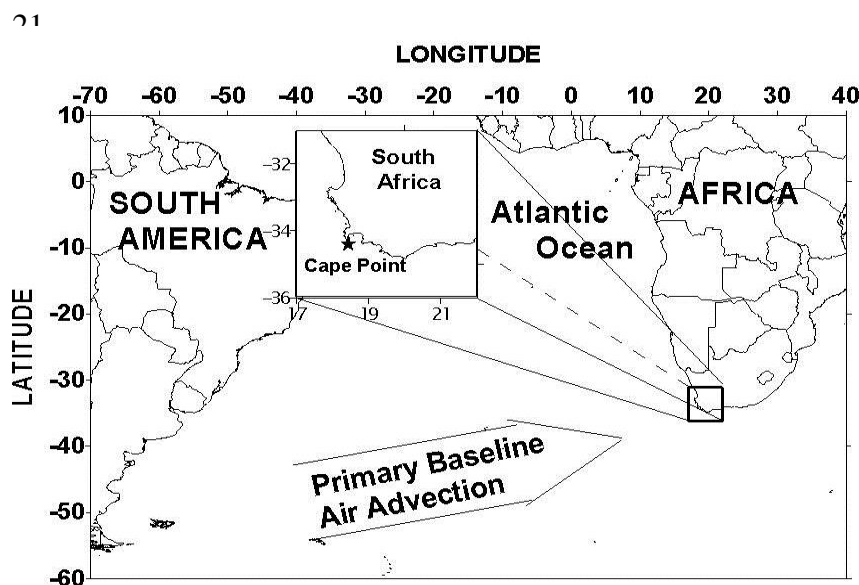term atmospheric measurements, representative of mid-latitudinal SH conditions.   20

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Figure 4. Map showing the geographic position of Cape Point and primary air advection sector. Adapted from   32
Brunke et al. (2004).   33

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Moreover, the trajectories indicate a strong contribution from descending air masses. Ac-   35

cording to calculations, a substantial number of trajectories (about 50%) from a representa-
tive sample spanning several months originate as far as 70-80 °S south of Cape Point and at
altitudes between 3000 and 7000 m (Brunke and Scheel, 2002) above the Southern Ocean.
Consequently, the air sampled at Cape Point can be viewed as being significantly affected by
free tropospheric conditions. It thus stands to reason that in the marine sector, air parcels ar-
riving at Cape Point do not only represent marine boundary layer air.

The air advected at the station can, furthermore, be divided into a marine component (typi-
cally from 120° to 280°), representative of BG air, contrasting a northerly continental com-
ponent (320° to 110°) that reflects continental air having a variable anthropogenic signature
(Brunke et al., 2004; Whittlestone et al., 2009). Two trace species, Radon 222 (^{222}Rn) and
CO, are sensitive indicators for human influences on these air masses (Brunke et al., 2004).
In 1999, a programme was launched at Cape Point GAW, together with the Australian Nu-
clear Science and Technology Organisation (ANSTO), to measure ^{222}Rn (Table 1), which is
primarily used as a tracer to distinguish maritime from continental air (Whittlestone et al.,
1998; Brunke et al., 2004). From a depiction of the angular distribution for both ^{222}Rn and
CO, it is evident that the latter corresponds more closely to the greater Cape Town area,
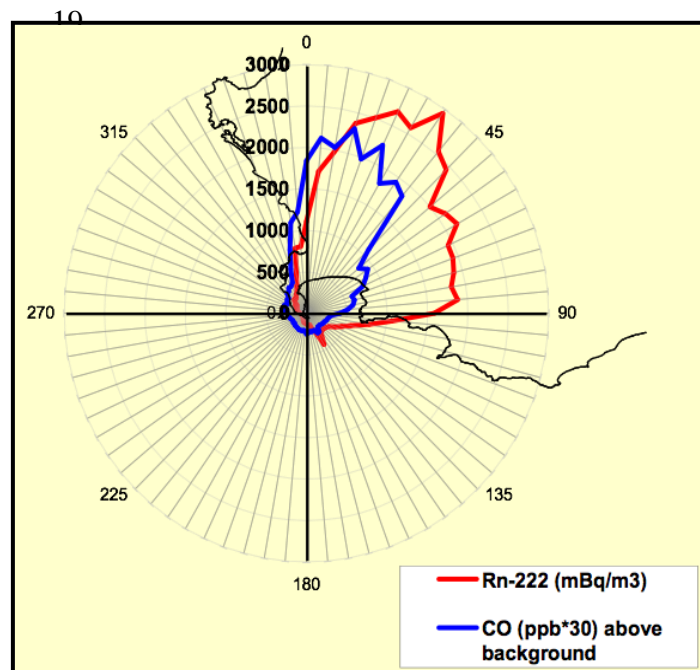whereas ^{222}Rn represents a larger continental fetch region (Figure 5).

Figure 5. Angular distribution of ^{222}Rn (red) and CO (blue) at Cape Point (1999-2002) showing a higher loading
of these gases in continental-urban air (NW to NE sector) compared to the marine sector (SE to W). The black
trace indicates the coast line of southern Africa with Cape Point at the origin of the axes. Adapted from Brunke et
al. (2004).

As part of the routine data processing, Cape Point trace gas data are subjected to statistical

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filtering methods, based on different moving percentile values (percentile filter, PF), as a   1
general tool to extract a subset of BG values from the complete data set (Brunke et al., 2004).   2
In particular, both the PF technique and the ^{222}Rn data filter have been compared for their   3
ability to classify trace gas data into BG predominantly marine and non-BG fractions. Good   4
agreement was found to exist between the two techniques, which were similarly effective in   5
excluding regional pollution episodes associated with air from the Cape Town metropolitan   6
area (Brunke et al., 2004; Whittlestone et al., 2009; Abiodun et al., 2013). The BG data set   7
has been used for the determination of long term-trends that are indicative of SH mid-   8
latitudes (Whittlestone et al., 2009). While the BG dataset is aimed at providing information   9
on long-term processes of the greater SH atmosphere, the non-BG data collected at Cape   10
Point yield insight into regional developments as well as air chemical mechanisms on shorter   11
time scales (ranging from months to hours). The latter applies predominantly to regional/local   12
biomass burning episodes.   13

 An example of the structure of the Cape Point CO_2 data, plotted as half-hourly values for a   14
randomly selected period such as 2005-2007 is illustrated in Figure 6. Statistical filtering is   15
used to extract data representative of CO_2 BG levels and is routinely applied. This subset of   16
data is shown by the black band in the figure. In particular cases, CO_2 values less than the BG   17
can occur. These are noteworthy, because of regional sink processes, which are discussed in   18
more detail in section 3.1 below.   19

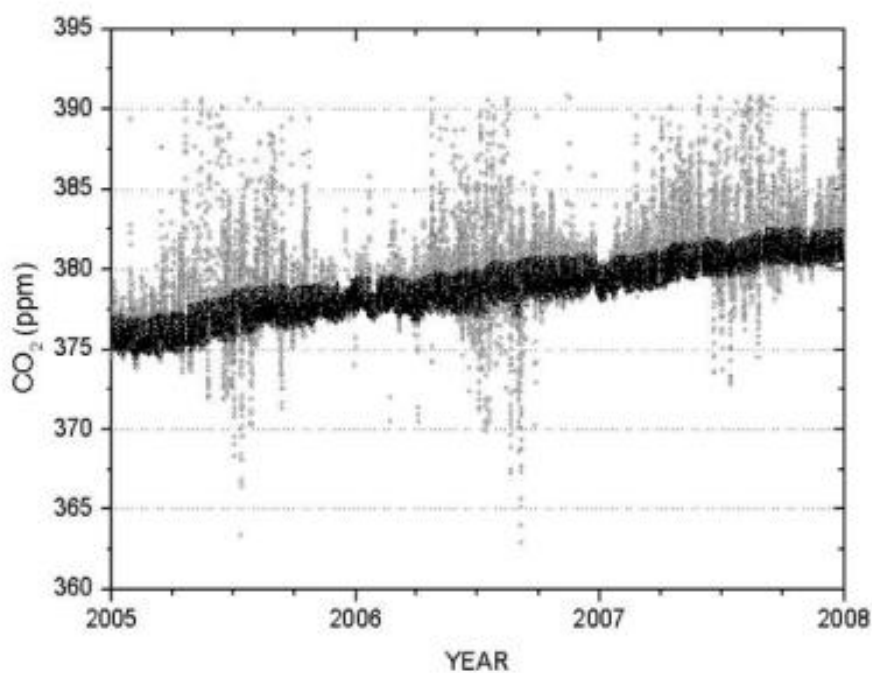   20
Figure 6. Half-hourly data for CO_2 collected at Cape Point from 2005-2007 showing the typical variation ob-   21
served. The black band represents the values categorized as BG mole fractions. Note the occasional draw down   22
events.   23

For investigating the long-term trend behaviour of Cape Point trace gas levels, different statistical tools have been employed. These range from simple linear regression to more sophisticated curve fitting, such as dynamic harmonic regression on the monthly means. The latter provides an informative temporal resolution of the trend curve and the seasonal component of the time series as part of this work.

3 TRACE GAS TIME SERIES

3.1 Carbon Dioxide (CO_2)

CO_2 is recognized as the most important anthropogenic, long-lived greenhouse gas in the atmosphere which contributes more than 60% of total radiative forcing of the long-lived greenhouse gases (IPCC, 2013; WMO, 2017; Zhang et al., 2016; Campbell, 2017). The temperature in the atmosphere is balanced by incoming and outgoing radiation. Radiative forcing is the measure of how much an atmospheric gas or particle can affect the net energy budget and therefore, atmospheric temperature. Interest in historic atmospheric CO_2 levels has led to studies of ice cores collected at different locations in the northern and southern Polar Regions by various research institutes (Petit et al., 1999; Pépin et al., 2001; Barnola et al., 2003; Raynaud et al., 2005; Zhou and Feng, 2015). The results show that the present atmospheric CO_2 levels have not been observed - at least not for the past 650000 years - and more likely, not during the past several million years either (Solomon et al., 2007; Lüthi et al., 2008; Wolff, 2011; Sloper et al., 2016).

Systematic measurements of the tropospheric CO_2 abundance commenced in 1958 at the Mauna Loa station in Hawaii and led to the now famous record for this gas (Keeling et al., 2009). Measuring programmes throughout the world, which followed the Mauna Loa initiative, all show similar long-term CO_2 increases (IPCC, 2013; WMO, 2017). However, subtle but important differences exist at the individual measuring sites, which are determined by source-sink processes related to regional conditions. Source-sink processes refer to the source of a particular gas emission and the natural absorption/decomposition of this gas in the environment (sink). Recent information based on CO_2 records over the past decades through 2016 is summarized in WMO (2017).

Since about 1750, atmospheric CO_2 mole fractions have increased by more than 100 ppm in the global atmosphere, reaching 400 ppm in 2015 (WMO, 2017). The unparalleled rate of CO_2 increase is primarily due to anthropogenic emissions, of which roughly 65% are from fossil fuel burning, whilst the balance has been attributed to land use changes (IPCC, 2013). Furthermore, it has been estimated that ~45% of the fossil fuel fraction has remained in the

atmosphere, whilst ~30% has been taken up by the world's oceans (Caldeira and Duffy, 2000; Solomon et al., 2007; Lenton et al., 2009; Le Quéré et al., 2009; 2016; Hauck et al., 2013).

Globally, short-term variations (inter annual) in CO_2 uptake/release are mainly associated with terrestrial fluxes. However, a smaller but significant fraction of CO_2 variability is also attributed to oceanic flux changes (Solomon et al., 2007; Le Quéré et al., 2007; 2009; 2016). Variations in CO_2 growth rates are also influenced by global climate oscillations like the El Niño-Southern Oscillation (ENSO) and volcanic eruptions (Hashimoto et al., 2004; Frölicher et al., 2013; Wang et al., 2013; Le Quéré et al., 2016).

The Cape Point CO_2 time series (1993-2017), based on filtered monthly means, is shown together with the calculated regression curve along with its trend component (Figure 7). Short-term variations attributed to local influences have been omitted by data filtering techniques. Consequently, the Cape Point BG CO_2 levels are largely representative of the greater south Atlantic Southern Ocean region (Brunke et al., 2004).
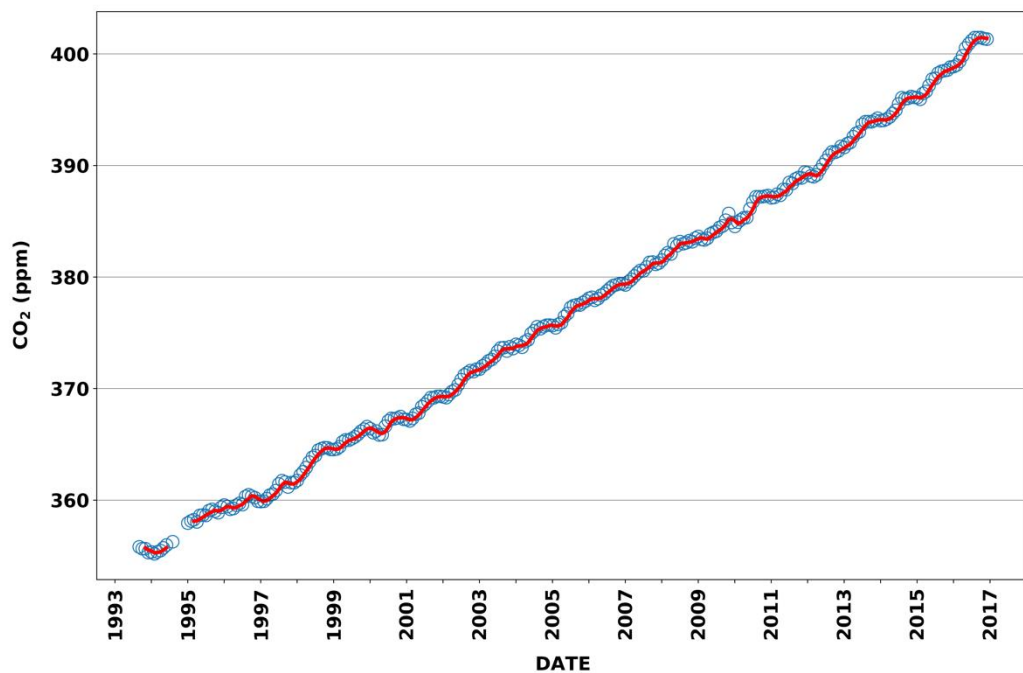

Figure 7. Cape Point CO_2 time series (1993-2016) showing monthly means, moving average (red).

The resolution of the CO_2 growth rate curve, can vary, and depends on the degree of smoothing applied. With a 5-year smoothing, the rates fluctuate between 1.5 and 2.2 ppm yr^{-1} (not shown), reflecting an overall increase. This is particularly evident from the linear regression with values of the fit ranging from 1.65 ppm yr^{-1} in early 1993 to 2.80 ppm yr^{-1} at the

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end of 2016. These rates are similar to those reported by other global sites where a CO_2 1

growth rate was reported as 2.08 ppm yr^{-1} for 2005-2015 period and of 2.3 ppm yr^{-1} specifi- 2

cally for the 2014-2015 period (WMO, 2017). 3

The Cape Point CO_2 data are shown within a global context in both latitudinal banding and 4

temporal scale (Figure 8). The seasonal variations of CO_2 are large in northern latitudes, but 5

the variations are insignificant in the southern latitudes (WMO, 2017). The seasonal peak-to- 6

peak values observed at Cape Point (which is also typical for other SH sites) are out of phase 7

with the corresponding NH latitudes, due to the shift in seasons. WMO (2017) reported that 8

the inter-annual variations in CO_2 growth rate are larger in the NH compared with that in the 9

SH. Generally, BG CO_2 seasonal variation has been largely a function of land mass (i.e. ab- 10

sorption or emission in the biosphere) in the NH. In contrast, oceanic processes primarily 11

drive the seasonal structure (Tanaka et al., 1987; Battle et al., 2000; Levin, 2012) in the SH, 12

due to the lack of continental landmass in the Southern Ocean. The main factors controlling 13

CO_2 uptake by the oceans comprises a complex combination of physical, chemical, and bio- 14

logical processes. The chemical process, for instance, involves the dissolution of atmospheric 15

CO_2 with water to form carbonic acid and its dissociation products. This specific process is 16

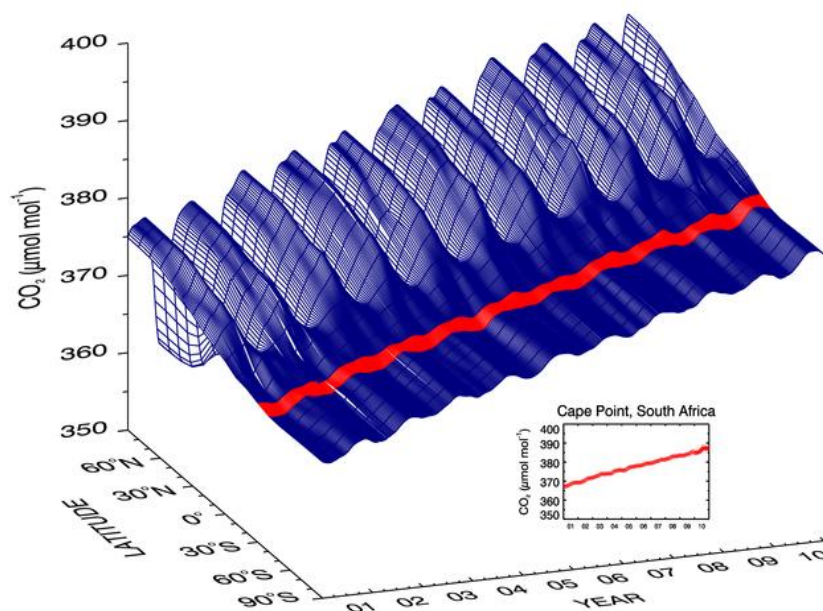also temperature sensitive and as a result, contributes to a CO_2 climate feedback mechanism. 17

Figure 8. Cape Point CO_2 (shown as red band) as a function of latitude and time (2001-2010, GLOBALVIW- 34
CO2, 2011) 35
  36
The Southern Ocean is a known sink of anthropogenic CO_2 in the atmosphere (e.g. 37

Calderia and Duffy, 2000), accounting for approximately 50% of all anthropogenic uptake 38

(Butterworth and Miller, 2016). Although the physical solubility plays a role in the uptake 39

15

and dissolution of atmospheric CO_2, the biological pump through photosynthesis accounts for ~80% of the Southern Ocean uptake (Moore and Abbott, 2000), particularly in mid-latitudes (Metzl et al., 1999; Takahashi et al., 2002). It has been shown that the ability of the Southern Ocean to continue to take up CO_2 might be reduced due to changing wind fields, as a result of climate change (Le Quéré et al., 2007). This may have an impact on the growth rates observed at Cape Point.

While the overall Cape Point CO_2 BG record parallels the global trend, if at a smaller scale, valuable information on local and regional processes can also be derived from the non-BG data (Brunke et al., 2009; Whittlestone et al., 2009). Elevated CO_2 levels are often associated with pollution events from the greater Cape Town region that are advected to the station from the northern sector, mainly during autumn and winter (April to August), when strong inversions and low wind speeds trap emissions - referred to as brown haze (e.g. Wicking-Bird et al., 1997; Walton, 2005; Jenner and Abiodun, 2013). Regional air masses occasionally contain significantly reduced CO_2 mole fractions (up to 5 ppm below the BG level) which are observed over the sampling site during August-October. As indicated, confirmed by back trajectories, these CO_2-depleted air masses have passed over agricultural areas in the Western Cape where wheat cultivars are grown (Brunke et al., 2009). It is speculated that wheat growing areas act as small local CO_2 sink (as can be observed in Figure 6).

3.2 Methane (CH_4)

CH_4 plays a pivotal role in the atmosphere due to its global warming potential (e.g. Lelieveld et al., 1998; Hofmann et al., 2006; IPCC, 2013; WMO, 2017). Methane is reported to be ~21 times more effective as a greenhouse gas as CO_2 for a time horizon of 100 years (Solomon et al., 2007). Furthermore, CH_4 has a strong influence on the oxidizing potential of the atmosphere via its reaction with the hydroxyl ($\cdot$OH) radical (Thompson, 1992; Thompson et al., 1993; Prather 1996; McNorton et al., 2016; Turner et al., 2017; Rigby et al., 2017).

CH_4 contributes ~18% to the radiative forcing attributed to long-lived GHGs and approximately 40% of CH_4 emitted into the atmosphere is estimated to have originated from natural sources such as wetlands and termites. Whereas anthropogenic sources, notably ruminants, rice agriculture, fossil fuel exploitation, landfills and biomass burning, account for about 60% (WMO, 2017). The increase of atmospheric CH_4 mole fractions has thus been linked to human activities (Crutzen, 1995; Wuebbles and Hayhoe, 2002; Nisbet et al., 2016), especially increasing numbers of cattle and sheep as well as rice cultivation (Lassey et al., 1992; Huarte et al., 2010; Broucek, 2014; Nisbet et al., 2016; Shindell et al., 2017). The atmospheric me-

thane burden prior to the industrial era was estimated to be around 750 ppb (Thompson et al., 1993; Lelieveld et al., 1998; Solomon et al., 2007; Kirschke et al., 2013). This has escalated to a globally averaged level of 1845 ± 2 ppb CH_4 in 2015 (WMO, 2017).

Furthermore, high CH_4 levels increase moisture in the stratosphere (Oltmans et al., 1995; Flemming et al., 2011; WMO, 2017), **thus** it promotes high-altitude O_3 depletion (Blake et al., 1988; Portman et al., 2012) via HO_x chemistry and the formation of polar stratospheric clouds. The global methane trend has been presented by various studies (Steele et al., 1992; Dlugokencky et al., 1994; Crutzen, 1995; Dlugokencky et al., 1997; Dlugokencky et al., 2000; Khalil et al., 2007; Bergamaschi et al., 2013, McNorton et al., 2016; Saunois et al., 2016; Nisbet et al., 2016, Turner et al., 2017). This includes a period of ~1% yr^{-1} increase in CH_4 in the 1970s and early 1980s, followed by a slowdown and stabilization in the 1990s. The levels of CH_4 in the SH varied little up to 2006 and since 2007 a sustained increase in CH_4 levels has occurred in most latitudinal zones of the planet (Rigby et al., 2008; Bousquet et al., 2011; Sussmann et al., 2012; Nisbet et al., 2016). Many uncertainties concerning source and sink processes remain unresolved (Kirschke et al., 2013; Hopecroft et al., 2017; Houweling et al., 2017; Rigby et al., 2017).

Tropospheric CH_4 measurements have been conducted at Cape Point since 1983. Observations made under BG conditions during the first few years (1983 to 1987) were reported by Brunke et al. (1990), whilst the entire data record until 2015 is discussed in WMO (2017). Within the context of selecting air masses that are representative of BG conditions, the relationship between CH_4 and the tracer ^{222}Rn has been explored (Brunke et al., 2004).

The BG measurements make up the bulk of the measurements observed (~80%, with a standard deviation of 12%). Non-BG measurements up to 200 ppb greater than the BG observations are recorded approximately 20% of the time. These non-BG events occur dominantly in austral winter. The complementary data set, i.e. the non-BG data, provides valuable information on regional processes. Although not covered here, as it is beyond the scope of this review, the non-background datasets are of great interest and will be covered in detail elsewhere.

Although atmospheric CH_4 mole fractions have shown an overall upward trend since measurements began at Cape Point, the growth-rate has decreased from 12 ppb yr^{-1} in 1982 to 2 ppb yr^{-1} in 2003. The growth rate then stabilized and remained just above zero (near equilibrium state) for approximately 3 years. From October 2007 onwards, CH_4 mole fractions have increased again reaching a growth rate by 2016 of about 11 ppb yr^{-1} which relates well to the global average of 9.0 ppb yr^{-1} for the years 2013 to 2015 (WMO, 2017).
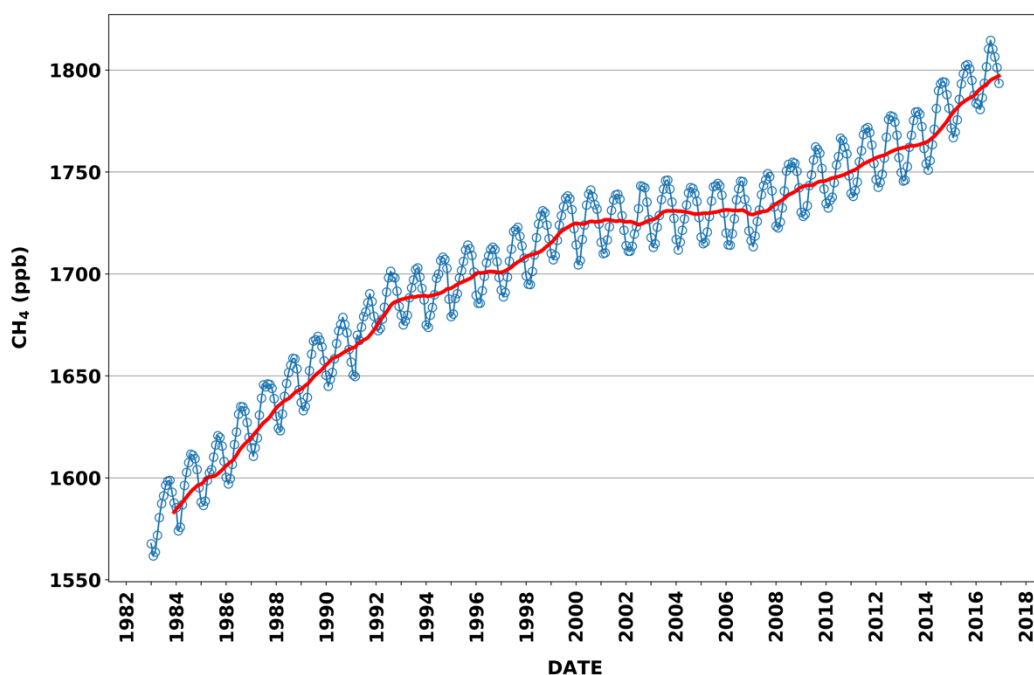
Figure 9. Cape Point CH$_4$ monthly means (1983-2016) for BG data. Red line highlights the moving average.

The seasonal cycle of CH$_4$, based on BG data has been highly consistent over the timespan of the Cape Point measurements (Figure 10). The structure of the CH$_4$ measurements at Cape Point exhibit a strong seasonal cycle (as do most of the trace gas species measured) with a maximum in austral winter and minimum in austral summer. This was primarily in response to the annual cycle in the rate of CH$_4$ removal by the $\cdot$OH radical (Prather, 1996; WMO, 2014):

$$CH_4 + \cdot OH \rightarrow \cdot CH_3 + H_2O \quad\quad\quad (E1)$$
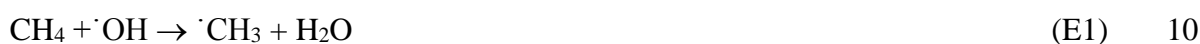
The $\cdot$CH$_3$ radical formed in this reaction initiates a chain reaction that leads ultimately to the formation of formaldehyde (HCHO) and CO (Thompson, 2002; Clarke and Tomlin, 1999).

In detail, the CH$_4$ amplitude values between summer and winter at Cape Point (Figure 10) showed a small decrease from 29 ppb in 1983 to 27 ppb in 1992, where after they increased again to about 29 ppb in 2000. Since 2010 the CH$_4$ seasonal amplitude has increased to approximately 40 ppb. The observed inter-annual variations in CH$_4$ peak-to-peak values are a function of different processes, notably changes in sink strengths, variations in seasonal source emissions, and changes in long-range transport (Dlugokencky et al., 1997).
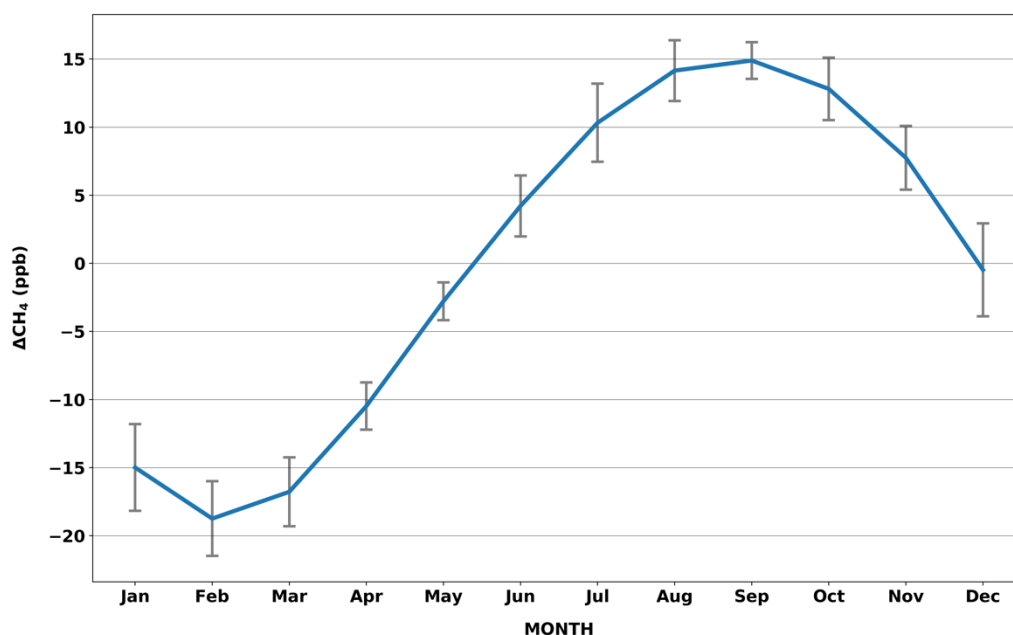
Figure 10. Composite CH_4 cycle (1983-2016) The error bars denote ± 1 standard deviation of the monthly means.

The variability in growth rates agrees well with observations made at several SH and NH locations. Possible causes, such as an increase in emissions (both natural and anthropogenic) in both hemispheres or a reduction in ˙OH mole fraction, are still under discussion (e.g., Rigby et al., 2008; 2017; Dlugokencky et al., 2009; McNorton et al., 2016; Rice et al., 2016; Turner et al., 2017). Based on modelling studies, Bousquet et al. (2006) explained the 2002-2006 near absence of any CH_4 growth to a general drying up of wetlands world-wide, which offset the concomitant anthropogenic increase. The increase observed during the latter part of the record (2007-2014), indicates that the growth rate is driven by biogenic sources particularly in the tropical region (Nisbet et al., 2016).

3.3 Nitrous Oxide (N₂O)

N_2O is emerging as one of the most important contributors to the radiative forcing by long-lived greenhouse gases (WMO, 2017). Its mole fractions in the troposphere have increased from about 270 ppb in pre-industrial times to a global abundance of 328 ppb in 2015 with a mean growth rate of approximately 0.89 ppb yr^{-1} over the past 10 years (WMO, 2017). N_2O has a Global Warming Potential (GWP) which is 280-300 times higher than that of CO_2 for a time horizon of 100 years (Solomon et al., 2007; IPCC, 2013). Its impact on the global climate is hence substantial. Furthermore, N_2O has one of the largest Ozone Depletion Poten-

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tials (ODP) estimated to be 0.017 relative to CFC-11, which has an ODP of 1 (Ravishankara et al., 2009; WMO, 2017) and depending on future CO_2 and CH_4 levels in the stratosphere may increase over the next century (Revell et al., 2015). It has both biogenic and anthropogenic sources (Kroeze et al., 1999; Crutzen et al., 2008; Davidson, 2009; Davidson and Kanter, 2014). These include natural sources such as soil, oceans, biomass burning as well as anthropogenic activities, such as agricultural fertilization, fossil fuel combustion and various industrial processes, with anthropogenic contributions constituting about 40% of all emissions (WMO, 2017). The major use of nitrogen fertilizers takes place in the mid-latitudes of the NH which is the underlying reason for the small north-to-south gradient of about 1.2 ppb (WMO, 2017). The primary removal process of N_2O from the atmosphere is via photochemical processes in the stratosphere (Minschwaner et al., 1993; Nevison and Holland, 1997), which leads to the long atmospheric residence time of ca. 131 years (Prather et al., 2012; Table 1) for this gas.

N_2O has been measured at Cape Point since 1983, although data prior to 1989 are deemed not reliable enough for detailed trends analysis (Brunke et al., 1990). Cape Point is one of only three continuous monitoring stations in the SH that reports N_2O measurements. There are extensive analytical challenges present in the measurements techniques of N_2O. Currently, fine scale processes cannot be adequately resolved. However, the N_2O data generated from Cape Point is still of great use in a global sense. The overall trend for this region is well characterised and evident within the CPT record. A linear regression fit to the monthly mean N_2O mole fractions indicates a local growth rate of 0.72 ppb yr^{-1} at Cape Point over this 23-year period (Figure 11). This agrees well with growth rates found at other GAW stations and with the recent global increase (WMO, 2017).
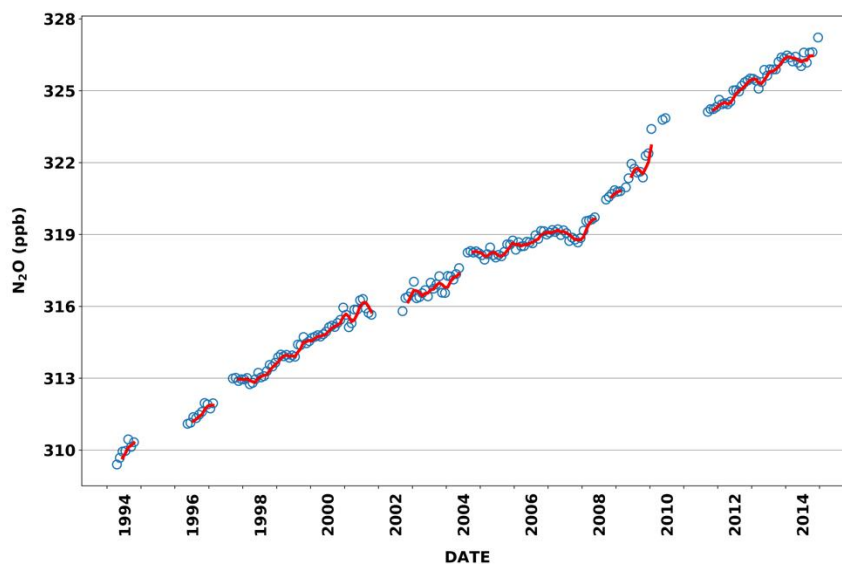
Figure 11. Monthly means of N_2O at Cape Point from 1993 till December 2016.

3.4 Ozone (O_3)

Tropospheric O_3 is the third most important tropospheric greenhouse gas (IPCC, 2013; Stevenson et al., 2013) which plays an important role in controlling the chemical composition of the troposphere (Logan et al., 1981; Ehhalt et al., 2001; Monks, 2005) and consequently exerts a significant influence on global climate (Fishman et al., 1979; Shindell et al., 2012; Monks et al., 2015). Ozone forms part of the reaction chain leading to the formation of the ˙OH radical, which in turn, is the removal agent for many atmospheric trace gases and pollutants. On a temporal and spatial scale, tropospheric ozone displays large variability, mainly as a result of its relatively short atmospheric lifetime-compared with other greenhouse gases (Table 1). The tropospheric O_3 abundance originates from both stratospheric influx (e.g. Danielsen and Mohnen, 1977; Viezee et al., 1983; Roelofs and Lelieveld, 1997; Olsen et al., 2002) as well as from photochemical production in the troposphere (e.g. Chameides and Walker, 1973; Crutzen, 1974; 1976; Lelieveld and Dentener, 2000, and references therein). Taken together, the lower tropospheric ozone mole fractions, as measured in-situ, are the results of production, transport, chemical destruction, and deposition processes.

Measurements of tropospheric O_3 at Cape Point are made at three air intake heights, 30 m, 14 m, and 4 m, of which the 30 m time series (1983 onwards) constitutes the longest-term record at this site (Scheel et al., 1994; Brunke and Scheel, 1998; Oltmans et al., 2006; Brunke et al., 2011a). Data from the 4 m air intake was collected from 1997 onwards, and those from the intermediate height (14 m) have been available since 2008. In-situ ozone observations at Cape Point indicate high variability (elevated or depleted in O_3) at time scales of hours to days. Results from 30 m and 4 m air intakes show small differences of less than 2 ppb under background conditions. However, differences of up to $\pm$ 60 ppb is occasionally observed under non-background conditions when air masses originate from Cape Town region (Brunke et al., 2009) and is trapped under inversion conditions.

The O_3 observations at Cape Point under BG conditions are very stable; however, measurements under non-BG conditions indicate high variability at various scales (i.e. elevated or depleted in O_3, Figure 12). For illustration purposes, data for the years 1997-2001 (Figure 12) show how statistical filtering is applied to the O_3 data (see section 2.3). The central band indicates BG data measured at Cape Point. In contrast to species such as CO_2 or CH_4 **(where the lowest data points are usually also indicative of BG conditions)** the statistically filtered O_3 data cannot *a priori* be regarded as representative of BG mole fractions, but only as the central part of the frequency distribution. **Air masses arriving at Cape Point can con-**

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tain both high and low concentrations of O₃. Typical filtering techniques usually involve 1

the subtraction of low mixing ratios from elevated mixing ratios to establish a baseline 2

or background. Instances of very low O₃ values have been associated with urban- 3

derived NOₓ chemistry, usually under heavily polluted pre-frontal conditions. Hence, the 4

BG data for O₃ at Cape Point is derived from **calculating** the most frequent mole fractions. 5

This is confirmed through the known air-flow regimes, where the data does reflect BG condi- 6
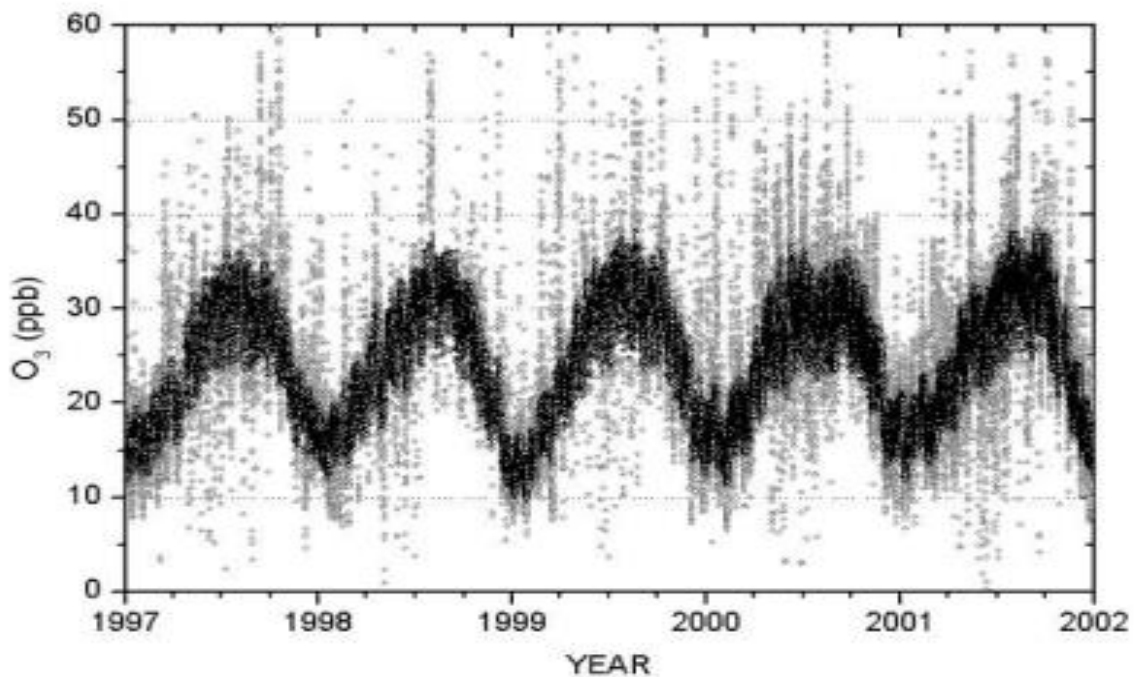
tions. 7

8

Figure 12. Half-hourly data for surface O₃ at Cape Point (30 m air intake) from 1997 to 2001. The bold data points represent filtered data (local pollution eliminated).
9
10
11

In the case of O₃ the monthly mean values of the complete data set and the statistically fil- 12

tered data usually agree very well with each other, because locally polluted air gives rise to 13

both elevated as well as depleted values, which can cancel each other. However, for the pur- 14

pose of determining long-term trends the BG data are used which is treated in a similar fash- 15

ion as for all other trace gases. 16

The monthly means for the 30 m air intake are depicted with the statistical filter together 17

with a moving average calculation (Figure 13). The time series can be roughly divided into 18

three parts: 1983-1989/90 showing no clear trend behaviour with two data gaps. From 1991- 19

2002 a statistically significant O₃ increase occurred followed by stabilization from 2003 on- 20

wards. Following a short rise in 2010 the concentrations followed a period of stability. The 21

positive trend for the period 1991 to 2002 of 0.35 ppb yr^{-1} was also accompanied by an in- 22

crease in seasonal peak-to-peak values, which has been shown to be statistically significant 23

using a range of tests.

The seasonal variations display a maximum in July-September and a minimum in January, yielding an average peak-to-peak value (amplitude) of 14.7 ppb (Figure 14). The overall seasonal cycle of O_3 in the BG marine atmosphere (low in NO_x) is primarily driven by O_3 photolysis (Ayers et al., 1997; Bremaud et al., 1998), which is a function of the annual solar cycle. In winter, when the solar intensity is at its minimum, the photochemical breakdown of O_3 is at a minimum, thus giving rise to the ozone maximum during austral winter and its minimum in summer.
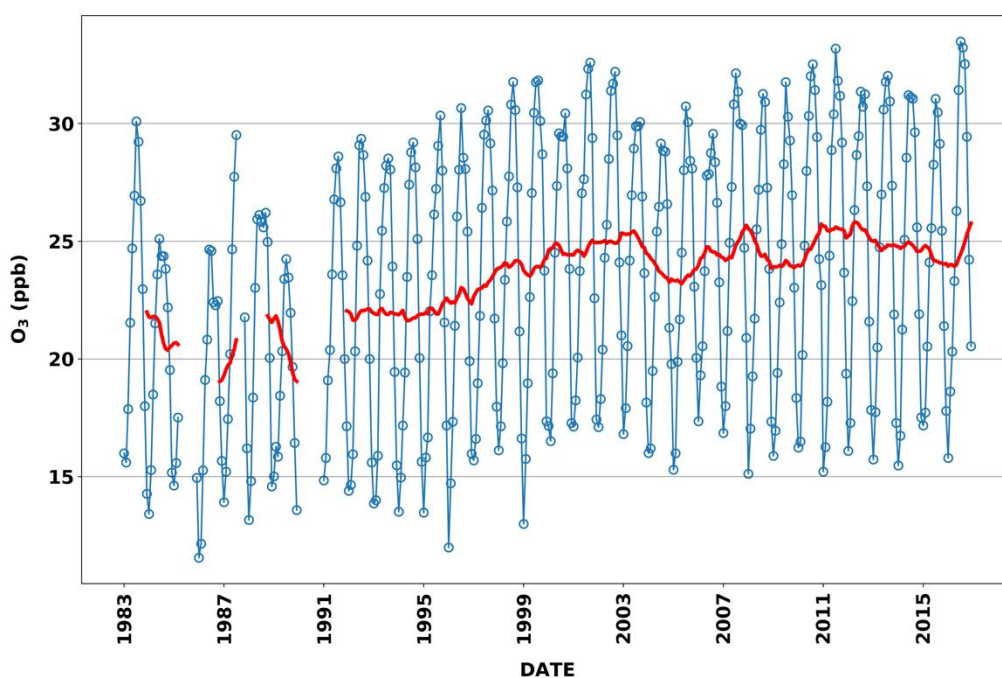

Figure 13. O_3 time series of monthly means (1983-2016) and moving average (red).
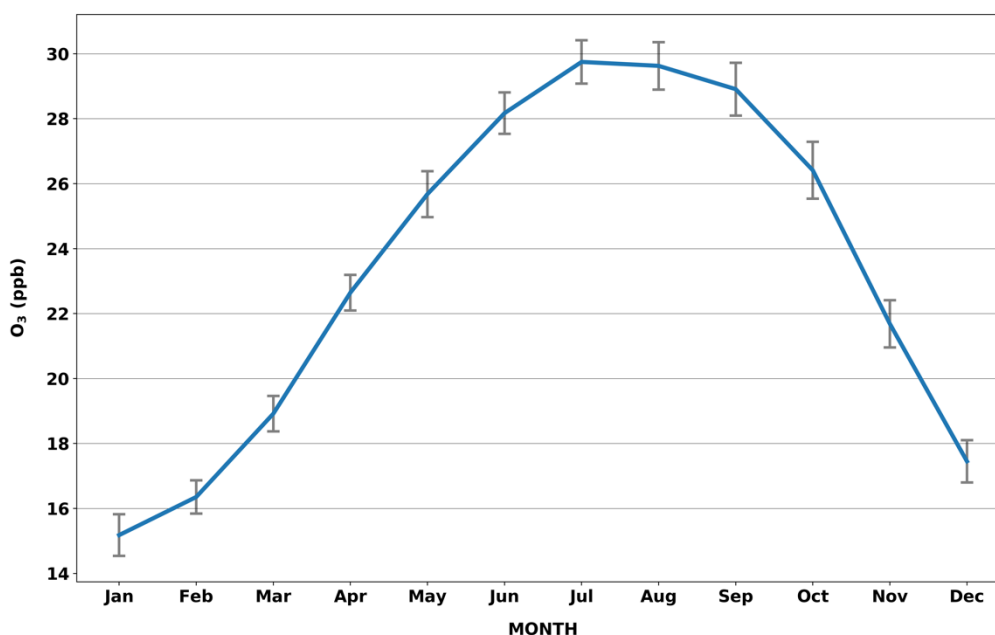
Figure 14. Average seasonal variations of O_3 (1983-2016). Error bars denote ± 1 standard deviation.

In a study of global ozone trends, the Cape Point time series was put into perspective with other SH locations, where it showed a relatively high O_3 increase (Oltmans et al., 2006). For the period 1990-1999, this is particularly evident from a comparison of the growth rates at Cape Point of 0.30 ppb yr^{-1} (Brunke et al., 2011a) with Cape Grim, showing a rate of 0.11 ppb yr^{-1} (Galbally et al., 2011). Interestingly, data from Lauder, New Zealand (850-700 hPa ozonesonde data) shows a similar increasing trend as the one observed at Cape Point (Oltmans et al., 2013). The underlying reasons for this disparity in ozone growth rates between Cape Point and Lauder relative to Cape Grim are still being **investigated but is most likely related to the sites' individual and unique NO_x and VOC chemical process pathways.**

3.5 Carbon Monoxide (CO)

CO is recognised as one of the most important atmospheric trace gases that plays a key role in the tropospheric oxidative chemistry (Chameides and Walker, 1973; Logan et al., 1981; Thompson, 1992). It is not a direct greenhouse gas, but it affects the atmospheric burden of some greenhouse gases e.g. O_3 and CH_4 and hence contributes in radiative forcing (Wigley et al., 2002; Myhre et al., 2013). It is mainly produced during the incomplete combustion from fossil fuels and biomass burning as well as being formed by the photochemical degradation of volatile organic compounds (VOCs). Measurements of CO in the atmosphere have been associated with anthropogenic sources and its tropospheric lifetime is about 2 months varying

24

with season and location (Cicerone, 1988). For instance, a strong gradient exists between NH and SH mixing ratios. This gradient exists because the NH displays proportionally much larger anthropogenic sources than the SH. Furthermore, the abundance of the ˙OH radical within the tropics prevents large scale inter hemispheric transport. At local scales, the short atmospheric lifetime makes CO an excellent marker for tropospheric transport processes and polluted air masses (Edwards et al., 2004; Sodemann et al., 2011).

The dominant sink of CO from the atmosphere is through reactions with O_3 and ˙OH radicals (WMO, 2017). At Cape Point, CO concentrations form a seasonal cycle with a maximum in winter (70-80 ppb) and minimum in austral summer (40-50 ppb; Seiler et al., 1984; Scheel et al., 1998). Reasons behind the maximum in winter may be two-fold, firstly, decreased reactions with ˙OH and secondly, an influx of CO from Cape Town carried on the north-westerly winds (Seiler et al., 1984; Toihir, 2015).

The El Niño Southern Oscillation (ENSO) is known to cause changes throughout the earth system. Large changes such as variations in temperature or precipitation have been reported. Other impacts might include changes in source and sink processes of various trace gases such as CO (Scheel et al., 1998; Toihir, 2015).

In October 1998, the measurements were specifically made to coincide with the NASA Modelling, Analysis and Prediction (MAPS) programme, to measure CO from an orbiting satellite (Scheel et al., 1998). The satellite measurements made by the MAPS orbiter compared well with ground based measurements at Cape Point, South Africa and Zugspitze, Germany (Scheel et al., 1998).

Further modelling studies of CO measurements in the southern African atmosphere have been moderately successful (Wagner et al., 2015). The Monitoring Atmospheric Composition and Climate (MACC) project compared O_3, CO and NO_2 measurements from GAW stations to model simulations (Wagner et al., 2015). Particularly for the southern Africa region, the MACC model captured the CO cycle realistically. The modified normalised mean biases used to assess the model accuracy ranged between -15 and 10% for different seasons. A small under prediction occurred during winter and an over prediction in summer (Wagner et al., 2015). The over and under prediction errors were more noticeable in Europe and North America. The authors ascribe the offset largely to errors in rate of dry deposition and limitations in the emissions inventories (Wagner et al., 2015).

The CO mixing ratio has been fairly consistent over the period from 1978-2000 thereafter a decreasing trend was observed. Since 2000, a declining trend was observed at Cape Point in-situ measurements (Figure 15). Similarly, satellite studies conducted on the same latitude reported a decreasing trend (Zeng et al., 2012; Yin et al., 2015; Toihir, 2015). The CPT de-

creasing trend in surface observations was confirmed by satellite observations (Tohir et al., 2015; Worden et al., 2013) and is consistent with global observations of CO (van der Werf et al., 2010; Worden et al., 2013; Tohir et al., 2015). The reported decreasing trend may be related to, *inter alia*, to a decrease in the occurrence of biomass burning especially on the African continent, as well as economical drivers such as the global recession which has resulted in an overall decrease in industrial manufacturing practices (Gaubert et al., 2017).
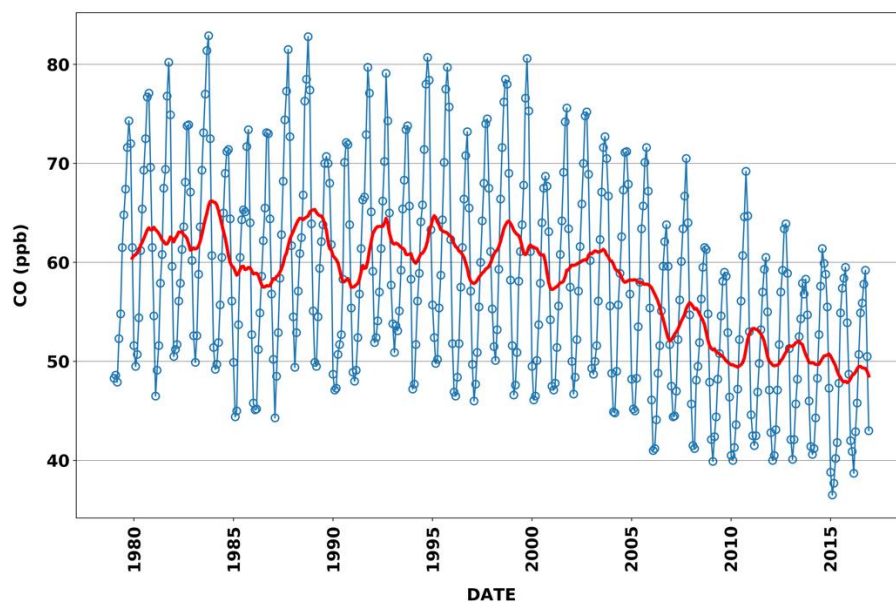

Figure 15. CO time series of monthly means for Cape Point. Monthly moving average shown in red (1979-2016).

3.6 Halocarbons

Halocarbons in the atmosphere play a number of roles relating to climate change and O_3 destruction (Daniel et al., 1995; Forster and Joshi, 2005; Ramanathan and Feng, 2009; Hodnebrog et al., 2013; IPCC, 2013). Whilst chlorofluorocarbons (CFCs) have no natural sources, having been synthesized for such diverse uses as refrigerants, aerosol propellants and cleaning solvents, halocarbons have both anthropogenic and biogenic sources. In the early 1980s, it was discovered that the anthropogenically produced chlorofluorocarbons (CFC) compounds used in refrigeration systems were resulting in the catalytic destruction of stratospheric O_3 (Ramanathan, 1975). The O_3 in the stratosphere is of critical importance to all life as it filters out harmful UV radiation from the sun. Modern halocarbons, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), were developed to replace the CFCs. Recent evidence suggests that these replacement HCFCs and HFCs are also problematic because of their capacity to act as potent greenhouse gases (Velders et al., 2009; Montzka et al.,

2011; Xu et al., 2013; Rigby et al., 2014).

The main halocarbons (including the classic CFCs) measured at Cape Point include: CFC-11, CFC-12, CFC-113, trichloroethylene (TCE) and CCl_4. These measurements have been made from 1979 (CFC-11; Table 1). Early measurements of $CFCl_3$ and CCl_4 at Cape Point were done manually on a GC-ECD system donated by James Lovelock. Later an automated system was introduced which improved the sampling frequency. The early measured concentrations of $CFCl_3$ (CFC-11) and CCl_4 were 182 and 143 ppt, respectively (Brunke and Halliday, 1983). The growth rates of these gases were found to be 11.5 and 6 ppt yr^{-1} for $CFCl_3$ and CCl_4, respectively (1978-1981). The rate for $CFCl_3$ compared well with other measurements while that for CCl_4 was 2.5 times elevated (Brunke and Halliday, 1983). It was subsequently established that this elevation was calibration scale related and the data was adjusted accordingly. The growth rate of $CFCl_3$ and CCl_4 decreased through the 1980s to 9.1 and 2.1 ppt yr^{-1}, respectively (Scheel et al., 1990). These growth rates agree well with other BG sites (Cape Grim and Antarctica). While CCl_4 in the atmosphere is thought to be mostly from anthropogenic sources, $CFCl_3$ is entirely man-made. TCE has been used as an industrial solvent and been used extensively as a marker for anthropogenically contaminated air (Dimmer et al., 2001).

Early work at Cape Point showed a slight seasonal cycle in CFC-11 (Figure 1 in Scheel et al., 1990). However, in contrast, no discernible seasonal pattern for CCl_4 was observed. This may be a function of a lack of emission gradient between NH and SH (Scheel et al., 1990). The rate of increase or growth of CCl_4 slowed through the 1980s to a rate of 1.0 ppt yr^{-1} most likely as result of decreased demand for CFCs **due to restrictions in production; a consequence of the Montreal Protocol**, of which CCl_4 is a precursor (Rossberg et al., 2006). This agrees well across numerous global sites (Scheel et al., 1990). This rate decreased from 2.7 ppt yr^{-1}, calculated for the first half of the decade (1980-1985) (Scheel et al., 1990). The presence or absence of CFCs observed in different air masses has been used to characterise air samples at Cape Point (Brunke et al., 2001). An elevated concentration of CFCs implies that anthropogenically modified air was sampled, conversely low concentrations would suggest clean air.

During a particular biomass burning event in the vicinity of the Cape Point GAW station (2000) the concentrations of numerous trace gases showed a marked increase. However, the concentrations of CFCs observed in the same air mass remained unvarying during this period (Brunke et al., 2001). The absence of CFCs observed in these samples confirmed that the air mass was of mainly biogenic origin and not from anthropogenic sources.

The atmospheric lifetimes of the CFCs ranges from days to years. Trichloroethylene (TCE)

is the shortest-lived CFC compound measured at Cape Point, with an atmospheric lifetime of ~5 days (Dimmer et al. 2001). CFC-11 and CFC-12 display significantly longer atmospheric lifetimes, typically around 55 and 140 years respectively (Elkins et al. 1993). The Montreal Protocol was established in 1987 to mitigate the CFC related damage to stratospheric ozone. A complete ban in the global production of CFCs was achieved in the early 1990s and reflected in the measurements (Figure 16). The decrease for the shortest-lived compounds have reached nearly zero (e.g. TCE). The longer-lived CFC compounds (11 and 12) show a much slower rate of decrease due to the long atmospheric lifetimes of these compounds (Figure 16). This is not a function of gas release but rather due to the slow destruction rates. The marked decrease in these compounds highlights the efficacy of the Montreal Protocol in curbing the production of these compounds.

In recent times, the monitoring of halocarbons has expanded from the classic CFCs to include the replacement HCFCs and HFCs (e.g. Prinn et al., 2000). All three types of species are potent greenhouse gases and predictions suggest that by 2050 the HFCs will be equivalent to between 9-19% of the projected CO_2 emissions (Velders et al., 2009; Rigby et al., 2014). **Due to their high GHG potential, HCFCs and HFCs were added to the list of banned species under the Montreal Protocol as the Kigali Amendment (2016).** Therefore, there is an urgency to measure these species, particularly in the SH sites where such measurements are sparse. Accordingly, a joint University of Bristol/University of the Western Cape halocarbon project has been started at the Cape Point GAW station and data for 33 different halocarbons is being acquired.
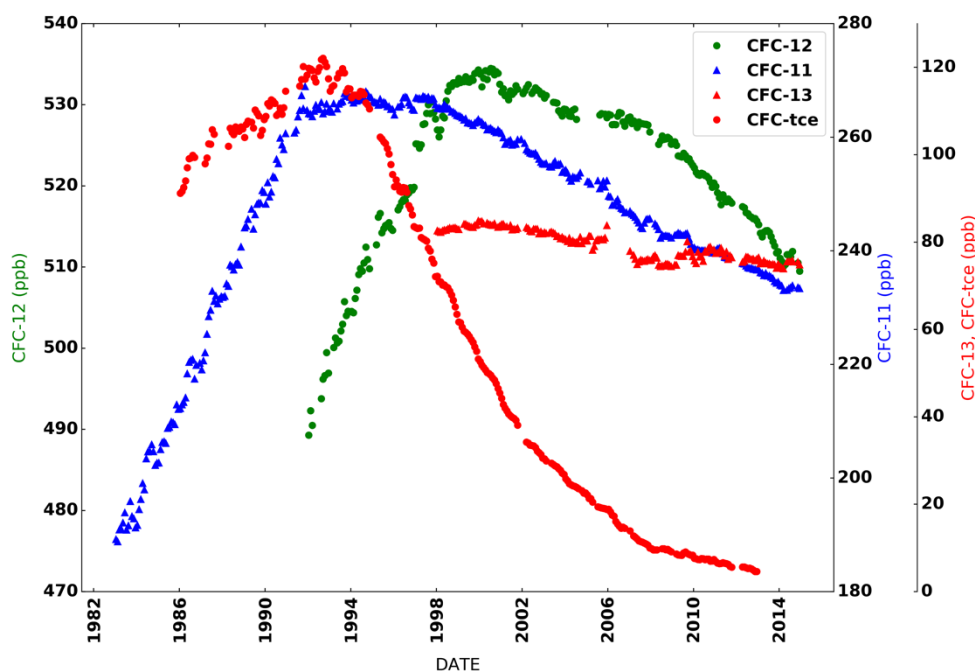
Figure 16. Time series of filtered monthly means of halocarbons measured at Cape Point. Halocarbons measured include: CFC-11 (blue triangles), CFC-12 (green points), CFC-13 (red triangles), and TCE (red points).

4 Summary

The Cape Point GAW monitoring station has provided a platform for extensive climate change and trace gas measurement for the past four decades. This monitoring station is unique in receiving clean marine air from the Atlantic sector of the Southern Ocean and is able to monitor local anthropogenic contributions to the Southern Hemisphere. The Cape Point GAW closes a latitudinal gap in measurements in the Southern Hemisphere, between Cape Matatula to the north and Cape Grim to the south and had recorded some of the longest Southern Hemisphere records for CO, CFCs and other gases.

Globally observations of CO_2 mixing ratios at Cape Point are consistent with other SH sites and these mixing rations have shown a similar increase over the last 40 years (WMO, 2017). Local processes, possibly linked to the wheat growing season, result in small, short lived drawdown events which briefly reduce CO_2 concentrations.

The mean CH_4 mixing ratios measured at Cape Point have also shown a general increase congruent with global trends. The seasonal variation has largely remained constant since the start of the CH_4 monitoring 34 years ago. Not unexpectedly the growth of the city of Cape Town, in terms of increased urbanisation and industrialisation, have been reflected in an increase in the local non-BG measurements of CH_4. Interestingly there was a short three year (2003-2006), plateauing of the CH_4 mixing ratios measured at Cape Point. Subsequently the growth rate of CH4 mixing ratios has returned to levels last seen in the 1980s.

Cape Point is one of the only sites in the Southern Hemisphere at which N_2O is measured and reported, possibly due to the analytical challenges of measuring concentrations of this gas in the atmosphere. While the variability of N_2O concentrations are not reported in detail in this review, the overall trend suggests a small annual increase (0.72 ppb yr^{-1}) under BG conditions.

The first measurements of CO were initiated in 1977 and now comprise the longest time series of CO measurements in the SH. Paradoxically, after two decades of minimal change in CO mixing ratios measured at Cape Point, the concentration of atmospheric CO has steadily decreased since 2005. A similar decline in CO mixing ratios has been reported from a number of global atmospheric monitoring sites and also from satellite observations. The reason behind this decline are not fully understood.

Given the relative proximity of city of Cape Town, the determination of the background for surface O_3 measurements at Cape Point is not simple. A small increase in the O_3 mixing ratio has been observed at Cape Point since surface measurements were begun in 1983. The interaction of O_3 with CO and OH radicals are thought to have an undetermined impact on the local CH_4 measurements.

A cohort of eight halocarbons, relevant to stratospheric ozone depletion, have been measured in the atmosphere at Cape Point since the early 1980s. The increase in mixing ratios of these gases observed when measurements began has been steadily reversed over the last two decades, thought to be related to the implementation of the Montreal Protocol which has limited the production of CFCs.

In conclusion, the data reviewed here provides an insight into the climate change processes occurring in the atmosphere of the Southern Hemisphere, and especially from the Atlantic sector of the Southern Ocean. A combination of the climatology of the Cape peninsula and the position of the Cape Point GAW station, relative to the city of Cape Town, provides a unique opportunity to monitor both background and non-BG air masses and processes. In addition to contributing to a global understanding of the atmosphere for the past four decades, the Cape Point GAW station continues to provide an internationally recognised platform for the training of future generations of South African atmospheric chemists and meteorologists. Finally, the Cape Point GAW station's ongoing contribution to our understanding of climate change in this region of the African continent cannot be underestimated.

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List of Abbreviations and Acronyms

ANSTO   Australian Nuclear Science and Technology Organisation
CPT   Cape Point
CRDS   Cavity Ring Down Spectroscopy
CSIR   Council for Scientific and Industrial Research
ECD   Electron Capture Detector
EMPA   Swiss Federal Laboratories for Material Science
ENSO   El Niño Southern Oscillation
ESRL GMD   Earth System Research Laboratory Global Monitoring Division (of   NOAA)
FID   Flame Ionization Detector
GAW   Global Atmosphere Watch
GAWSIS   Global Atmosphere Watch Station Information System
GC   Gas Chromatograph
GHGs   Greenhouse Gases
ICP   InterComParison
IMK-IFU   Institute of Meteorology and Climate Research-Atmospheric Environmental Research (part of KIT)
IPCC   Intergovernmental Panel on Climate Change
KIT   Karlsruhe Institute of Technology
NDIR   Non-dispersive infrared
NOAA   National Oceanic and Atmospheric Administration

SAWS   South African Weather Service   1
UNFCCC   United Nations Framework Convention for Climate Change   2
UV   Ultraviolet   3
WDCGG   World Data Centre for Greenhouse Gases   4
WMO   World Meteorological Organization   5