

LONG-TERM OBSERVATIONS OF TRACE GASES AT CAPE POINT

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1. INTRODUCTION

Over the past decades, scientists around the world have gathered evidence showing that atmospheric change is taking place on a global scale. While the problems related to stratospheric ozone depletion are now widely accepted as being established fact, the debate on whether global climate change is real or not, has not yet been conclusively resolved. However, an increasing number of observations have given compelling evidence that the anthropogenic signal is perturbing the earth system (see for e.g. the report of the Working Group I of the Intergovernmental Panel on Climate Change¹, which summarises the past five years of climate change research). Global temperature data have shown that the 1990s constituted the warmest decade in the instrumental records (started in 1860) and that 1998 in particular, was the warmest year. It was also determined that during the 20th century the global temperature had increased by as much as 0.6 °C. The warming over the past 50 years due to anthropogenic emissions of greenhouse gases can be identified despite uncertainties due to forcing by anthropogenic sulphate aerosol and natural factors (example: volcanoes and solar irradiance). Furthermore, it is also likely that the 20th century warming has contributed significantly to the observed sea level rise, through thermal expansion of seawater and widespread loss of ice (particularly in the Northern Hemisphere). In view of the need for sound information about the earth's atmosphere, South Africa has committed itself towards the World Meteorological Organization's Global Atmosphere Watch Programme (GAW), and amongst other projects is running a GAW station at Cape Point. Environmentally important trace gases (CO₂, CH₄, N₂O, CO, surface O₃ and halocarbons) have been measured at this station (34°S, 18°E) with records dating back to the early

1980s²⁻⁴. The environmental significance of these gases lies in their respective impacts on the enhanced greenhouse effect, on stratospheric O₃ as well as on the oxidising capacity of the troposphere. In this paper updated secular trends are presented for these gases and compared to measurements conducted at other baseline stations around the globe. Furthermore, attempts are also made to explain the Cape Point trace gas trends in terms of air-chemical processes and recent budget considerations published in the literature.

2. DATA BASE

Practically none of the existing trace gas measurement methods constitute an absolute technique. Instead, the atmospheric concentrations are related to external standards.

Since inter-comparability of results on a global scale is a prerequisite for sound data, great efforts are being made in this regard, particularly within the GAW network⁵. In line with this, all trace gases measured at Cape Point are linked to internationally accepted scales. When endeavouring to make representative long-term trend determinations, care has to be taken to remove all values reflecting local and/or regional pollution from the respective data sets. Various routines for this baseline filtering have been tested over the years, and continued development in this direction is an ongoing process of the station's staff. The baseline data sets thus obtained are used for internal research work, but also constitute valuable input for models developed by different groups⁶. In this context, a particularly noteworthy project to which Cape Point has contributed is GLOBALVIEW-CH₄⁷. This project is aimed at providing modellers with geographically evenly spaced data, spanning the whole globe.

3. TRACE GAS TRENDS

3.1 Carbon Dioxide

CO₂ is the largest contributor towards global warming and can be classified as the most significant greenhouse gas, which has a large anthropogenic signal. It was estimated that the present CO₂ concentration has not been exceeded during the past 420 000 years, and probably did

not either during the past 20 million years. The currently observed rate of increase hence seems to be unprecedented at least for the past 20 000 years¹. From a global perspective, the atmospheric CO₂ concentration has increased by 31% since 1750. About 75% of the anthropogenic emissions of CO₂ to the atmosphere, during the past two decades, can be attributed to fossil fuel burning. The rest (25%) has predominantly been due to land use change, especially deforestation¹.

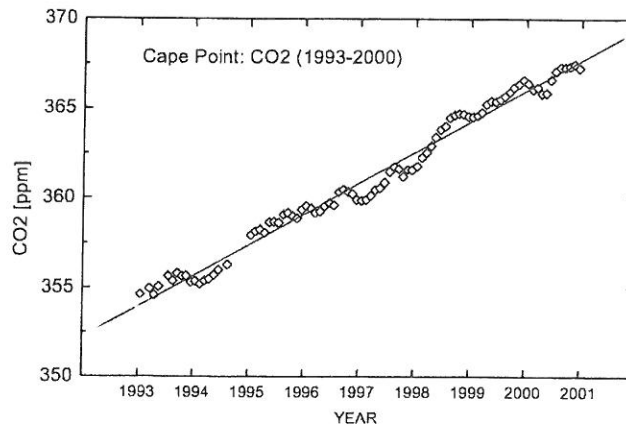


Fig. 1: Cape Point CO₂ time series (monthly means) with straight line fitted to the data.

CO₂ measurements have been conducted at Cape Point since 1993 (Fig. 1). For the period 1993 to 1999, the ambient CO₂ concentration increased by approximately 13 ppm, with observed growth rates varying between 0.5 ppm yr⁻¹ (1993) and > 3 ppm yr⁻¹ (1994 – 1995, and 1998). Similar growth rate variations have also been seen at other global measuring sites, such as Mauna Loa, Hawaii^{8,9}.

The inter-annual variability in the CO₂ trend, as seen globally, suggests a significant variation in the activity of sources and sinks. Changes in growth rates are also known to be associated with El Niño - Southern Oscillation (ENSO) events. Results obtained from various GAW stations reveal high CO₂ growth rates for 1994/1995, but a low growth rate in 1992. The low growth rate observed for that year was probably due to a lower global temperature after the Mt Pinatubo eruption (1991), which reduced the northern terrestrial biosphere emission significantly and increased the CO₂ uptake of the global oceans. An anomalously strong El Niño event occurred in 1997/1998. The entire climate system deviated from “normal” observations for this period, as was also shown by the Cape Point data. These extreme events perturbed the carbon cycle and accelerated

the increase of CO₂ concentration build-up in the atmosphere¹.

3.2 Methane

Methane (CH₄), which has a lifetime of about 9 years¹⁰, is the second most important greenhouse gas after CO₂ in terms of its contribution towards global warming. The atmospheric CH₄ concentration has increased by 1060 ppb since the year 1750 (151 %) and is still rising. Ice core data show that the present concentrations have not been exceeded in the past 420 000 years¹. On a global scale, the annual growth of CH₄ slowed down and became more variable during the 1990s compared to the 1980s. Atmospheric CH₄ is emitted mainly from anaerobic processes, both natural and anthropogenic, including natural wetlands, oceans, rice paddies, landfills, biomass burning, enteric fermentation, and gas drilling operations. The major removal processes is by its reaction with the hydroxyl radical (OH) and by reacting with chlorine atoms in the stratosphere.

The Cape Point CH₄ record (Fig. 2), which spans 18 years (1983 - 2000), reveals a steadily rising trend. However, the actual annual growth rates are

showing significant inter-annual variations. According to the magnitude of the trend, the Cape Point time series can empirically be divided into two periods: 1983 - 1991 and 1992 - 2000. The first period is characterised by an average growth rate of 10 ppb yr⁻¹, which slowed down to about 6 ppb yr⁻¹ for the period 1992-2000. The first eight years reveal on average a decreasing growth with undulating variations, which showed a prominent maximum towards the end of 1991 (18 ppb yr⁻¹). After 1992, the growth rate seems to have stabilised with maxima at the end of 1994, the beginning of 1997 and at the end of 1998. A short period of near zero growth occurred at the beginning of 1996. Growth rate variations similar to those observed at Cape Point have also been

observed at other locations in both hemispheres^{11, 12}.

Although the major contributors to the global CH₄ budget are likely to have been identified, most of them are uncertain quantitatively, because of the difficulty in assessing emission rates of highly variable biospheric sources. The limitations of poorly quantified and characterised CH₄ source strengths inhibit the prediction of future CH₄ atmospheric concentrations (and hence its contribution to radiative forcing) for any given anthropogenic emission scenario, particularly since both natural emissions and the removal of CH₄ can be influenced substantially by climate change¹.

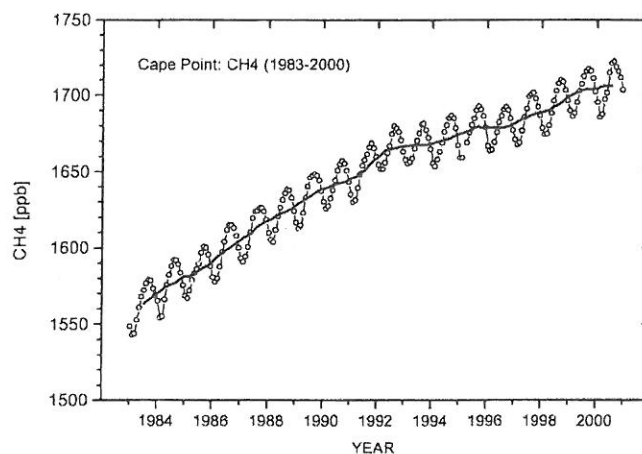


Fig. 2: Cape Point CH₄ time series (monthly means) and 12-month moving averages (solid line).

In global terms, the decreasing CH₄ growth rate can be explained in terms of a system approaching steady state, where CH₄ emissions and OH have remained fairly constant over the past twenty years of measurement¹⁰. Methane growth rate variations were found to have fluctuated in the 1990s in response to global mean temperatures¹. Studies of CH₄ in ice core samples and global temperature anomalies suggests that a large growth rate for the CH₄ concentration may follow an exceptionally high global mean temperature as was the case in 1998, associated with the strong El Niño event in 1997/1998. Furthermore, natural events, such as the Mt. Pinatubo eruption in 1991, can also induce photochemical changes in the troposphere, which in turn lead to CH₄ growth rate perturbations¹⁰.

3.3 Carbon Monoxide

CO is not a greenhouse gas, but has significant influence on the oxidising capacity of the atmosphere by virtue of its reaction with the hydroxyl (OH) radical¹³. As a result, a lowering of the atmosphere's oxidising capacity would invariably lead to concentration increases in other important trace gases, such as CH₄. Most of the important sources and sinks of CO have been identified, but there are still large areas of uncertainty in the CO budget. Sources include fossil fuel combustion, biomass burning and the oxidation of CH₄ and non-methane hydrocarbons. Major sinks primarily comprise the reaction with OH and secondly soil uptake. The seasonally varying OH concentration is the primary driving force for the shape of the annual cycle of CO, in addition to biomass burning and long-range transport processes.

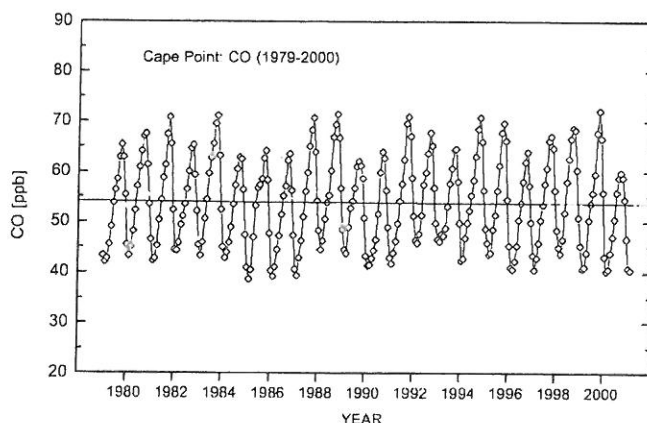


Fig. 3: Cape Point CO time series (monthly means) and straight line fitted to the data.

Up to date, the 22-year-long Cape Point CO record (Fig. 3) has shown no statistically significant long-term trend, which suggests that the oxidising capacity of the SH midlatitudes is still capable of maintaining the CO levels. In spite of the absence of a long-term trend, strong inter-annual variations up to 10 ppb characterise the CO time series¹⁴. As has been observed for CO₂ and CH₄, some of these variations showed correlations with ENSO events. During the El Niño years of 1982 and 1987, for example, rather low CO maxima were observed. ENSO events are known to temporarily alter global air transport processes and can lead to droughts in Africa. This in turn affects the fuel loading for biomass burning. It is assumed that such changes in source strength have a stronger effect on the hemispheric CO levels, as observed at Cape Point, than changes in transport pathways.

3.4 Nitrous Oxide

Nitrous oxide (N₂O), which has a lifetime of 120

years, is both an important greenhouse gas as well as a depleter of stratospheric ozone¹⁵. Atmospheric N₂O increased by 46 ppb (17%) since 1750 and has continued to increase ever since¹. Approximately one third of the current N₂O emissions are from anthropogenic agriculture (fertiliser), cattle feed, fuel combustion and the chemical industry. N₂O removal from the atmosphere is primarily via photo-dissociation in the stratosphere^{1,9}.

Long-term N₂O measurements made at Cape Point display an average growth rate of 0.88 ppb yr⁻¹ over the period from 1994-2000. This is in good agreement with trend estimates made for other stations in both hemispheres, such as South Pole, Mauna Loa (Hawaii) and Point Barrow (Alaska). Fig. 4 puts the Cape Point measurements in perspective with these three sites. The slight difference between the levels in the northern and southern hemisphere reflects a small constant inter-hemispheric gradient related to differences in source strength.

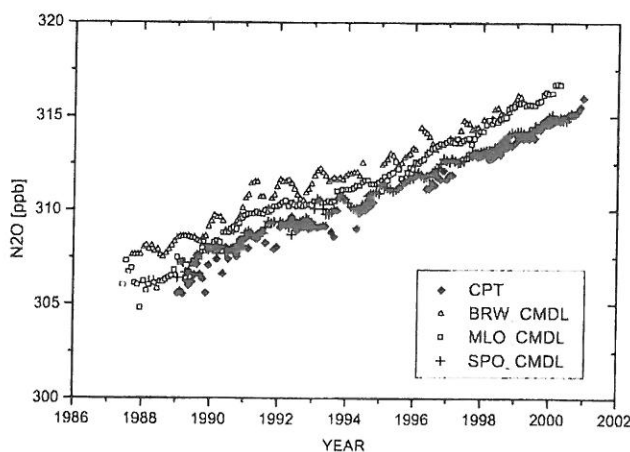


Fig. 4: Comparison of the monthly mean N₂O values for Cape Point (CPT) with results from three NOAA CMDL stations: South Pole (SPO), Mauna Loa (MLO) and Point Barrow, Alaska (BRW). Source of data: www.cmdl.noaa.gov.

3.5 Halocarbons

The halocarbons CFCl_3 , CF_2Cl_2 , $\text{CCl}_2\text{FCCl}_2\text{F}_2$ and the chlorinated solvents CH_3CCl_3 and CCl_4 are both ozone depleting species as well as contributors towards the enhanced greenhouse effect. After the commercial production of these halogen-containing gases had ceased in the developed countries, in accordance with the Montreal Protocol (1978), atmospheric levels have since either grown at a slower rate or even started to decline.

Halocarbons have been measured at Cape Point since the beginning of the 1980s, with CFCl_3 (CFC-11) having the longest record (1980 onwards). Whilst the growth rate for CFC-11 has recently dropped below zero (-0.8 ppt yr^{-1}) that of CFC-12 is still positive. The growth rate of the latter has decreased from 16 ppt yr^{-1} (1987-1991) to 6.1 ppt yr^{-1} (1992-1996), and then to 2.4 ppt yr^{-1} (1997-2000). However, large emissions of CFC-12 are still occurring, which is reason for concern. Amongst others, leaks in old industrial products

are an important source. The trend for CCl_4 has also dropped below zero, reaching an average value of -2.0 ppt yr^{-1} for the 1997-2000 period. In the case of CH_3CCl_3 , which is relatively short-lived, the growth rate has come down dramatically to about -10 ppt yr^{-1} (1995-2000 period) (Fig. 5). At Cape Point, CH_3CCl_3 levels amounted to 120 ppt in 1992, whilst seven years later in 1999 they had already reached 50 ppt.

Based on observations made by the Climate Monitoring and Diagnostics Laboratory (CMDL) network, total equivalent chlorine ($\text{Cl} + 45 * \text{Br}$) peaked in the troposphere between mid-1992 and mid-1994¹⁶. The chlorine loading within the stratosphere, which is currently estimated at 3.5 ppt^{17} , is expected to decline steadily over the coming decades. Model calculations predict that, if the Montreal Protocol is being adhered to internationally, stratospheric O_3 levels should have recovered to "pre-CFC days" by the year 2060.

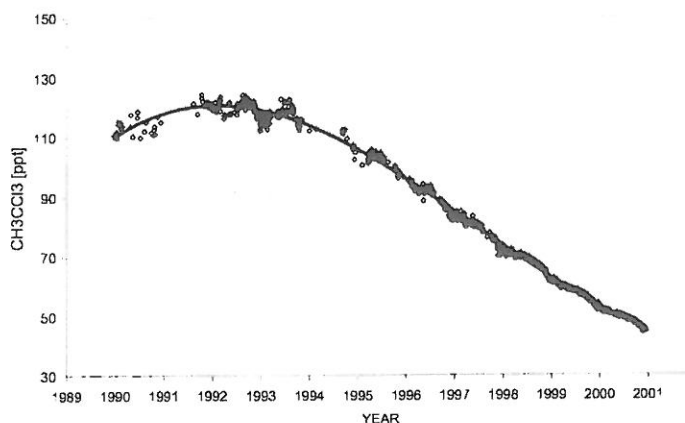


Fig. 5: Cape Point methyl chloroform (CH_3CCl_3) time series (1990 - 2000) showing daily means and a 3rd-order polynomial fit (solid line).

4. SUMMARY AND CONCLUSIONS

The Cape Point trace gas data for CO_2 , CH_4 and N_2O have shown steady increases with time in response to anthropogenic emissions. Although the trend for CH_4 has remained positive over the past 18 years, the average growth rate has declined from 10 ppb yr^{-1} for the period 1983-1991 to about 6 ppb yr^{-1} for the years 1992-2000. The ambient CO_2 concentration at Cape Point increased by approximately 13 ppm (1993 - 1999), with growth rates varying between 0.5 and 3 ppm

yr^{-1} . Nitrous oxide has displayed an average growth rate of 0.88 ppb yr^{-1} over the period from 1994-2000 in accordance with data collected at other global sites. No

statistically significant trend has been detected for CO when taking the entire 22-year-long record into account.

Inter-annual concentration variations in the time series for CO_2 , CH_4 and CO indicate correlations with the ENSO phenomenon, which affects global transport processes as well as the source/sink strengths of these trace gases.

As a result of reduced emissions (Montreal Protocol), the atmospheric concentrations of several halocarbons and chlorinated solvents have stopped growing or have started decreasing, even rapidly as in the case of methyl chloroform (-10 ppt yr^{-1}). Although the growth rate of CFC-12 has slowed down to a rate of currently 2.4 ppt yr^{-1} (Cape Point observations), the concentration

increase of this species still merits special attention in the years to come.

Whilst the problem of stratospheric O₃ depletion seems to be largely understood and under control, the continued anthropogenic emission of greenhouse gases is still a cause for concern. The general consensus by atmospheric research groups is hence that the anthropogenic signal, as a result of these gases, is making itself felt on the environment with climate change being an issue to be dealt with by both environmentalists and policy makers.

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<http://jcdc.kishou.go.jp/wdcgg.html>

5. REFERENCES

- (1) IPCC Third Assessment Report: A Report for Working Group I of the Intergovernmental Panel on Climate Change (2000). Summary for Policymakers [see also Technical Summary report], Daniel L Albritton, LG Meira Filho (Co-ordinating lead Authors) *et al*, path <http://www.ipcc.ch/>, 63 pp.
- (2) Brunke E-G, Scheel HE and Seiler W, Trends of tropospheric CO, N₂O and CH₄ as observed at Cape Point, South Africa. *Atmospheric Environment* 1990, 24A, 3, pp 585-595.
- (3) Scheel HE, Brunke E-G and Seiler W, Trace gas measurements at the Monitoring Station Cape Point, South Africa, between 1978 and 1988. *Journal of Atmospheric Chemistry* 1990, 11, 3, pp 197-210.
- (4) Labuschagne, C, Brunke, E-G and Scheel, H.E, Cape Point trace gas observations under baseline and non-baseline conditions. NOAA Climate Monitoring and Diagnostics Laboratory Annual Meeting, Boulder, Colorado, U.S.A. 12-13.05.1999, Abstracts, p 6.
- (5) WMO GAW Report No. 113, The strategic plan of the Global Atmosphere Watch (GAW), 1995 [WMO-TD No. 802].
- (6) Marufu L, Dentener F, Lelieveld J, Andreae MO and Helas G, Photochemistry of the African troposphere: influence of biomass-burning emissions. *Journal of Geophysical Research*, 2000, 105, D11, pp 14,513-14,530.
- (7) GLOBALVIEW-CH₄: Cooperative Atmospheric Data Integration Project – Methane. CD-ROM, NOAA CMDL, Boulder, Colorado [Also available on Internet via anonymous FTP: <ftp.cmdl.noaa.gov>, Path: [ccg/ch4/GLOBALVIEW](ftp://ftp.cmdl.noaa.gov/ccg/ch4/GLOBALVIEW/)], 1999.
- (8) WMO WDCGG Data Summary Report No. 22, World Meteorological Organization, Global Atmosphere Watch, 2000, WDCGG [Japan Meteorological Agency in co-operation with WMO]. Path
<http://jcdc.kishou.go.jp/wdcgg.html>
- (9) Conway, TJ, Tans, PP, Lang, PM, Masarie, K, Paynter, N, Thoning, K, Kitzis, D, White, J and Vaughn, B, The CO₂ Growth Rate and the Global Carbon Sink, 1979-1999. NOAA Climate Monitoring and Diagnostics Laboratory Annual Meeting, Boulder, Colorado, 2001, U.S.A., 16-17.05.2001, Abstracts, p 28.
- (10) Dlugokencky, EJ, Masarie, KA, Lang, PM and Tans, PP, Continuing decline in the growth rate of the atmospheric methane burden. *Nature* 1998, 393, pp 447-450.
- (11) Dlugokencky, EJ, Dutton, EG, Novelli, PC, Tans, PP, Masarie, KA, Changes in CH₄ and CO growth rates after the eruption of Mt. Pinatubo and their link with changes in tropical tropospheric UV flux. *Geophysical Research Letters* 1996, 23, 20, pp 2761-2764.
- (12) Dlugokencky, EJ, Walter, BP, Masarie, KA, Lang, PM, Kasischke, ES, Measurements of an anomalous global methane increase during 1998. *Geophysical Research Letters* 2001, 28, 3, pp 499-502.
- (13) Khalil, MAK, and Rasmussen, RA, The global cycle of carbon monoxide: Trends and mass balance. *Chemosphere* 1990, 20, pp 227-242.
- (14) Harris, JM, Oltmans, SJ, Dlugokencky, EJ, Novelli, PC, Masarie, KA, Scheel, HE and Brunke, E-G, CO and O₃ Measurements at Cape Point. NOAA Climate Monitoring and Diagnostics Laboratory Annual Meeting, Boulder, Colorado, U.S.A., 03-04.05.2000, Abstracts, p 2.
- (15) Atmospheric Change: An Earth System Perspective (1992). Graedel, TE, Crutzen, PJ (Eds.), pp: 446 [W.H. Freeman and Company, New York].
- (16) Elkins, JW, Montzka, SA, Butler, JH, Thompson, TM, Dutton, GS, Hall, BD, Balkwin, PS and Wofsy, SC, Measurements of the ozone-depleting chemicals regulated by the Montreal Protocol. NOAA Climate Monitoring and Diagnostics Laboratory Annual Meeting, Boulder, Colorado, 2001, U.S.A., 16-17.05.2001, Abstracts, p 15.
- (17) Romashkin, PA, Hurst, DF, Elkins, JW and Dutton, GS, Distinction between vortex and midlatitude air masses from tracer-tracer correlations, and lower stratospheric halogen burdens from SOLVE. NOAA Climate Monitoring and Diagnostics Laboratory Annual Meeting, Boulder, Colorado, U.S.A., 16-17.05.2001, Abstracts, p 12.