

Baseline

2005-2006

30th Anniversary Edition

Cape
Grim



ATMOSPHERIC PROGRAM (Australia) 2005-2006

Australian Bureau of Meteorology
and
CSIRO Marine and Atmospheric Research

Baseline Atmospheric Program Australia 2005-2006

Edited by J M Cainey, N Derek and P B Krummel

2007

Cover: Images showing views of Cape Grim Baseline Air Pollution Station over the past 30 years. Main photograph by Paul Krummel[©]. The photographs used in the map of Tasmania are by Richard Bennett and Australian Bureau of Meteorology[©] (bottom panel); CSIRO Division of Atmospheric Research[©] (top two panels).

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FOREWORD

Despite the image evoked by its name, Cape Grim is a brilliant place, especially for anyone who loves nature and is optimistic that mankind can manage its way out of the difficult environmental situation in which we have been placed by a burgeoning global population of carbon-consumers. Its shining star is the Cape Grim baseline station perched high on a promontory jutting into the roaring forties wind-belt of the Southern Ocean and flanked to the south by a fleet of giant electricity-generating windmills. The symbolism is wonderful: a cornerstone in global research on climate change for the past thirty years rests side-by-side with one of the solutions to our carbon-free energy needs.

Underlying the success story of Cape Grim is a unique collaboration between two Australian agencies dating back to the early 1970s. The Australian Bureau of Meteorology and the Commonwealth Scientific and Industrial Research Organisation have given the world a role model used by many countries that now contribute to more than 250 observatories in the World Meteorological Organization's Global Atmospheric Watch (GAW) programme. These two agencies showed great managerial and scientific creativity in combining the full power of the meteorological and atmospheric chemistry research communities into a world class global change research programme involving systematic atmospheric composition observations, analysis and understanding the weather and climate system. They demonstrated that the most successful mode of making systematic atmospheric chemistry observations involves continuous research and development, analysis and assessment coupled with a strong institutional commitment to infrastructure.

When research on atmospheric composition at Cape Grim began 31 years ago in 1976, the impetus was traceable back to preparations for the International Geophysical Year (1957), when C. D. Keeling of the Scripps Institution of Oceanography (USA) established the first 'global' network comprising Mauna Loa, Hawaii (1956) and South Pole, Antarctica (1957) to measure the content and temporal variability of carbon dioxide in the background atmosphere. Significant temporal trends and seasonal cycles of carbon dioxide were quantified for the first time and related respectively to combustion of fossil fuels and biological photosynthesis and respiration on a global scale. More than a decade later in 1969, the ~180 Member countries in the World Meteorological Organization (WMO) recommended the establishment of a global network of remote stations specifically to monitor changes in atmospheric composition which might impact climate.

In 1971, Australian scientists considered the possibility of observing background atmospheric composition in the Australian region. In 1972, the United Nations Conference on the Human Environment echoed the WMO recommendation. During the next three years, the project to establish a permanent

Australian background observatory, in fulfilment of the Australian commitment made at the UN conference, was developed.

After exploratory measurements in Tasmania of carbon dioxide, ozone, halocarbons, oxides of nitrogen, particulates, precipitation chemistry, solar radiation and meteorological variables, Cape Grim was chosen as the permanent site for the Australian Station in early 1976.

In January 1984 a significant managerial development took place. The Bureau of Meteorology assumed full administrative responsibility for Cape Grim with the avowed intent to ensure that relevant, high quality monitoring continued there for at least the next 50 to 100 years and a cooperative science steering activity was declared. This meant that more energy could be focused on quality research, observations and analysis. Regular science and managerial steering committee meetings and an annual international science meeting were added as part of the winning recipe.

In 1989 in Dookie, Australia, a major international atmospheric chemistry workshop took place that was the birthplace of the International Global Atmospheric Chemistry (IGAC) project that is now in its 17th year as part of the International Geosphere Biosphere Programme (IGBP). It is no coincidence that this meeting was held in Australia. The strong atmospheric chemistry and meteorology research that evolved out of Cape Grim's international research programme and leadership was a major factor. The underlying science on climate change that has led to the success of the science assessments performed under the Nobel Peace Prize winning Intergovernmental Panel for Climate Change (IPCC) owes its success to such bottom-up national foresight and sustained support.

It was my great pleasure to represent WMO at the 30th anniversary of the Cape Grim observatory in 2006 and to renew acquaintance with the vibrant Australian and international research activities catalysed by this centre. In 1986, I was awed on my first visit to the annual research workshop and to the observatory and I am still awed by the breadth, depth and quality of activities described in this 2007 annual report. If I may be granted one wish, it would be that the Australian government, agencies and research community continue to recognize the power of combining research and development with strong institutional observational infrastructure support to meet the environmental, weather and climate challenges of the future.

Leonard Barrie
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October 2007

PREFACE

Baseline 2005-2006 reports on the activities and scientific program at the Cape Grim Baseline Air Pollution Station in North West Tasmania, Australia, for the two calendar years of 2005 and 2006. Included are scientific papers, based on research at Cape Grim, as well as operational reports on the various experiments and monitoring conducted at the station over the two year period.

For this edition of *Baseline*, we are fortunate to have a 'Foreword' provided by Len Barrie, who is the Director of the Atmospheric Research and Environment Program for the World Meteorological Organization, including the Global Atmosphere Watch Program.

We were delighted that Len Barrie could attend the 30th Anniversary Celebrations at Cape Grim in April 2006.

Len Barrie has been a strong advocate for global monitoring, through various World Meteorological Organization programs and has been closely associated with the Cape Grim Baseline Air Pollution Station, while a researcher with Environment Canada and as the Chief of the Environment Division of the World Meteorological Organization where he had direct responsibility for the Global Atmosphere Watch Program, of which Cape Grim is part.

Baseline 2005-2006 incorporates additional material to celebrate the 30 years of continuous operation. This includes a brief 30 history of significant events at the Cape Grim Baseline Air Pollution Station and detailed lists of personnel and publications over the 30 years of activities.

Following the style of recent issues of *Baseline*, the layout of this edition includes both research papers and reports from the various scientific programs in operation at the Cape Grim station. Program reports contain the status of the research programs for only the two year period. The research papers are stand-alone scientific articles that may present research results and data up to the final time of submission. The research papers have been scientifically peer-reviewed by at least two independent referees before being considered for publication.

The research papers follow the American Geophysical Union (AGU) publications formatting and referencing styles. Limited numbers of reprints of these papers are available from the lead author of each paper.

J M Cainey, N Derek and P B Krummel

October 2007

CONTENTS

Special Report

A brief history of the Cape Grim Baseline Air Pollution Station – <i>P J Fraser</i>	1
1. STATION SPECIFICATION	
1.1 General	7
1.2 Site plan	8
1.3 Program summary	9
2. REPORT FROM THE OFFICER-IN-CHARGE	
2.1 Introduction	11
2.2 Buildings and maintenance	11
2.3 Staff and students	12
2.4 International activities and visitors	13
2.5 Operational budget	14
3. RESEARCH PAPERS	
Interpretation of the MiniLidar data recorded at Cape Grim 1998 – 2000 – <i>Stuart A Young</i>	15
Effect of temperature on the Cape Grim UV-B record – <i>Stephen R Wilson</i>	25
Aerosol composition at Cape Grim: an evaluation of the PM10 sampling program and baseline event switches – <i>Melita Keyword</i>	31
4. PROGRAM REPORTS (CALENDAR YEARS 2005-2006)	
4.1 Introduction	37
General	
4.2 Data management report – <i>S McEwan and S Baly</i>	37
4.3 Meteorology/Climatology 2005-2006 – <i>A Downey</i>	39
4.4 Radon and radon daughters – <i>W Zahorowski</i>	46
Trace gases	
4.5 Baseline carbon dioxide monitoring – <i>L P Steele, P B Krummel, D A Spencer, C Rickard, S B Baly, R L Langenfelds and M V van der Schoot</i>	50
4.6 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 in baseline Cape Grim air: 2005-2006 – <i>C E Allison, S A Coram and L P Steele</i>	52
4.7 Archiving of Cape Grim air – <i>P B Krummel, R L Langenfelds, P J Fraser, L P Steele and L W Porter</i>	55
4.8 Continuous measurements of ^{14}C in atmospheric CO_2 at Cape Grim, 1997-2006 – <i>I Levin, B Kromer, L P Steele and L W Porter</i>	57
4.9 SF_6 from flask sampling – <i>I Levin, R Heinz, J Ilmberger, R L Langenfelds L P Steele and P B Krummel</i>	60
4.10 Measurements of atmospheric O_2/N_2 ratios at Cape Grim – <i>R F Keeling, B Paplawsky, K Bracchi, A Cox and L W Porter</i>	61
4.11 Atmospheric methane, carbon dioxide, hydrogen, carbon monoxide and nitrous oxide from Cape Grim flask air samples analysed by gas chromatography – <i>L P Steele, R L Langenfelds, P B Krummel, M V van der Schoot, D A Spencer and P J Fraser</i>	62
4.12 The AGAGE <i>in situ</i> program for non- CO_2 greenhouse gases at Cape Grim, 2005-2006: methane, nitrous oxide, carbon monoxide, hydrogen, CFCs, HCFCs, HFCs, PFCs, halons, chlorocarbons, hydrocarbons and sulfur hexafluoride – <i>P B Krummel, P J Fraser, L P Steele, L W Porter, N Derek, C Rickard, B L Dunse, R L Langenfelds, B R Miller, S Baly and S McEwan</i>	65

4.13	Reactive gases in near surface air at Cape Grim, 2005-2006 – <i>I E Galbally, C P Meyer, S T Bentley, S J Lawson and S Baly</i>	77
4.14	Phytoplankton dynamics and the production of methyl bromide and methyl iodide at Cape Grim: 2005-2006 – <i>J Caine, M Grose, A McMinn, C Parr, P Fraser, C Reeves and S Penkett</i>	80
Precipitation, particles and multi-phase species		
4.15	Particles – <i>J L Gras</i>	85
4.16	Fine particle sampling at Cape Grim – <i>D D Cohen and E Stelcer</i>	87
4.17	Measurement of natural levels of tritium in precipitation for years 2005-2006 at Cape Grim – <i>B Neklapirova and R Chisari</i>	88
4.18	The stable isotopic composition, δD and $\delta^{18}O$, of rainfall – <i>R G Creswell, J C Dighton, M L E Lefournour and F W J Leaney</i>	89
4.19	Aerosol samplers – <i>M D Keywood, J Ward, R W Gillett, P W Selleck and K Boast</i>	89
4.20	Precipitation chemistry – <i>R W Gillett, M D Keywood, P W Selleck and K Boast</i>	95
Radiation		
4.21	Spectral solar radiation – <i>S R Wilson and B W Forgan</i>	97
4.22	Passive solar radiation – <i>S R Wilson and P Shinkfield</i>	98
APPENDICES		
A.	Publications	101
1.	Carbon dioxide and carbon isotopes	
1.1.	Research and technical papers	101
1.2.	Conference papers	105
1.3.	<i>Baseline</i> research reports.....	111
1.4.	<i>Baseline</i> data summaries	113
2.	Non-carbon dioxide greenhouse gases, carbon monoxide and hydrogen	
2.1.	Research and technical papers	114
2.2.	Conference papers	118
2.3.	<i>Baseline</i> research reports.....	124
2.4.	<i>Baseline</i> data summaries	125
3.	Precipitation, particles and multi-phase species	
3.1.	Research and technical papers	128
3.2.	Conference papers	130
3.3.	<i>Baseline</i> research reports.....	133
3.4.	<i>Baseline</i> data summaries	134
4.	Ozone, oxides of nitrogen and volatile organic compounds	
4.1.	Research and technical papers	136
4.2.	Conference papers	137
4.3.	<i>Baseline</i> research reports.....	139
4.4.	<i>Baseline</i> data summaries	139
5.	Radiation	
5.1.	Research and technical papers	140
5.2.	Conference papers	141
5.3.	<i>Baseline</i> research reports.....	143
5.4.	<i>Baseline</i> data summaries	143
6.	Radon	
6.1.	Research and technical papers	144
6.2.	Conference papers	144
6.3.	<i>Baseline</i> research reports.....	146
6.4.	<i>Baseline</i> data summaries	146

7. Climatology	
7.1. Research and technical papers	147
7.2. Conference papers	147
7.3. <i>Baseline</i> research reports.....	147
7.4. <i>Baseline</i> data summaries	148
8. Data Management	
8.1. Research and technical papers	148
8.2. Conference papers	148
8.3. <i>Baseline</i> research reports.....	148
8.4. <i>Baseline</i> data summaries	149
9. Reviews, Policy Papers (Cape Grim data used in a wider context).....	149
B. Personnel	153
C. Definitions	159

A Brief History of the Cape Grim Baseline Air Pollution Station

P J Fraser

CSIRO Marine and Atmospheric Research

Background

Although observations of background atmospheric composition at Cape Grim commenced 30 years ago in 1976, the impetus for such a program can be traced back to preparations for the International Geophysical Year (1957), when C. D. Keeling of the Scripps Institution of Oceanography (SIO, USA) established the first 'global' network, comprising Mauna Loa, Hawaii (1956) and South Pole, Antarctica (1957), to measure the content and temporal variability of carbon dioxide in the background atmosphere. The value of such an approach to geophysical monitoring was considered doubtful by some, but was clearly demonstrated within a few years, when significant temporal trends and seasonal cycles of carbon dioxide were quantified for the first time and related respectively to combustion of fossil fuels and biological photosynthesis and respiration on a global scale. A few years of careful research and measurement ended 100 years of speculation as to whether it was possible for anthropogenic activities, such as the use of fossil fuels, to affect the composition of the background atmosphere. The answer was a resounding 'yes'.

More than a decade later (1969), the World Meteorological Organization (WMO) recommended that member countries establish a global network of remote stations (BAPMoN: Background Air Pollution Monitoring Network) specifically to monitor changes in atmospheric composition which might impact on climate. By this time, relevant activities within the United States were well advanced, and the USA was soon to have established four fully operational stations - Mauna Loa, Hawaii (1956); South Pole, Antarctica (1957); Barrow, Alaska (1971) and Cape Matatula, American Samoa (1973).

The Australian Baseline Station

Australian scientists (W. Gibb, Bureau of Meteorology; C. Priestley, CSIRO) considered the possibility of observing background atmospheric composition in the Australian region in 1971. In 1972, G. Pearman and J. Garratt (CSIRO) established an aircraft based observational program to measure possible long-term trends of carbon dioxide in the background atmosphere of the south-east Australian region. Also in 1972, the United Nations Conference on the Human Environment followed the WMO in recommending that a global network of atmospheric observatories be established, with a particular emphasis on climate change research. During the next three years, the project to establish a permanent Australian background observing Station, in fulfilment of the Australian commitment made at the 1972 UN conference, was developed.

In September 1972, Australian scientists lead by Pearman reported that the most suitable location for a baseline Station would probably be found in the southern highlands of Tasmania and recommended that surveys be commenced to identify the preferred site. Honey Smith Hill, near the South East Cape, was identified as the preferred location in 1975, and by early 1976 an instrumented caravan was ready to be installed at this site. However, uncertainties about the long-term viability of, and the problems of access to, the South East Cape site resulted in the caravan being installed temporarily on Commonwealth property at Cape Grim, northwest Tasmania, during March 1976, so that field trials could begin, while the search for the preferred site continued.

During 1976-1977 initial measurements were made of carbon dioxide, ozone, halocarbons, oxides of nitrogen, particulates, precipitation chemistry, solar radiation and meteorological parameters. After considerable investigation and discussion of a range of possible sites (Figure 1), Cape Grim was chosen as the permanent site for the Australian Station in early 1978 and approved by the Australian Government.

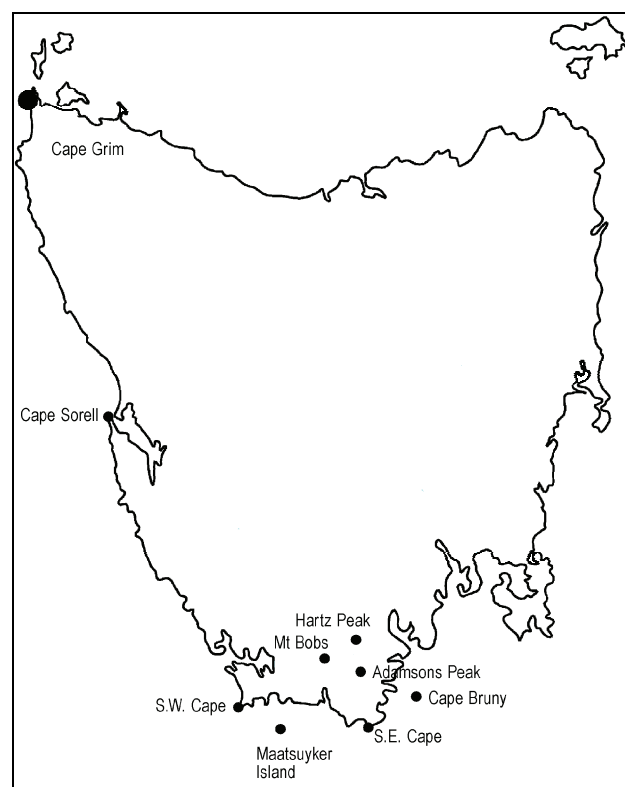


Figure 1. Sites evaluated in 1975-1977 for possible location of the Australian Baseline Station

In 1977 the laboratory and accommodation functions of the original caravan were separated with the acquisition of an additional caravan for accommodation. Despite this, it was clear by mid-1978 that the instrument and accommodation caravans were too small to house all the experiments at Cape Grim. In early 1980, the halocarbon gas chromatographs were moved to a separate caravan (about 500 m north-west) in anticipation of possible contamination problems associated with the construction of permanent facilities immediately adjacent to the original caravan site, throughout 1980 (Figure 2). Construction was finished in early 1981 and throughout the rest of that year the original instruments were transferred from the caravans, and new instruments were installed, in the permanent facilities. The Australian BAPMoN Station was officially opened in December 1981.

Since that time there has been a steady growth in the observational program, both *in situ* and involving other cooperating agencies. Measurements now include all of those originally made plus isotopologues of carbon dioxide, methane (including isotopologues), carbon monoxide, nitrous oxide (including isotopologues), additional halocarbons (about

thirty), hydrogen (including isotopologues), oxygen/nitrogen ratios, aerosol chemistry including several sulfur species (dimethylsulfide, methanesulfonic acid), other sulphur species (carbonyl sulphide, sulphur hexafluoride, sulfuryl fluoride), several volatile organic compounds (including ethane, ethylene, acetylene, isoprene, benzene, toluene), radon and radon daughters, radionuclides, black carbon and lead isotopes. In addition, more sophisticated technology, often developed by Cape Grim scientists or in partnership with their national and international colleagues, has allowed increases in frequency and accuracy of all these measurements.

In 1984-1985, a 74 m high telecommunications tower (the Telstra tower) was constructed at Cape Grim, which involved associated extensions to the Cape Grim building. This allowed the addition of air intakes at 70 m and meteorological instruments at 30 m and 50 m, to supplement the standard 10 m intake and instruments. It also made available additional laboratory space at the north-east end of the building.

Significant dates and events in the evolution of the Cape Grim facility and observational program are given Table 1.

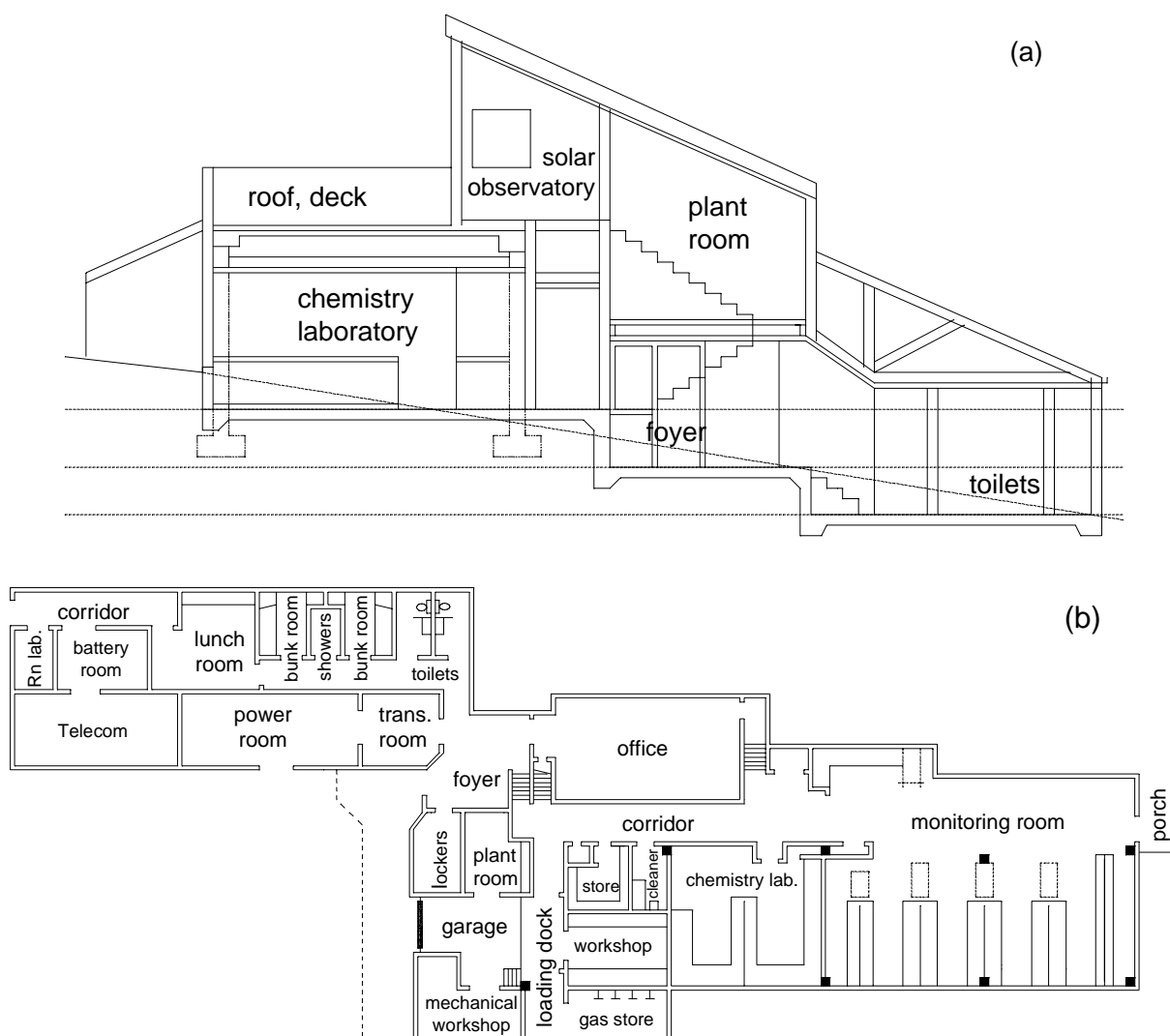


Figure 2. Building plan for the Cape Grim site, (a) the south east elevation (b) the floor plan of the Station.

Table 2. Significant dates and events in the evolution of the Cape Grim Baseline Station and Program.

Year	Cape Grim events
1972	Australia informs the UN of its intention to participate in the Earth Watch Programme, including the WMO BAP-MoN program.
1973	Australia informs UNEP of its intention to set up a Southern Hemispheric Baseline Station.
1975	Tasmanian Baseline Station site evaluations conducted by CSIRO (Pearman, Fraser, Helmond, O'Toole) at Hartz Mountains, Cape Bruny, Cape Sorrell, South West Cape, Honey Smith Hill, Adamsons Peak, Mt Bobs and Cape Grim. Original NASA instrument caravan equipped at CSIRO Aspendale. CGBAPS Project Manager appointed (Department of Science). CGBAPS Working Group established. First Australian/international baseline science meeting held at CSIRO Aspendale.
1976	NASA caravan installed at Cape Grim by CSIRO (Pearman, Beardsmore, Fraser, Garratt, Helmond, O'Toole). Two full time CGBAPS staff (Briggs, Wise) appointed. NASA conducts Cape Grim overflights (CV990). First measurements of CO ₂ , O ₃ , CFC-11, CCl ₄ , meteorology, aerosol and precipitation chemistry at Cape Grim.
1977	First measurements of solar radiation (direct, global, diffuse, UV), turbidity, N ₂ O and CN. Temporary Smithton depot established. Maatsuyker Island site evaluated.
1978	Scientists (CSIRO, AGAL, DST) recommend, and Australian Government approves, Cape Grim as the Baseline Station site. Funds for capital works of \$1.25M approved. <i>In situ</i> N ₂ O, CFC-12 and CH ₃ CCl ₃ measurements commence; Cape Grim <i>in situ</i> halocarbon and N ₂ O measurements incorporated into global network (ALE). Air archive commenced; first issue of <i>Baseline</i> published; first NO _x measurements made. Air flows around Cape Grim studied. Additional caravan installed to house first short-term international experiment at Cape Grim (aerosol and hydrocarbon measurements, Max Planck Institute); caravan later converted to accommodation/store facility.
1979	Seven Lead Scientists appointed (precipitation - Ayers, Ivey, particulates - Bigg), halocarbons/N ₂ O - Fraser), O ₃ /NO _x - Galbally, CO ₂ - Pearman, radiation - Platt). High quality surface O ₃ measurements begin. Department of Science and Technology assumes administrative responsibility for CGBAPS. CSIRO assumes responsibility to provide long-term scientific leadership/guidance and conduct research in support of CGBAPS.
1980	OiC (Wise) resigns. Commence CH ₄ (flask) and CO (flask) measurements. Cape Grim CSIRO overflights begin. Road access to Cape Grim upgraded. Construction of permanent facilities at Cape Grim and Smithton. Separate caravan installed to house halocarbon GCs away from construction site. CGBAPS Management Group established.
1981	CGBAPS permanent staff increased from two to five (4 new appointees: Francey, Harrison, Muir-Wilson, Watson; Briggs resigns). First scientist/OiC and additional Lead Scientist (Francey, C-isotopes, total 8) appointed. Four CGBAPS funded staff appointed to CSIRO-DAR, one to CSIRO-DCP. CCN, Rn and NH ₃ measurements commence. GAGE GC installed in new building. Permanent building occupied and officially opened. 10 m air intake commissioned. Review of Commonwealth Functions ('razer gang') recommends that CGBAPS be contracted out to private enterprise.
1982	New permanent CGBAPS staff members (Emmertson, Helmond) appointed, Watson resigns. Measurements of elemental C, CFC-113 (<i>in situ</i>) on GAGE GC, high precision δ ¹³ C and δ ¹⁸ O CO ₂ and δ ¹⁴ CO ₂ commence. NASA and GC caravans removed from site. Tenders called for private companies to manage and operate the CGBAPS facility.
1983	OiC (Francey) resigns. Two additional Lead Scientists appointed (Forgan - radiation, Whittlestone - radon, total 10). CGBAPS permanent staff reduced from 5 to 4. Sulfur program commences (SO ₄ ²⁻ , nss-SO ₄ ²⁻ and MSA). New Australian government rejects CGBAPS privatisation proposal.
1984	New OiC (Forgan) appointed. CGBAPS permanent staff increased from 4 to 5 (Sibson, Porter and Walford appointed, Muir-Wilson resigns). <i>In situ</i> CH ₄ and CO measurements commence. Air sampling commenced for NOAA-CMDL and OGI. GRIMCO installed at Cape Grim; Telstra tower and building extensions constructed. First SABOAC Meeting. Administrative responsibility for CGBAPS transferred to the Bureau of Meteorology, Department of Science and Technology.
1985	10 th year of observations; additional Lead Scientist appointed (particles, total 11). GRIMCO operational. Precipitation chemistry and Hivol sampling frequency increased from monthly to weekly. ALE GC shut down. Construction of Telstra tower completed. Lightning strike causes significant instrument damage.
1986	Lead Scientist resigns (Bigg - particles), new Lead Scientist appointed (Burton - sulfur, total 11). Permanent CGBAPS staff member (Emmertson) resigns. Sampling booms installed on Telstra tower, 70 m air intake installed.
1987	Two additional Lead Scientists appointed (Downey, Jasper - meteorology, climatology, total 13). New CGBAPS staff member (Eisman) appointed, Sibson resigns. Raschig ¹⁴ CO ₂ , ⁸⁵ Kr and ¹³ CH ₄ sampling commence.
1988	OiC (Forgan) resigns, new OiC (Wilson) appointed. Price appointed to Working Group. Weekly DMS sampling and Quadropod aerosol sampling commenced. Southwest door porch constructed. Second SABOAC Meeting held. Lead Scientist (Pearman) awarded CSIRO Medal. New CGBAPS staff member (Leonard) appointed.
1989	Lead Scientist resigns (sulfur - Burton, total 12). CGBAPS permanent staff increased from 5 to 6. New CGBAPS staff members (Paterson, Schrank) appointed, Eisman resigns. Cape Grim staff awarded DAS Award for Excellence. Lead Scientist (Pearman) presented UNEP Global 500 Award. COCl ₂ (phosgene) measurements begin.
1990	New Lead Scientist appointed (methane - Steele, total 13). New CGBAPS staff member (French) appointed. GASLAB opened at CSIRO-DAR. Lightning strike causes significant instrument damage at Cape Grim. Smithton office wins Keep Australia Beautiful award. The CGBAPS ASM commemorates 15 years of Cape Grim observations, 10 years in the permanent building.
1991	Lead Scientist (radiation - Forgan) resigns.

Table 2. continued....

Year	Cape Grim events
1992	New CGBAPS staff member (Britton) appointed, Schranck resigns. New OiC (Dick) and new Lead Scientist (radiation - Wilson, total 13) appointed. High resolution UV-B measurements commence; new Rn detector installed; GASLAB $^{13}\text{CH}_4$ measurements commence; ASASP measurements initiated; pilot hydroxyl radical program commenced; significant exterior maintenance to Cape Grim building carried out.
1993	New CGBAPS staff member (Torr) appointed. AGAGE GC installed; in situ H_2 measurements begin. Automated DMS measurements by GC commence. MOUDI commenced sampling of size segregated aerosols; sulfur program intensive field experiment; winter phase of SOCEX carried out involving lidar and microwave radiometer. LAN installed. CGBAPS air conditioning upgraded. CGBAPS ASM held at University of Tasmania (Hobart).
1994	Lead Scientist (Jasper, climatology) resigns (total 12). New CGBAPS staff members (Munday, Weymouth) appointed, Patterson resigns. SOAPEX1 background winter phase carried out. GAGE GC shut down. Strategic Review of CGBAPS commissioned by Management Group. CGBAPS ASM held at Monash University (Clayton).
1995	20 th year of observations at Cape Grim. Lead Scientist (Pearman, CO_2) resigns (total 11). Lead Scientists (Ayers and Fraser) awarded Priestley Medal (AMOS) and Eureka Prize (Australian Museum) respectively. GASLAB O_2/N_2 measurements begin; field campaigns SOAPEX1 (summer and winter), SOCEX (summer) and ACE-1 carried out. First CGBAPS PhD (University of Melbourne) and summer scholarships (University of Wollongong) awarded. Fire causes damage at Cape Grim. CGBAPS ASM held at Monash University (Clayton).
1996	20 th anniversary celebrations held at Cape Grim, distinguished guests: Prof. M. Molina (Nobel Laureate, MIT), Hon. P. McGauran, Dr. M. McIntosh (CSIRO), Dr J. Zillman (Bureau), Dr G. Pearman (CSIRO), Dr J. Miller (WMO). Strategic Review of the Cape Grim Program completed and submitted. Lead Scientists (Ivey – precipitation chemistry, Platt - radiation) resign (total 9). CSIRO PDF (Sturrock) located at Cape Grim to install/run new halocarbon GC-MS. New CGBAPS staff member (Baly) appointed, Munday resigns. Overseas visitors: A. Jackson (U. Lancaster), K. Masarie (NOAA), P. Salameh (SIO), E. Dlugokencky (NOAA). AGAGE team visits Cape Grim. CGBAPS ASM held at Stanley (Tasmania).
1997	Lead Scientist (Boers – radiation) appointed (total 10). New CGBAPS staff member (Gough) appointed. AGAGE GC-MS-ADS installed at Cape Grim to measure minor CFCs, HCFCs, HFCs, halons and halomethanes. GAGE GC-ECD retired. Major upgrade of solar radiation program, with new instrument site 300 m north of the Station. New aerosol sampler installed for the ANSTO program. Overseas visitors: G. Brailsford, D. Ferretti (NIWA, NZ), S. Montzka, J. Butler (NOAA, USA), S. Yonemura, A. Miyata (NIES, Japan). CGBAPS ASM held at CRC for Southern Hemisphere Meteorology, Monash U. CGBAPS ASM held at CRC for Southern Hemisphere Meteorology, Monash University (Clayton).
1998	OiC (Dick) resigns, new OiC (Tindale) appointed. Lidar installed at Cape Grim. CSIRO flask air sampling for VOC analyses commenced. Maintenance work carried out on Telstra tower. Record wind recorded at Cape Grim: 177 km hr^{-1} with some Station damage. Overseas visitors: L. Carpenter, N. McArdle, W. Broadgate, T. Elsayed, D. Oram (UEA, UK), S. O'Doherty (U. Bristol, UK), A. Lewis (U. Leeds, UK). CGBAPS ASM held at CRC for Southern Hemisphere Meteorology, Monash University (Clayton).
1999	SOAPEX2 hosted at Cape Grim. Smithton office sold into private ownership. International visitors: many SOAPEX2 scientists (U. Leeds, U. Leicester, UEA, UK), B. Suhardi and U. Nasrullah (Indonesian GAW staff), P. Hoan and N. Huong (Hydrometeorological Service of Vietnam), L. Peng and I Neo (Malaysia), R. Turco (U. California, USA), J. Elkins (NOAA, USA), J. Ju (Chinese Ministry for Science and Technology). CGBAPS ASM held at CSIRO Atmospheric Research, Aspendale.
2000	Lead Scientist (Whittlestone - radon) resigns (total 9). New CGBAPS staff member (Wheaton) appointed, Gough resigns. Lidar and LWR ceased operation. NIES (Japan) flask air sampling commences, particularly for short-lived halocarbon species. BoM/CSIRO/UEA seawater sampling and analysis (methyl halides) commences. UCSD flask air sampling for N isotopes commenced. New CSIRO CO_2 analyser (LoFlo) installed. VDL celebrates 175 anniversary. International visitors: K. Mace (Texas A&M U., USA). CGBAPS ASM held at CSIRO Atmospheric Research (Aspendale).
2001	Lead Scientist (Zahorowski – radon) appointed, (Ayers – multi-phase atmospheric chemistry) resigns and (Boers – radiation) resigns (total 8). Price resigns from Working Group. CGBAPS staff member (Weymouth) resigns. Lead Scientists (Francey, Steele) awarded the Victoria Prize. CGBAPS staff member L. Porter achieves 30 years service with the Bureau. Station struck by lightning. AGAGE GC-ECD SF_6 analyser installed. Phase 1 Woolnorth wind farm constructed. International visitors: K. Suda (JMA, Japan), G. Sturrock (UEA, UK), C. Lindley (CalTech, USA), B. Hall and P. Sheriden (NOAA, USA), C. Simmonds (Bowdoin College, USA), M. Hitoski and Dr Katsumoto (NIES, Japan). CGBAPS ASM held at Antarctic CRC, University of Tasmania (Hobart).
2002	OiC (Tindale) resigns. Lead Scientist (Francey – C isotopes) resigns (total 7). Forgan appointed to Working Group. CGBAPS permanent staff reduced from 6 to 5. CGBAPS staff member L. Porter awarded National Australia Day Medal. Lead Scientist (Galbally) elected to Australian Academy of Technological Sciences and Engineering (ATSE). Lead Scientist (Fraser) awarded US EPA Stratospheric Ozone Protection Award. ANU rainwater sampling and UCSD air sampling for N isotopes closed down. NO_x analyser turned off. International visitors: C. Zellweger and S. Reimann (EMPA, Switzerland). CGBAPS ASM held at CSIRO Atmospheric Research (Aspendale).
2003	OiC (Cainey) appointed. CGBAPS permanent staff increased from 5 to 6 (Quartararo appointed and later resigns). CSIRO flask sampling for O_2/N_2 terminated. Telstra tower refurbishment commenced. Phase 2 of Woolnorth wind farm commenced. International visitors: B. Bryson (author), C. Leck (U. Stockholm, Sweden), J. Petersen (NZ), H. Jansen (centre for Isotope Research, The Netherlands), J. Elkins (NOAA, USA). CGBAPS AGM held at CSIRO Atmospheric Research (Aspendale).

Table 2. continued....

Year	Cape Grim events
2004	Lead Scientists (Gorman – meteorology, Krummel – CO ₂ and non-CO ₂ GHGs, Keywood – multi-phase atmospheric chemistry) appointed (total 10). New CGBAPS staff members (Hood, Rickard, McEwan) appointed, Britton, Wheaton resigns. Lead Scientist (Galbally) awarded the CASANZ Werner Strauss achievement Award. Lead Scientist (Fraser) awarded CSIRO Lifetime Achievement Award. Rn instrument HURD-1 and CO ₂ analyser BASGAM shut down after 24 years and 14 years operation respectively. AGAGE GC-MS Medusa installed and PFC measurements commence. AWS, new O ₃ instrument CN counter (TSI 3010) installed. Six new air inlets installed on Telstra tower at 70 m. Phase 2 of Woolnorth wind farm commences operation. International visitors: R. Weiss, B. Miller (SIO, U. California at San Diego, USA), J. Duplissey (U. Claremont-Ferrand, France), D. Moller (Brandenburg Institute of Technology, Germany), A. Hirsch (NOAA, USA), N. Hayati (Indonesian Baseline Station, Indonesia), R. Moss (NIWA, NZ); AGAGE scientists visit Cape Grim. CGBAPS ASM held at CSIRO Atmospheric Research (Aspendale).
2005	30 th year of observations at Cape Grim. Former Lead Scientist (Pearman) and Lead Scientist (Fraser) elected to Australian Academy of Technological Sciences and Engineering (ATSE). Station struck by lightning, damaging several instruments. New gas cylinder store constructed, kitchen and bedrooms upgraded. Ceilometer, four-stage impactor aerosol sampler (U. Colorado, 50m) installed. Second Telstra tower refurbishment commenced. Precursors to Particles 2005 campaign. International visitors: N. Cassar (Princeton U., USA), G. Jennings (National U. Ireland, Ireland), R. Derwent (U. Bristol, UK), D. Moller (Brandenburg Technical U., Germany). CGBAPS ASM held at CSIRO Marine and Atmospheric Research (Aspendale).
2006	30 th anniversary celebrations held at Cape Grim. Visitors included Dr L. Barrie (GAW, WMO, Switzerland), Dr G. Foley (Bureau), Dr G. Ayers (CSIRO). Management Group member and former Lead Scientist (Ayers) elected to ATSE. CGBAPS permanent staff member Porter seconded to CSIRO. Precursors to Particles 2006 campaign. Telstra tower refurbishment completed. Monthly rain sampler (CSIRO), O ₂ /N ₂ instrument (CSIRO) and sea state camera installed. Construction of Stage 3 of Woolnorth wind farm. International visitors: D. Shallcross (U. Bristol, UK), A. Gomez, M. Harvey, P. Johnston, T. Hay, A. Fraser (NIWA, NZ), T. Stein, O. Ibrahim (U. Heidelberg, Germany), A. Goldstein (U. California, Berkeley, USA), Z. Lingxi (CMA, China), N. Hayati (BMG, Indonesia), L. See Fook (Malaysian Met. Service, Malaysia), C. Labuschagne, J. Mphepya (S. African Weather Service, S. Africa). CGBAPS ASM held at CSIRO Marine and Atmospheric Research (Hobart).

Publications

Appendix A. (p. 95-145) details the publications listed or contained in *Baseline*, the annual/biennial report of activities in the Cape Grim program. *Baseline* records that, up to 2006, 202 papers have been published by Lead Scientists (lead or co-author) or other Australian scientists reporting and interpreting Cape Grim data in peer-reviewed international journals, including 15 in *Nature/Science* (average 1 every 2 years), 62 in the *Journal of Geophysical Research* (2 per year), 27 in the *Journal of Atmospheric Chemistry* (1 per year), 19 in *Tellus*, 16 in *Geophysical Research Letters* and 13 in *Atmospheric Environment*. The average peer-reviewed international journal publication rate is 7 per year; the peak year for these publications was 1998 with 22 papers, including 13 in the *Journal of Geophysical Research*.

Up to 2006, *Baseline* contained 409 research reports and data summaries, about 20 per *Baseline* issue and typically 30 per issue in the past 5 issues of *Baseline*. *Baseline* also details about 600 conference papers reporting Cape Grim activities, authored/co-authored by Australian scientists involved in the Cape Grim Program.

Personnel

Appendix B. (p. 146-151) lists personnel involved in the Cape Grim program since 1975, including members of the Management Group, the Working Group, Lead Scientists, CGBAPS on-site staff, off-site staff and post-graduate students.

Since 1984, the Management Group (2) has consisted of senior appointments from the Bureau of Meteorology and CSIRO. Working Group members have varied from 9 to 17, typically 13.

Since 1979 Lead Scientist numbers have varied from 7 to 13, typically 10. Since 1976 CGBAPS permanent on-site staff numbers have varied from 2 to 6, having remained at 6 since 1989.

Post-graduate students involved at Cape Grim commenced in 1991 (1), reached peak numbers in 1998 (14), gradually declining to 3 in 2006. Not surprisingly, there is a significant correlation between numbers of post-graduate students and peer-reviewed papers in international journals, the latter peaking at 22 in 1998 (Figure 3).

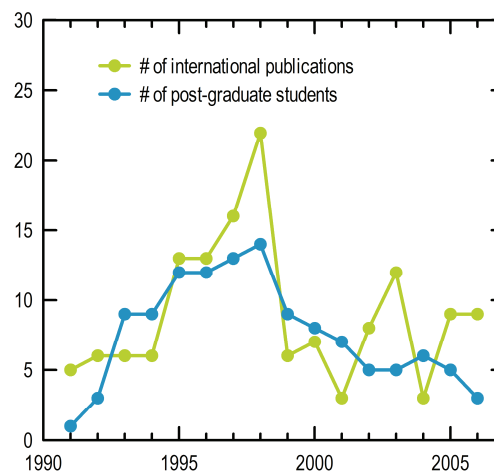


Figure 3. Cape Grim international peer-reviewed publications and post-graduate student numbers 1991-2006.

Budget

The evolution of the Cape Grim budget since 1980 is shown in Table 2 and Figure 4.

From 1980 to 1995 the Cape Grim budget grew by 11-12% per year and since 1995 the research and station budget has remained stable at close to \$700,000 per year. The equipment budget has varied significantly, averaging about \$50,000 per year for most years except 1982-1983, 1999-2003 and 2006-2007, in which equipment expenditure averaged about \$200,000 per year.

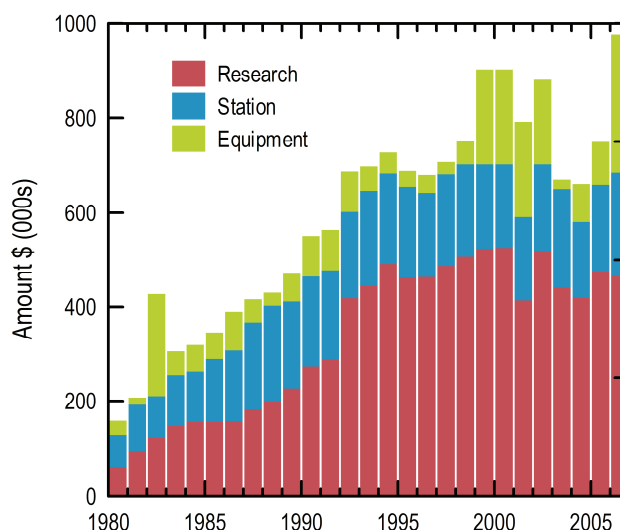


Figure 4. DST/Bureau of Meteorology Cape Grim budget, 1980 – 2006.

Table 2. DST/Bureau of meteorology Cape Grim budget (1980-2007): research, Station (operational) and equipment

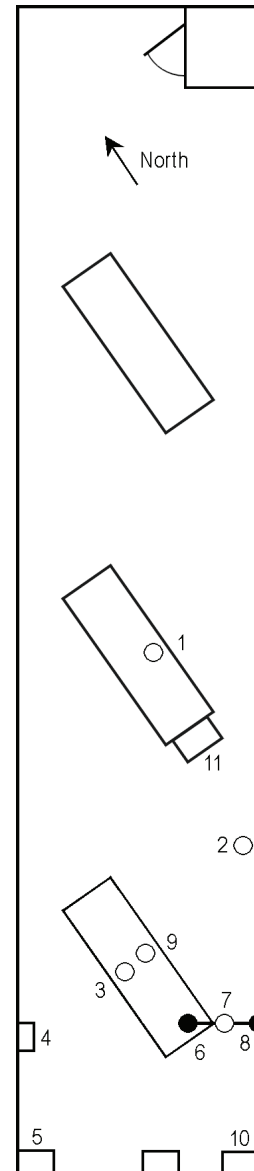
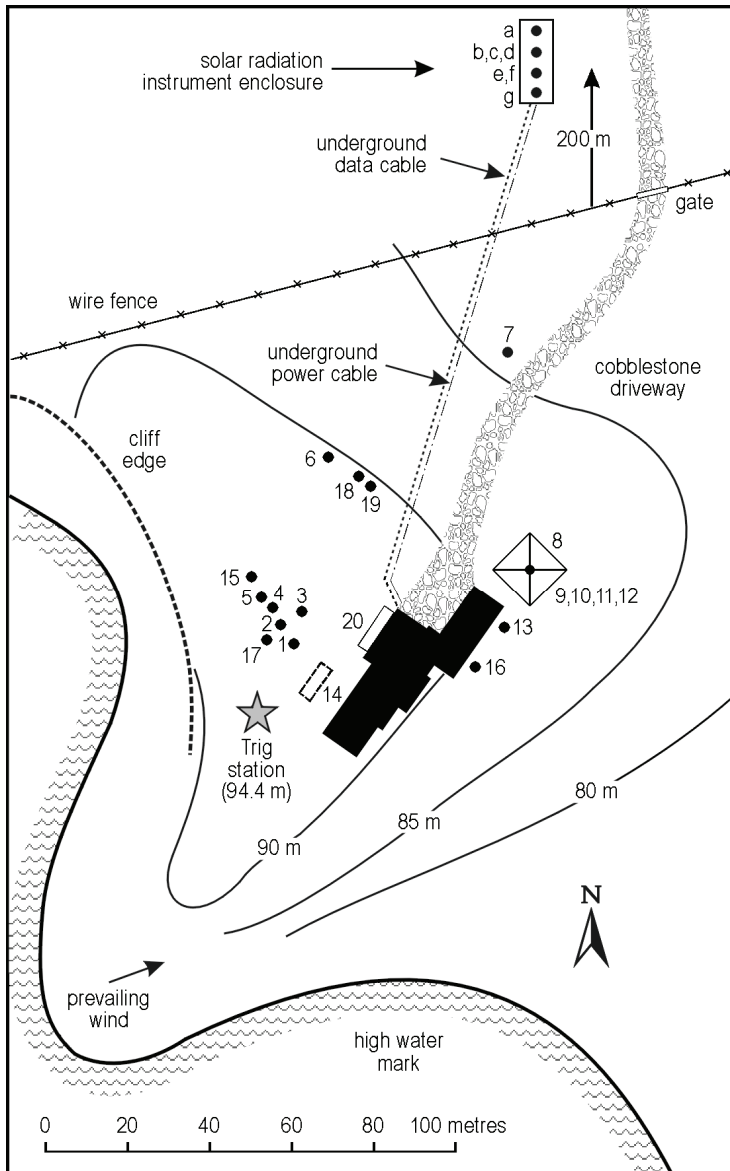
Period	Research	Station	Equipment	Total	Period	Research	Station	Equipment	Total
1980/1981	61,500	66,500	30,000	158,000	1994/1995	491,000	191,800	44,200	727,000
1981/1982	94,000	98,000	15,000	207,000	1995/1996	461,800	193,100	33,100	688,000
1982/1983	122,250	87,750	217,000	427,000	1996/1997	463,000	179,000	38,000	680,000
1983/1984	147,100	107,945	50,955	306,000	1997/1998	487,000	194,000	26,000	707,000
1984/1985	155,700	106,900	56,900	319,500	1998/1999	507,200	194,800	50,000	752,000
1985/1986	155,500	133,844	56,896	346,240	1999/2000	522,270	179,730	200,000	902,000
1986/1987	156,700	151,000	82,100	389,800	2000/2001	524,310	177,690	200,000	902,000
1987/1988	181,750	185,448	46,645	415,843	2001/2002	413,447	177,000	201,000	791,447
1988/1989	198,700	203,800	27,500	430,000	2002/2003	517,260	184,000	178,000	880,000
1989/1990	226,500	184,600	58,900	470,000	2003/2004	440,000	210,000	20,000	670,000
1990/1991	273,300	190,400	86,300	550,000	2004/2005	418,366	161,634	81,000	661,000
1991/1992	288,200	188,700	86,000	562,900	2005/2006	474,184	185,000	90,000	749,184
1992/1993	418,200	183,300	85,500	687,000	2006/2007	464,500	220,000	292,000	976,500
1993/1994	443,450	202,950	51,100	697,500					

1. STATION SPECIFICATION

1.1 GENERAL

Name	Cape Grim Baseline Air Pollution Station	
Latitude	40° 41' 00" (40.683°) S	
Longitude	144° 41' 22" (144.689°) E (DATUM GDA94)	
Roofdeck elevation	94 metres	
Air intake elevations	104 metres	(10 m intake)
	164 metres	(70 m intake)
WMO station classification	Baseline (global)	
Status	Fully operational	
Station ID indices	WMO station code 94954 WMO index number A2000 101 WMO turbidity code number 03 050 WMO ozone code number 230 AWS station code 94954	
Time zone	Australian Eastern Standard Time (AEST) (AEST = UTC + 10 hours; the station operates on AEST year-round)	
Office hours	0845-1700 local time (AEST plus 1 hour in summer)	
Telephone	Smithton office	(03) 6452 1629
	International dialling	+61 3 6452 1629
	Station	(03) 6452 2181
	Facsimile Smithton	(03) 6452 2600
	Facsimile Station	(03) 6452 2582
E-mail	capegrim@bom.gov.au	
Postal address	P.O. Box 346, Smithton, Tasmania 7330, Australia	
Freight address	159 Nelson Street, Smithton, Tasmania 7330, Australia	

1.2 SITE PLAN



Site Plan

1. Baseline ERNI
2. Continuous ERNI
3. Raindrop sensor
4. Tipping-bucket rain gauge
5. Standard 203 mm rain gauge
6. Stevenson screen
7. Station exhausts
8. Telstra tower (74 m)
9. 70 m intake
10. Wind vane and anemometer (50 m)
11. 50 m Temperature sensor
12. Wind vane and anemometer (30 m)
13. Radon detector (HURD2)
14. Concrete slab & power box for containers
15. Passive dioxin
16. BHURD
17. CSIRO Land and Water monthly rain sampler (GNIP)
18. Ceiliometer
19. Tipping bucket rain gauge
20. Cylinder store

Solar Radiation Instruments

- a. Global pyranometer
- b. Sunphotometer (SPO-1A)
- c. Direct pyrheliometer
- d. Diffuse pyranometer
- e. Sunphotometer (SPO-2)
- f. Long wave radiometer (Pyregeometer)
- g. Spectral radiometer (SRAD)

Roof deck plan

1. UV pyranometer
2. Barometer static head and DOE transmitter
3. Elemental carbon LVS
4. DOE HVS
5. Ecotech B HVS
6. 10 m anemometer and wind vane
7. 10 m air intake
8. 10 m anemometer
9. ANSTO ASP sampler
10. Ecotech A HVS
11. Dual flow aerosol sampler

1.3 PROGRAM SUMMARY

This section summarises programs in operation at Cape Grim during the calendar years 2005 and 2006.

(a) Automated measurements

Species	Instrument
CO ₂ Major CFCs, CHCl ₃ , CH ₂ CCl ₃ , CCl ₄ , N ₂ O	CMAR LoFlo Mark 2 (based on a LI-COR model 6252 IR analyser) AGAGE GC-Multi Detector (GC-MD) system: {HP5890 GC (two electron capture detectors); Carle (flame ionisation detector); Trace Analytical RGA-2 / RGD-2 (mercuric oxide reduction detector)}
CH ₄ CO, H ₂ Minor CFCs, HCFCs, HFCs, PFCs, methylhalides chlorinated solvents, halons	AGAGE GC-Mass Spectrometry ADS (GC-MS-ADS) system (decommissioned January 2005)
Minor CFCs, HCFCs, HFCs, PFCs, methylhalides chlorinated solvents, halons SF ₆ Surface O ₃	AGAGE GC-Mass Spectrometry Medusa (GC-MS-Medusa) system Shimadzu GC-ECD TECO 2 Thermoelectron 49 & 49-PS calibrator (UV)/ TECO 3 Thermoelectron 49C & 49C-PS calibrator (UV) alpha detector / delay tank (x2)
Rn	
Irradiance	
Direct	Eppley pyrhelimeter tracker eye 862 nm
Direct Spectral/Aureole	SPO-1A (341.5, 500, 610, 778 nm), SPO-2 Carter-Scott (368,412,500,812 nm)
Global	Eppley long-wave radiometer
Diffuse	Kipp & Zonen CM11
UV-B	Optronics Spectral Radiometer OL-752 Biometer - Solar Light 501A
Condensation Nuclei (CN)	TSI 3010
Ultrafine Condensation Nuclei (UCN)	TSI 3025a
Cloud Condensation Nuclei (CCN)	auto static CCN counter
Aerosol size distribution	auto-Pollak and diffusion battery
Particulate carbon	Magee Scientific Aethalometer
Temperature (wet & dry)	Rosemount (Pt) / Vaisala DTS12 (50 m)
Wind speed	Synchrotac 3-cup (10 m) / Vaisala WAA-15 (10 m, 30 m, 50 m)
Wind direction	Vaisala WAV-15 (10 m, 30 m, 50 m)
Pressure	Setra / static head
Rainfall	Rauchfuss (0.2, 0.1 mm)
Radionuclides	Gamma detector
Ceilometer	Viasala (installed December 2005)

(b) Component collections

Component	Method	Nominal number per month	Species analysed	Analysing Agency [^]
CO ₂	Cryo	4	δ ¹³ C, δ ¹⁸ O	CMAR
CO ₂	Raschig tubes	2	Δ ¹⁴ C	UH
Soluble ions	HVS* (Ecotech A)	4	inorganic ions	CMAR
Soluble ions	HVS* (Ecotech B)	4	inorganic ions	CMAR
Soluble ions	Dual Flow LVS*	4	organic aerosol	CMAR
Particulate matter	HVS	4	radionuclides	DOE (ceased October 2005)
Particulate matter	LVS*	4	elemental carbon	U Stockholm
Aerosol	LVS	8	metals	ANSTO
Rain	ERNI*	4	pH, conductivity, inorganic ions	CMAR
	ERNI	1	tritium, δD, δ ¹⁸ O	ANSTO; CSIRO-Land & Water
	Standard gauge	20	oxygen isotopes	UTAS
	GNIP bottle	1	inorganic ions, isotopes	CSIRO-Land & Water (commenced June 2006)
Marine gases	Sea water sampling	2	methyl halides & alkyl nitrate	CGBAPS/UEA
Marine biology	Sea water sampling	1	phytoplankton, salinity, temperature, etc.	UTAS
Dioxin	Passive	1/3	persistent organic pollutants	Environment Canada

* operated on baseline events switch (BEVS); ^ - Appendix C (p. 159)

STATION SPECIFICATION - Program summary

 (c) Whole air collections – episodes⁺

Flask type (litre)	Pressure (kPa)	Drying	Nominal number per month*	Species analysed	Analysing Laboratory [^]
G (0.5)	100 p	Dehydrite	4	CO ₂ , CO, CH ₄ , H ₂ , N ₂ O $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO ₂	CMAR
G (2.5)	100 p	Cryo	4	CO ₂ , CO, CH ₄ , H ₂ $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO ₂	NOAA-ESRL (formerly CMDL)
	0 p	Cryo	4	O ₂ /N ₂ , CO ₂	U Princeton (ceased Apr 2005)
	0 p	Cryo	2	O ₂ /N ₂ , CO ₂ (automated sampler)	U Princeton
G (5)	0 p	Cryo	2	O ₂ /N ₂ , CO ₂	SIO
SS (0.8/2.5/3.0)	280 p	-	4	N ₂ O, halocompounds	NOAA-ESRL (formerly CMDL)
G (2.5)	150 p	-	1	N ₂ O, halocompounds	NOAA-ESRL (formerly CMDL)
SS (34)	3000 c	-	(6)	archive / AGAGE standards	CMAR/CGBAPS
SS (3.2)	500 p	-	(6)	halocarbons by GC-MS	UEA
SS (1.6)	100 p	Dehydrite	1	SF ₆ [also G (0.5) CMAR species]	CMAR/UH
SS (6.0)	150 p	-	2	methyl halides, SF ₆ , halocarbons, N ₂ O	SIO (ceased Sep 2003)
G (2.0)	100 p	Dehydrite	1	CO ₂ , CO, CH ₄ , N ₂ O, $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ of CO ₂	LSCE
SS (1.0)	100 p	Dehydrite	1	CO ₂ , CO, CH ₄ , $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ of CO ₂	U Tohoku (ceased Jun 2003)
SS (6.0)	100 p	-	2	methyl halides and halocarbons	NIES
SS (3.2)	150 p	-	2	methyl halides and alkyl nitrates	CGBAPS/UEA
SS (3)	500 p	-	1	HFC-365mfc, -227ea, -236fa, -245fa	Empa (commenced 2006)

p - pump; c - cryogenic trap; * () indicates per year, ⁺ each episode may include multiple flask traps; [^] - Appendix C (p. 159)

G - glass; SS - stainless steel

(d) Discrete sampling

Parameter	Method	Occasion
Temperature (wet & dry)	Mercury-in-glass	1/day
Temperature (max & min)	Mercury-in-glass	1/day
Condensation Nuclei (CN)	Manual Pollak	1/day
Rainfall	Standard 203 mm rain gauge	1/day

2. OFFICER-IN-CHARGE'S REPORT

2.1. INTRODUCTION

2005-2006 saw a great deal of building activity at the station with the construction of the new gas cylinder store and continuing works on the Telstra Tower. Work on both commenced in October 2005 and continued into early 2006.

Two campaigns, Precursors to Particles 2005 and Precursors to Particles 2006 (P2P 2006) occurred in February of each year. The campaign in February 2005 was a small affair allowing for development of the much larger Surface Ocean Lower Atmosphere Study (SOLAS) endorsed P2P 2006 campaign in February 2006. This involved groups from New Zealand, Germany and Australia and focused on the possible role of iodine emissions from the local Bull Kelp (*Durvillaea potatorum*) in Valley Bay, on particle events.

In April 2006 the Cape Grim Baseline Air Pollution Station celebrated 30 years of continuous operation. We hosted a number of international visitors from other Global Atmosphere Watch (GAW) Stations in the region and a large number of current and past staff and scientists. A reception was held at the station and was followed by a dinner in Stanley.

Roaring 40s commenced construction of Stage 3 of the Woolnorth Wind farm in 2006. This is a significant distance from the station and stages 1 and 2 of the wind farm and is unlikely to have any impact on measurements at the station, although Woolnorth Road did not survive the constant passage of large gravel trucks and the local Circular Head Council had to be prompted several times to repair the holes. Stage 3 of the Woolnorth Wind farm is expected to be operational in early 2007.

January 2005 started with a bang when the station was struck by lightning. The strike caused damage to a board in the new Almos automatic weather station and a port on the Passive Radiation computer. In February damage to the A/D board in one of the ozone instruments was also tied to the strike on the 10-m mast.

New instruments installed at the station included a ceilometer (December 2005) as part of the Almos automatic weather station. Another monthly rain sampler for CSIRO Land and Water, was installed in June 2006, as part of the Global Network of Isotopes in Precipitation (GNIP) program. A four stage impactor aerosol sampler for Herman Sievering (University of Colorado at Denver) was installed on the 50-m platform in August 2005 and this included contracting Telstra to run the power and fit the pump on the 50 m platform and staff undergoing training to obtain their tower climbing and rope rescue tickets. In August 2006 a sea state camera was installed at the station and provides real-time images of Valley Bay, looking towards Hippo Point.

In September 2005 the link between the Smithton Office and the Bureau of Meteorology was converted to a private ADSL link, which instead of going via the Hobart regional office goes direct to Melbourne, with a speed of 512 kbps. In August 2006 the speed of

the link between the Smithton Office and the Cape Grim Station was doubled to 256 kbps. Other significant IT events included the demise of Jacob (March 2006) and Virazon (September 2006). Both had been showing signs of age and some preparations had been made to replace both, but were not complete when Jacob failed. The failures led to a number of issues which were resolved over time, with the major issue still not resolved being access to hourly data through the Cape Grim internal website. In December 2005 network renumbering was undertaken at the station and office. Prior to the 30th Anniversary celebrations in April a major clean up at the station was undertaken and this included all the old Hewlett Packard servers, Alf and Bet. These were all removed to Smithton and eventually found a home at the Hewlett Packard Museum in Melbourne.

There were a number of problematic instruments throughout 2005 and 2006. The wind instruments at 50 and 10 m gave a few problems with the 10-m Syncrotac anemometer needing replacement in April due to water encroaching on the data cable. In November 2006 the Vaisala wind vane was reporting the wind direction +40°. A visual check indicated that the vane was pointing into the wind correctly and the fault was finally traced to the data conversion board. This affected the Almos automatic weather station data, but not station data, which does not get processed by the conversion board and the comparison between Cape Grim data and Almos data was useful in diagnosing the problem. The faulty board was replaced within a month.

A new oxygen instrument was installed in September 2006 following a visit by Patrick Sturm, a CSIRO fellow. This instrument has not functioned well since being installed due to problems with the cryo-cooler and software. The SRAD was problematic for most of 2006, requiring much attention from both staff and the lead scientist who affected miracle cures to keep the instrument running. A replacement instrument is being developed, but is not yet ready.

2.2. BUILDINGS AND MAINTENANCE

Major activities external to the station building were centred on the construction of a new gas cylinder store and a second refurbishment of the Telstra tower.

The unsuitability of the current gas store was raised by the in occupational health and safety assessment in November 2004 and in October 2005 work commenced to construct a new store abutting the current store. Work was projected to take 12 weeks, but due to delays with obtaining the steel framework, problems with the contractor and poor weather, the store was not completed until March 2006. As part of the building works for the gas cylinder store an assessment of asbestos at the station was performed and only the roof lining of the porch and garage were found to contain asbestos.

In February 2005 the upper King Island communication dish needed repair and while the lowering of the dish on a winch was successful, the lifting rig

failed while attempting to return the dish to its position. Fortunately the spare safety line prevented the dish from falling to the ground. The dish was left restrained at the base of the tower and a 100 tonne crane was brought to Cape Grim in April 2005 to complete the lift.

The refurbishment of the Telstra tower that was undertaken in mid to late-2003 was found to be sub-standard and refurbishment work recommenced in October 2005, with the Cape Grim booms and supporting crossbeams at 30, 50 and 70 m being replaced (free of charge) and all the crossbeams for all the Telstra equipment also being replaced. The four main legs of the tower were stripped and any rust ground off, before the legs were spray coated with a protective paint. The refurbishment of the tower was completed in March 2006.

With all this construction on site Cape Grim looked very untidy, but operations were largely unaffected with only the loss of one ^{13}C sample due to Telstra contractors working around the 70-m inlet height and particle measurements affected occasionally by the building of the gas store.

The replacement of the booms did require some modifications to the control of the baseline switch and the wind direction criteria was switched between the 10, 30 and 50-m instruments as required. The 50-m wind instruments failed in April 2005 and this appeared to be the result of a data cable problem. In December 2005, the 50-m instruments could not be returned to the end of the boom following the replacement of the boom, as the winch had jammed. The instruments were finally 'shoved' into position using a long pole from the 50-m platform in May 2006, with the 30-m instruments being used to control the baseline switch until the 50-m instruments were in position.

The air conditioning in the main laboratory had been experiencing problems in maintaining the specified temperature and in July 2005 Steve Montzka (NOAA) reported unusually high levels of HCFC-22 in a supposedly 'clean' baseline flask sample from late April. The AGAGE record was checked and spikes in HCFC-22 were detected between 28 April and 31 May 2005. Newmans Plumbing were contacted and it was found that a seal on one of the gas units had failed, venting the refrigerant. The seal was replaced and the unit recharged.

The additional instrumental load during P2P 2006 presented a challenge to the air conditioning unit and it was not able to maintain the laboratory temperature during the campaign. In addition problems with fan belts lead to icing up of the unit in the ceiling and flooding resulted when the ice melted.

In December 2005 the alternator on the back up generator blew up as a result of a short circuit in the windings. A portable generator set was hired from Coates and this was wired into the Station by BSH Electrical who responded rapidly to this emergency. In January 2006 a new alternator was fitted and the portable generator set removed.

The numerous problems with infrastructure, including the generator, domestic water pumps and

the air conditioning has given some concern over the standard of care shown by our regular contractor Newmans Plumbing and their response to urgent issues and so towards the end of 2006 alternative contractors were being investigated.

The cleaner at the station had been significantly underperforming and in July 2005 were replaced with another local contractor.

In May 2005 the kitchen and bedrooms at the station were upgraded. Both were redesigned to make better use of space and the bunk beds in each bedroom were replaced with two single beds.

In December 2005 the quality of the drinking water at the station deteriorated. A water cooler and bottled water supply was organised and in early January 2006 the rainwater tank was drained to discover the corpse of a Spotted Quoll. The tank was sanitised and the water treated and in September 2006 all the down pipes were fitted with diverters to remove debris and to prevent critters making their way into the tank.

Plans for the refurbishment continued with discussions on a Cape Grim tower based on the standard Bureau of Meteorology radar tower.

2.3. STAFF AND STUDENTS

2005 and 2006 were challenging years in terms of technical support. Laurie Porter (TO4) took long service leave in mid-2005 and then was seconded at his request to CSIRO Marine and Atmospheric Research. Chris Rickard (TO3) commenced acting in the TO4 position from August 2005 and the search for a temporary TO3 became an on-going mission. The lack of technical support was compounded by the absence of Stuart Baly (ITO2) who had successfully applied for the Bureau of Meteorology's undergraduate scholarship in late 2004 and was studying his Mechatronics degree as a fulltime student at Deakin University.

Aaron Humphries was eventually employed on a three month contract in early November 2005 to provide technical support, but due to qualification issues he was released at the end of this contract in January 2006. The position was advertised locally and attracted only one applicant who was deemed unsuitable and operations limped on with only one technical officer. IT staff, Stuart returning in late 2005, and the Officer in Charge providing the additional technical support required. This placed a great deal of stress on the only technical officer and limited the ability of other staff to work on their own projects. During this time there was a major campaign at Cape Grim (P2P 2006) and we celebrated the 30th Anniversary of the Cape Grim Station and it is a testament to the staff's abilities and dedication that we kept routine operations running while handling these additional events.

In July 2006 Paul Armstrong, a PhD Student from CSIRO Marine and Atmospheric Research in Hobart, joined us on a 6 month contract as a temporary TO3, providing much needed support to Chris

and allowing other staff to focus on their usual duties.

In January 2006 Jane Arnold joined the Smithton office as a contractor to provide support to Cindy Hood, working one day a week.

In October 2006 Stuart Baly graduated from Deakin University with a Bachelor of Engineering (Mechatronics) and in May 2006 Laurie Porter was awarded a NOAA 'Environmental Hero Award' at the Region IV World Meteorological Organization Meeting in Adelaide.

Station staff attended AGFEST, an agricultural show near Launceston, in May 2005 and 2006, assisting the Tasmanian Region team in the Bureau of Meteorology tent. Much fun was had with dry ice in water and tornadoes in a bottle. While none of the public were actually able to correctly guess the strongest gust ever measured at Cape Grim (2005) nor the significant rainfall event of 2006, we still managed to give away our prizes to those that got close.

2.4. INTERNATIONAL ACTIVITIES AND VISITORS

International visitors during 2005 included Nicolas Cassar of Princeton University who visited the station following a trip to Antarctica to upgrade the Aardvark automated flask sampling system and Gerry Jennings from the National University of Ireland. The Greenhouse 2005 conference in Melbourne generated only two visits to the station from Richard Derwent (rdscientific, UK) and Detlev Möller (Brandenburg Technology University). Dudley Shallcross (Bristol University) also visited the station in April 2006.

The NOAA attendees at the Cape Grim Annual Science Meetings in 2005 and 2006 were Debbie Mondeel and David Hoffman respectively. The 2006 Annual Science Meeting was held in Hobart at CSIRO Marine and Atmospheric Research following the merger of Atmospheric Research and Marine Research in June 2005. The Cape Grim attendees at the NOAA Annual Science meetings in May 2005 and 2006 were Ian Galbally (CMAR) and Matt Tully (BoM) respectively.

International travel by Cape Grim staff was confined to the Officer in Charge who travelled to Beijing, China in August 2005, accompanied by Wlodek Zahorowski (ANSTO), to attend the Symposium on Global Atmosphere Watch and to visit the Mt Waliguan Station as part of the 10th anniversary celebrations of the station. The visit was partially funded by the Chinese under the bilateral agreement between the Bureau of Meteorology and the Chinese Meteorological Association.

In September 2006 Jill Cainey travelled to Cape Town, South Africa to attend the Joint International Global Atmospheric Chemistry (IGAC)/Commission on Atmospheric Chemistry and Global Pollution (CACGP)/World Meteorological Organization (WMO) Conference 'Atmospheric Chemistry at the Interfaces'. This trip included a visit to the Cape Point

GAW Station to assess operations on behalf of the South African Weather Service.

There were two occupational health and safety assessments performed at the station. Michael Berechree (BoM) and Bruce Wilson (CMAR) visited the station and office in April 2005 and then Michael Tessier (BoM) visited the station in June 2006. The Cape Grim Management Group made two visits during 2005 and 2006. The first in June 2005 involved Bob Brook (Deputy Director Services, BoM), Greg Ayres (Chief, CMAR), Steve Morton (Group Executive, CSIRO Environment and Natural Resources), Tim Moltman (Deputy Chief, CMAR) and Geoff Willis (CEO, Hydro). This formed part of an introduction to activities at Cape Grim to the wider CSIRO community, prior to the merger of Atmospheric and Marine Research. Greg Ayres then visited again in September 2005 to introduce the Bureau of Meteorology's new Deputy Director Services, Gary Foley, to the Cape Grim station and staff.

The Precursors to Particle 2006 (P2P 2006) campaign in February 2006 resulted in a large number of visitors to the station to participate in the campaign. International visitors included Anthony Gomez, Mike Harvey, Paul Johnston, Karin Kreher, Tim Hay and Anitra Fraser all from NIWA, NZ. Torsten Stein and Ossama Ibrahim from the University of Heidelberg, Germany were also involved in the campaign. Allen Goldstein (University of California, Berkeley, USA) assisted Ian Galbally with the Proton Transfer Reaction Mass Spectrometry measurements during the campaign. Other local scientists involved with the campaign were: Ken Barker (BoM), Sarah Lawson, Melita Keywood, Jason Ward, Mick Meyer, Ian Morrisey, Rob Gillett, John Gras and Ian Weeks (all CMAR), Michael Grose (UTas), Zoran Ristovski, Graham Johnston, Cathie Flechter and Nic Meyer (all QUT) and Keith Bigg and Peter Grose.

During the campaign the BBC visited to film activities at the station for a David Attenborough documentary on climate change that was shown on television in the UK in May 2006.

By far the most major event of 2005 and 2006 was the 30th Anniversary celebrations on 11 April 2006. Many staff and scientists, past and present attended the Cape Grim Station for a plaque unveiling and reception and this was followed by dinner in the evening. The event at the station involved Dr. Len Barrie (Chief, Environment Division, Global Atmosphere Watch, World Meteorological Organization) and Mr. Mark Baker, Federal Liberal Member for Braddon and the Cape Grim Management Group of Gary Foley (DDS, BoM) and Greg Ayres (Chief, CMAR). International visitors included Zhou Lingxi (CMA, China), Noer Hayati (BMG, Indonesia), Lim See Fook (Malaysian Meteorological Service, Malaysia), Casper Labuschagne (Cape Point, South Africa) and Jonas Mphopya (Acting CEO, South African Weather Service). This group, including Len Barrie, also visited Cradle Mountain National Park during their time in Tasmania and Prof Zhou and Jill Cainey attended the AGAGE meeting in Hobart the previous week.

2.5. OPERATIONAL BUDGET

The Cape Grim program expenditure allocations for the financial years 2004-2005, 2005-2006 and 2006-2007 are detailed below. Staff salaries, road and building maintenance are not included as they are covered by other parts of the Bureau of Meteorology budget. Personnel costs of staff at CMAR assisting with Cape Grim related research are included in the Research allocation.

	2004-2005	2005-2006	2006-2007
	\$	\$	\$
Station Operation	161,634	185,000	220,000
Research	418,366	474,184	464,500
Equipment	81,000	90,000	292,000
Total	661,000	749,184	976,500

Compiled by J. M. Cainey

INTERPRETATION OF THE MINILIDAR DATA RECORDED AT CAPE GRIM 1998 – 2000

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Abstract

Data acquired during the mostly continuous operation of a lidar at Cape Grim (40.482°S, 144.688°E) during the years 1998 – 2000 are now available from the Bureau of Meteorology. The data record fascinating details of the structure and variability of clouds and aerosol layers associated with various atmospheric conditions occurring over Cape Grim during this period. By describing examples of the lidar signals from different types of clouds, precipitation, aerosol layers and frontal phenomena, presented both as profiles and as height-versus-time plots of attenuated backscatter, this work provides a guide to the interpretation of the data.

1. Introduction

A lidar, called the MiniLidar because of the small and simple laser transmitter and relatively unsophisticated detection and amplification system, was modified to permit continuous, autonomous operation and installed at the Cape Grim Baseline Air Pollution Station (CGBAPS) in June 1998. The aim of the deployment was to provide information on variations in cloud base height and in the depth of the boundary layer, partly to support other work at CGBAPS concerned with the evolution and transport of atmospheric chemical species. Apart from a break in operations for refurbishment in early 1999, the MiniLidar operated almost continuously until it was retired from service in late 2000.

The data acquired during the deployment period are now available from the Bureau of Meteorology by contacting the Officer-in-Charge of the Cape Grim Baseline Air Pollution Station (cgbaps@bom.gov.au). Details of the coverage and completeness of the data set can be found in Young [2006].

This paper will present several examples of MiniLidar data on such atmospheric phenomena as the passage of fronts, the atmospheric boundary layer, and various types of clouds and precipitation. By presenting the data as daily records of attenuated backscatter (see below) plotted on height versus time axes, supported by relevant profile and meteorological data, this work provides a guide to the interpretation of the data.

2. Summary of the lidar technique

Various constituents of the atmosphere, including air molecules, aerosol particles, water droplets and ice crystals in clouds, fogs and precipitation, can be studied by remote sensing techniques using their ability to scatter electromagnetic radiation. Because the sizes of many aerosol particles and cloud droplets are comparable to or larger than the wavelengths of visible light, lidar (light detection and ranging) has proven to be a powerful technique for studying these atmospheric constituents.

In the lidar technique, a short pulse of laser light is transmitted into the atmosphere where a small fraction is scattered back toward a receiving telescope, usually located along side the laser transmitter. The collected light is focussed onto a detector that converts the time-varying optical signal into an electrical signal that is digitised and recorded for subsequent analysis.

Because atmospheric constituents are distributed throughout any unit volume of the atmosphere, rather than forming a solid wall-like target, only a small fraction of the energy in the laser pulse is scattered at each range increment with most of the energy propagating away from the lidar to be scattered at more distant ranges. The lidar signal is, therefore, a continuous profile of the atmospheric scattering along the path of the laser beam, rather than a single pulse or 'echo' that would be detected from a solid target. The progressive loss of energy from the original pulse is proportional to the amount of scattering encountered at any particular range and constitutes a gradual attenuation of the signal. This attenuation occurs both as the pulse propagates away from the lidar and also as the scattered energy travels back to the receiver. The lidar signals thus contain information on both the concentration of atmospheric constituents and their distances from the lidar. The lidar equation gives the backscattered power $P(r)$ that is received by the lidar from range r as

$$P(r) = C\beta(r)T^2(0,r)/r^2 + P_0 \quad (1)$$

where $\beta(r)$ is the atmospheric volume backscatter function and $T^2(0,r)$ is the two-way transmittance between the lidar and the scattering volume. The product of these two, purely atmospheric factors is called the attenuated backscatter and is the quantity most commonly reported in lidar studies. The scaling constant, C , is a product of various factors relating to the instrument and P_0 represents the signal offset or background power.

The lidar equation is usually solved for profiles of backscatter, which is related to particle concentra-

tion, by assuming a relationship between the backscatter and the transmittance factor. The retrieval of the concentrations of atmospheric particulates requires specific information on their optical scattering properties. This is not the focus of this paper. However, much useful information on the atmosphere and its variable nature can be inferred from the study of the variation of the lidar signals over time. Although much information can be gained from the study of individual lidar profiles, considerably more information can be gleaned from the study of height versus time plots of attenuated backscatter, and this form of presentation will be used in this paper to illustrate changes in atmospheric structure.

3. The MiniLidar

Full details of the MiniLidar, its development history and operation at Cape Grim are provided in Boers *et al.* [2001] and Young [2006] and in references therein, so only the salient features will be provided here.

The transmitter was a Nd:YAG laser with a pulse length of 10 ns and a typical maximum energy of 15 mJ at the operating wavelength of 1064 nm. Backscattered energy was detected using a YAG-444 PIN photodiode mounted behind a 1.1-nm FWHM narrow band filter located at the prime focus of the 40-cm diameter mirror of the receiving telescope. The detector signal was amplified with a computer-controlled, gain-programmable amplifier before digitisation at 20 Msps using a plug-in, two-channel digitiser card installed in the control computer. Data were recorded using both channels of the digitiser, but with different gains on each, in order to increase the 8-bit dynamic range.

The MiniLidar was operated in the zenith through a window in the roof of the laboratory. A washer and wiper unit was controlled by the lidar computer to clean the window before each laser pulse, thus permitting operations during the frequent periods of rain and showers experienced at Cape Grim. To avoid multiple reflections of the transmitted pulse within the window glass reaching and saturating the detector, the laser beam exited through a separate port in the window. The port was isolated from the main window by a cylindrical metal tube from which hung a black fabric tube that completely enclosed the path of the laser beam within the laboratory. Because Cape Grim is sufficiently far south and the window was over 4 m above the lidar, there was no need to cease operations because of sunlight entering the receiver around local noon. Profiles were recorded every minute throughout the day until midnight when the file for the day was closed, compressed and copied to the network server before deletion from the lidar computer in order to prevent the hard disk from becoming full.

Because the laser output exceeded maximum permissible exposure levels for eye safety and posed a potential hazard to the eyesight of crew and passengers of aircraft encountering the laser pulse,

a restricted zone was set up over CGBAPS by the aviation authorities.

The MiniLidar was installed in June 1998 and operated until February 1999 when the system was returned to Aspendale for refurbishment and replacement of the original laser, the energy of which had dropped to such low levels that the quality of the data was severely degraded. Operations with the new laser began in June 1999. The energy levels of the replacement laser began falling significantly from the early part of 2000, thereby causing a steady decline in data quality, and the system was withdrawn from service in September 2000 pending the installation of a new system of higher performance. Despite the problems caused by the limitations of the components of the MiniLidar system, a large amount of useful data on the variability of the cloud and aerosol layers during the period 1998 – 2000 was obtained. Data were recorded on 671 days in 25 months during that time.

4. Examples of MiniLidar data

The data presented below are of the attenuated backscatter coefficient as defined above. The raw signals from which these values have been calculated have first been corrected for various signal anomalies; these include glitches caused by digitiser errors and energy monitor errors caused by multiple pulsing of the laser [Young, 2006]. Also, rather than calculating the signal offset (Equation 1) as the average of the last few points in the profile, this quantity has been determined using the most common (modal) digital level in the raw lidar signal. Although this method gives the signal offset only to the nearest whole digital level and is, therefore, less precise than the former method under ideal conditions, it is more accurate when multiple-pulse signals occur near the end of the profile.

4.1. Profile data

4.1.1. 'Clean' conditions

A typical signal profile obtained by the MiniLidar during 'clean' atmospheric conditions when there was relatively weak aerosol scattering is plotted in Figure 1. (Note that the MiniLidar detector is negatively biased, causing increases in the detected, backscattered power to produce an increasingly negative output voltage. This is accommodated in the digitizer by applying a positive digital offset (242 levels in the example shown) and the increasing detected power is recorded as decreases in the digitised signal.)

It can be seen from Figure 1, and from Equation (1), that, in the absence of strong variations in the atmospheric backscatter, the lidar signal decreases with the square of the range from the lidar. It can also be seen in Figure 1 that the atmospheric signal from the MiniLidar becomes less than the electronic noise for ranges beyond about 500 m under these conditions.

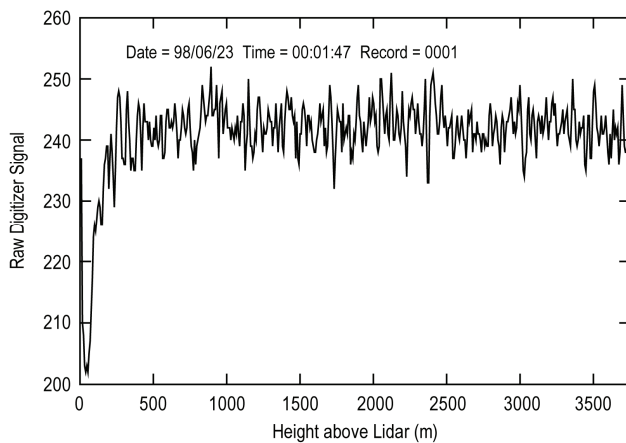


Figure 1. A typical raw MiniLidar digitizer profile recorded under conditions of low aerosol scattering. A positive digital offset of approximately 242 levels has been used to accommodate the negatively-going voltage from the detector-amplifier.

A more useful form of output used in reporting most lidar data is the attenuated backscatter defined in Section 2. As can be seen from Equation (1) this purely atmospheric quantity can be obtained by removing the background signal, correcting the resulting signal for the instrumental constant and multiplying by the square of the range at each point in the profile. The attenuated backscatter that corresponds to the raw signal in Figure 1 is presented in Figure 2. No significant particulate scattering is detectable above the noise level, which now increases with the square of the range.

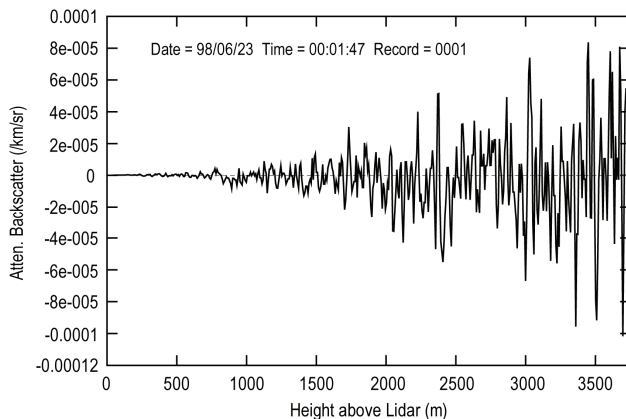


Figure 2. The attenuated backscatter profile corresponding to Figure 1.

4.1.2. Atmospheric Boundary Layer

The atmospheric boundary layer (ABL; see Garratt, 1992) is the layer immediately above the surface in which exchange between the surface and the atmosphere takes place. The height of the ABL plays an important part in air quality, atmospheric chemistry and in the transport and dispersal of airborne pollutants. The ABL height is defined in various ways, including the height of the lowest temperature inversion, the height at which a parcel of air becomes neutrally buoyant, the height to which sensible heat is transported, and so on. (See, for example, Gar-

ratt, [1992], Stull [1988], and Boers [2001] for discussion of this topic.)

Operationally, the height of the ABL is most commonly determined from thermodynamic data obtained from radiosoundings. However, even these soundings can produce ambiguous results in some atmospheric conditions [Seibert *et al.*, 2000]. Even under ideal conditions, radiosonde data are of limited temporal and spatial extent and are expensive to acquire. Therefore, alternative methods have often been employed, especially where high temporal resolution has been needed. Since the late 1960s, lidar has been used to measure ABL heights by determining the height to which passive tracers, including aerosols [Viezee and Oblanas, 1969, Russell *et al.*, 1974] and water vapour [Lammert and Bösenberg, 2006] have been mixed. However, even here there are caveats [Russell *et al.*, 1974, Sicard *et al.*, 2005]. While the methods work very well during the growth of the Convective Boundary Layer, care must be taken to discriminate against residual lofted layers during the decline of the ABL height in the evening and during less well-mixed conditions when other sources of aerosols may produce strong layers within the ABL. Generally, however, the situation is improved by studying the changes in the lidar data during the whole day in order to determine the evolution of the ABL.

Profiles of attenuated backscatter measured during periods when there was a well-defined boundary layer are plotted in Figures 3, 4 and 5. A region of enhanced aerosol backscatter can be seen in Figure 3 extending to a height of approximately 350 m where there is an abrupt decrease. Above this height there is insufficient aerosol scattering to be detected above the noise. This illustrates a limitation of the performance of the MiniLidar. Because of the low signal-to-noise ratio (SNR) of the system, the ABL can only be detected when aerosol loadings are at least moderate. The top of the ABL may be missed if there is insufficient aerosol or if the ABL top is high enough that it is in a region where the noise has exceeded the signal. (Remember that the SNR decreases approximately with the square of the range from the lidar.) The other feature to note is in the region from 0 m to approximately 50 m. The receiver field of view and the diverging laser beam form two narrow cones centred on the axes of the receiver and transmitter. As these axes are separated, the cones, the common volume of which determines the region in which the backscattered signal is detected, do not intersect completely for the first 50 m or so with the result that the detected signal is reduced in this region. This is called the overlap region and the ratio of measured to expected signals is called the overlap function. Data should not be used quantitatively in this region without correction for the overlap function.

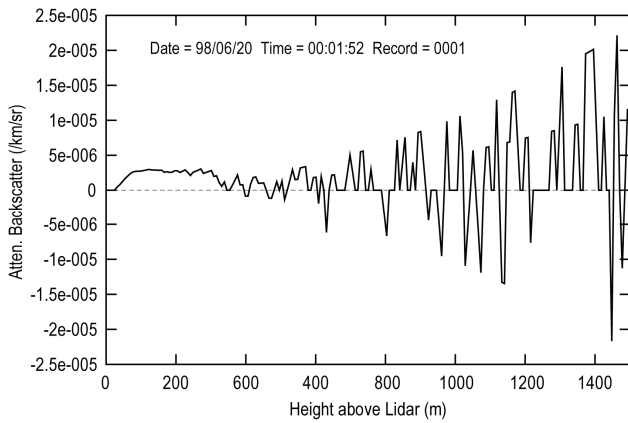


Figure 3. Attenuated backscatter profile showing a clearly-defined atmospheric boundary layer.

As the ABL grows, the determination of the top becomes more difficult. Figure 4 is an example of a profile where the upper limit of discrimination between aerosol scattering and noise is being approached. In such cases the ABL is more easily determined from height versus time plots as will be illustrated below. The ABL top is approximately 600 m above the lidar. Note that the single-profile plots in this paper are graphed against range, or height above the lidar. The height versus time plots below include the 90-m height of the lidar above mean sea level and are plotted against altitude AMSL.

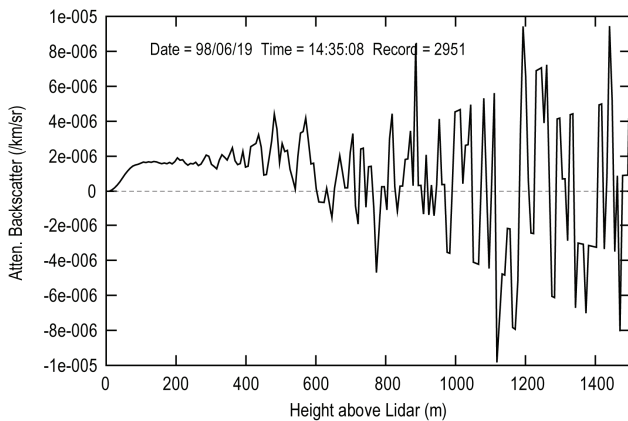


Figure 4. Attenuated backscatter profile showing an ABL with a top almost indiscernible in the noise.

Sometimes the ABL is capped by cloud. In these circumstances the range of aerosol loadings over which the ABL extent may be determined can be increased. However, if there is a gap between the apparent vertical extent of the aerosol and the base of the cloud, height versus time plots should be used in preference to profile data. Figure 5 illustrates a profile of attenuated backscatter with a developing cloud atop the ABL. If, however, the cloud is sufficiently opaque, the lidar pulse will be totally attenuated before the top is reached. There is also the situation where the cloud tops do not extend to the top of the ABL. So, again, caution must be used.

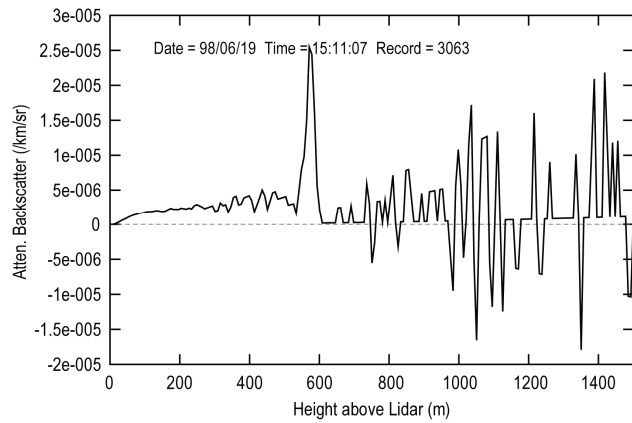


Figure 5. Attenuated backscatter profile for a cloud-topped ABL recorded 35 minutes after Figure 4.

4.1.3. High (ice) clouds

High clouds are the most distant atmospheric features detectable by the MiniLidar. Because high clouds are often tenuous and because the sensitivity and SNR of the MiniLidar decrease with the square of the distance, some of the weaker ('sub-visible') clouds are difficult to detect. (The highest cloud detected by the MiniLidar was at an altitude of approximately 7 km.) Improved detection is achievable by either averaging consecutive profiles, or applying a smoothing filter to the profile, or both. Both methods have advantages and disadvantages. Changes in the cloud profile between successive laser shots may cause a reduction in the SNR while noise at consecutive points in a profile may be correlated and smoothing may cause spurious features. Caution needs to be used in either case.

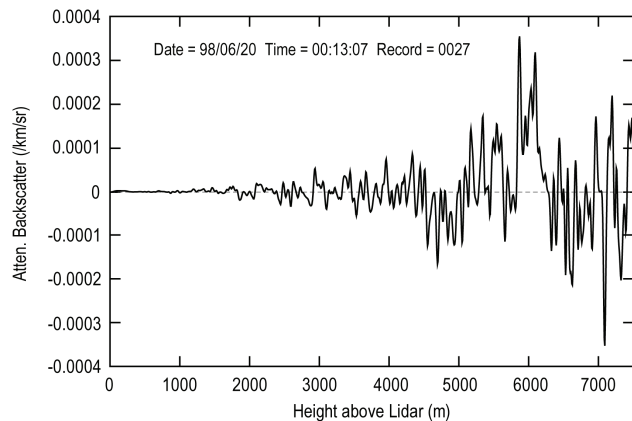


Figure 6. Attenuated backscatter profile of a deep but tenuous high cloud. The profile has been smoothed using a Gaussian filter with a width of 5 points. (There are 5 points between $\pm 1\sigma$ in the Gaussian smoothing function.)

A profile of a tenuous, high cloud (most likely cirrus) is plotted in Figure 6. The multilayered nature of the profile is typical of these clouds. The sharp top of the cloud at 6.3 km indicates that the cloud has not attenuated the lidar signal completely and that the true top of the cloud is being seen. This behaviour can be contrasted with that of dense clouds, typified by the low water cloud described below, where an exponential decrease in the signal is seen. The con-

siderably lower SNR at the higher altitudes, compared with Figures 3-5 is apparent. Even after smoothing with a 5-point Gaussian filter, the cloud still barely stands out above the noise, making interpretation of single profiles often difficult. Such clouds are more easily detected in height versus time plots.

High clouds can often be several kilometres deep as can be seen in Figure 6. However, these clouds exhibit a large range of behaviours. Cloud can range from the tenuous and deep cloud seen in Figure 6 to the appreciably stronger and much shallower cloud seen in Figure 7. The cloud in Figure 7 was detected some seven hours earlier than that in Figure 6.

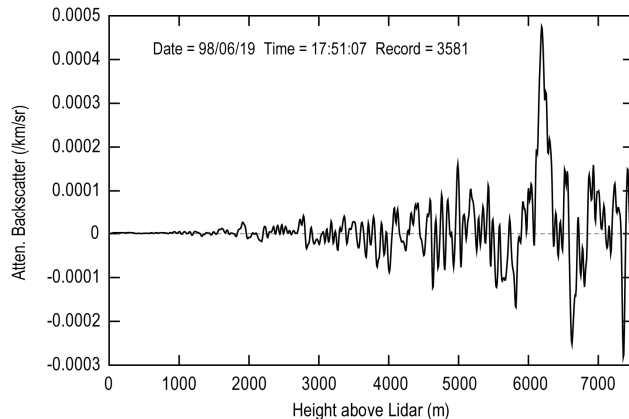


Figure 7. Attenuated backscatter profile of a strongly scattering, but thin high cloud. A 5-point Gaussian smoothing filter has been applied.

4.1.4. Middle-level clouds

As might be expected, being lower, these clouds are more easily detected by the MiniLidar. Again, these clouds vary considerably in strength, depth and form. Occasionally these clouds can attenuate the lidar signal, although this is difficult to determine from single profiles. Precipitation can often be seen falling from these clouds as will be illustrated below. Occasionally the precipitation attenuates the lidar signal sufficiently to mask the cloud signal almost completely. A profile of a multi-layered, middle-level cloud is plotted in Figure 8.

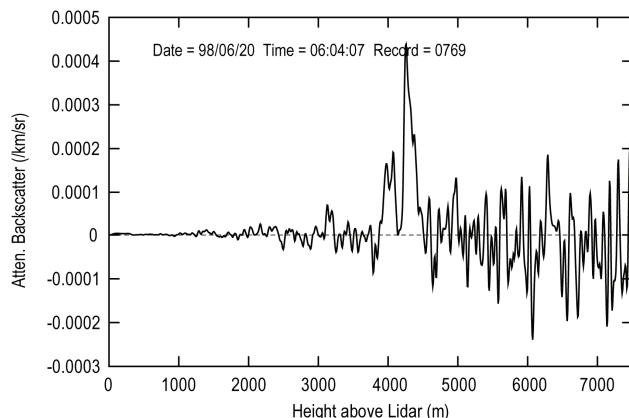


Figure 8. Attenuated backscatter profile of a multi-layered middle-level cloud at an altitude of around 4000 m.

4.1.5. Low (water) clouds

In the absence of precipitation, the atmospheric feature that is most easily detectable with the MiniLidar is low cloud. The droplets in these water clouds scatter the laser radiation very strongly creating a strong signal with high SNR. However, strong scattering also means strong attenuation and the lidar signal is usually attenuated before the top of the cloud is reached. An exponential decrease of the signal down into the noise can be seen on plots of attenuated backscatter when expanded on the height axis. Note that no information is available above the apparent cloud top; only noise is seen. In this way, attenuating low clouds may prevent the detection of overlying clouds. An example of the signal from a dense water cloud is plotted in Figure 9.

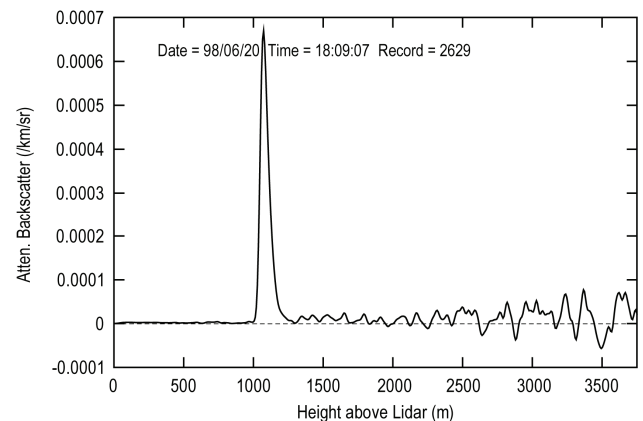


Figure 9. Attenuated backscatter profile of an attenuating water cloud with a base 1000m above the lidar. Note the exponential decrease of the signal up to the apparent top at 1250m. No information is available above this height.

4.1.6. Fog

From the foregoing discussion on the decrease of detectability of clouds as they are further from the MiniLidar, one might expect that fog would give the strongest signal with the highest SNR. However, this is not the case because the fog occupies the overlap region of the lidar described above. The laser beam illuminates the fog, which scatters the light strongly, thereby also attenuating the beam strongly. However, because the scattering is outside of the field of view of the receiver, most of this light is not detected. The result is that the detected signal is very much reduced from what would be expected and it is usually down to the noise level in the first 100 m above the lidar. Figure 10 illustrates an attenuated backscatter profile measured during fog. No information is available above about 100 m where the signal has been totally attenuated leaving only noise.

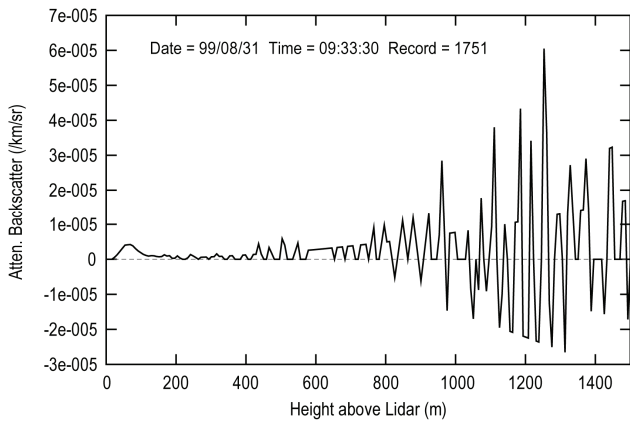


Figure 10. Attenuated backscatter profile obtained during fog showing an apparently weak layer near the surface, but only noise above.

4.1.7. Precipitation

The signatures of precipitation in lidar profiles are extremely variable. As would be expected, precipitation is usually seen below clouds, which can be identified as described above. However, precipitation can sometimes be heavy enough to extinguish the lidar signal before it reaches cloud base. Probably the most obvious characteristic that distinguishes precipitation from clouds in lidar profiles is the lack of a sharp lower boundary in the former. This is most likely a consequence of the different fall velocities of the various components in the precipitation droplet size distribution. (The author has, in fact, successfully employed the magnitude of the derivative of the attenuated backscatter signal with range to distinguish precipitation from clouds in an automatic cloud detection algorithm).

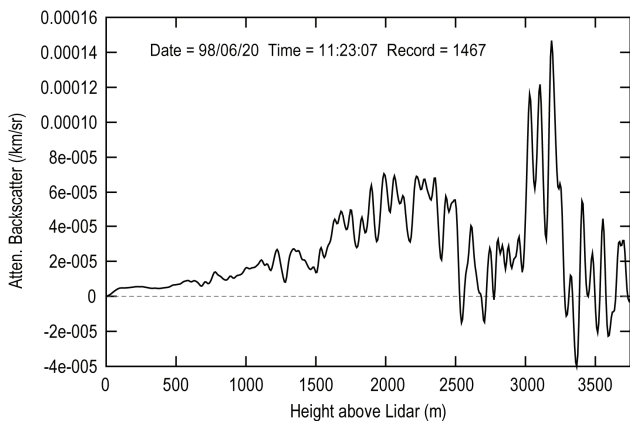


Figure 11. Precipitation, probably a mixture of ice and water, from a cloud with a base at 3000 m.

An example of precipitation from a mid-level, ice cloud is presented in Figure 11. The precipitation, based on the irregular signal profile and the altitude, is most likely a mixture of ice and water. In contrast to the ice precipitation shown in Figure 11, the smoother profile usually associated with rain is shown in Figure 12. The contrast between the 'rounded' base of the precipitation profile and the sharp increase in signal at cloud base is obvious. The precipitation profile changes with time as a re-

sult of the in-cloud rain formation processes and the different fall velocities mentioned above. The situation just 13 minutes after that depicted in Figure 12 is shown in Figure 13 and a quite different precipitation profile is apparent. The rain now extends from cloud base to the surface.

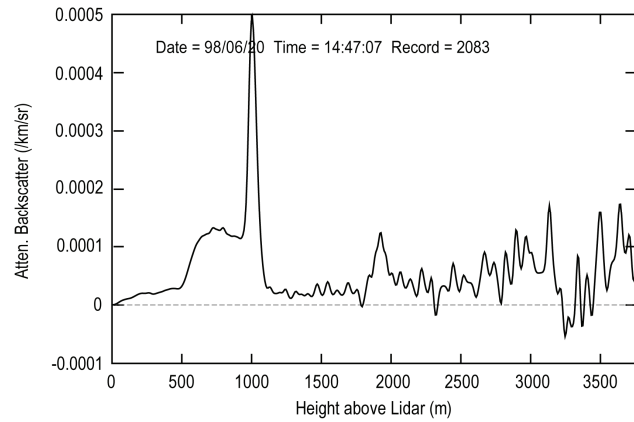


Figure 12. Rain falling from below a water cloud with a base near 950 m.

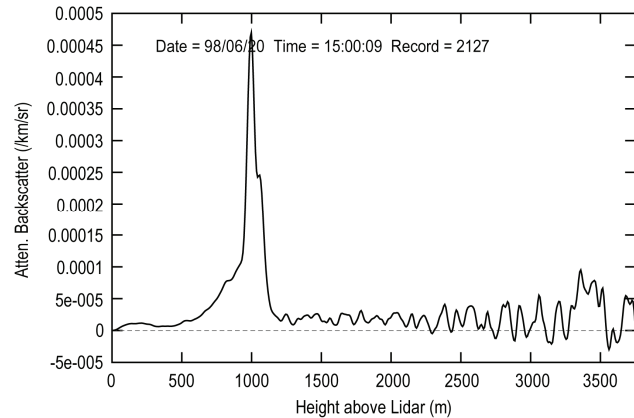


Figure 13. Rain extending from cloud base near 950 m down to the surface. The profile was recorded 13 minutes later than that in Figure 12.

4.2. Height versus Time Plots

In this section, attenuated backscatter data are plotted in two dimensions as a function of height (in km AMSL) and time. This form of presentation permits a better appreciation of changing atmospheric conditions during the 24-hour period.

Individual backscatter profiles have been smoothed with a 3-point (45-m) Gaussian filter. Then, in order to improve the SNR of the resulting plot, while at the same time recognising that finer temporal detail would be lost in the printing process, the horizontal resolution has been reduced to five minutes, five profiles being averaged at every plotted time interval. Data are plotted on a logarithmic scale with the magnitude of the attenuated backscatter indicated by a colour bar at the base of the figures. Also, the top ten range bins have been coloured magenta to indicate when 'baseline' conditions were prevalent at CGBAPS; black signifies that the conditions were not baseline.

4.2.1. Frontal Phenomena

A wide variety of atmospheric phenomena associated with the arrival of a cold front over CGBAPS on 20 June 1998 can be seen in Figure 14. Winds on that day backed from the NE to the NW while increasing from about 35 km hr^{-1} in the morning to up to 50 km hr^{-1} in the evening. The surface temperature at CGBAPS climbed steadily from 9.5 degrees, reaching 12.5 degrees at 1230 when the arrival of rain was associated with a drop in the temperature until around 1530.

For the period from midnight until about 0930, the figure shows an aerosol layer, extending to around 250 m, beneath high cloud at 6 km, indicated by the red patches; with lower layers of cloud between 4 and 5 km. Occasional fall streaks can be seen as orange streaks below the clouds during this period. Another layer of cloud with a base around 1500 m can be seen arriving over CGBAPS at 1130. Precipitation from this cloud (yellow and orange streaks) can be seen reaching the surface at this time. Evidence of the 'lidar dark band' (see below) just below cloud base indicates that the melting level was near this altitude. From midday, the cloud backscatter signal can be seen to strengthen, indicating an in-

crease in the number density or size of the cloud droplets, while the cloud base dropped further, occasionally to below 1000 m. Heavy rain can be seen from midday until about 1430 with shorter periods of precipitation occurring during the remainder of the day.

Note that the dense water clouds seen during the afternoon attenuate the lidar signal completely and prevent the detection of any clouds at higher altitudes, except during breaks in the lower cloud as occurred briefly at 1900.

The single-profile plots shown in section 4.1 can now be related to the atmospheric features shown in Figure 14 via the times shown in the headings of the profile plots and the ordinate in this figure. Note, in particular, the ABL shown in Figure 3 (0002), the high cloud in Figure 6 (0013), the multi-layer, mid-level cloud in Figure 8 (0604), the strongly attenuating water cloud in Figure 9 (1809) and the precipitation moving to lower levels during the period 1123 to 1500 as plotted in Figures 11, 12 and 13.

The increase in the noise with range shown in Figure 2 can be seen in Figure 14 as a change in the colour of the speckled background from dark blue near the bottom of the figure to yellow at the top.

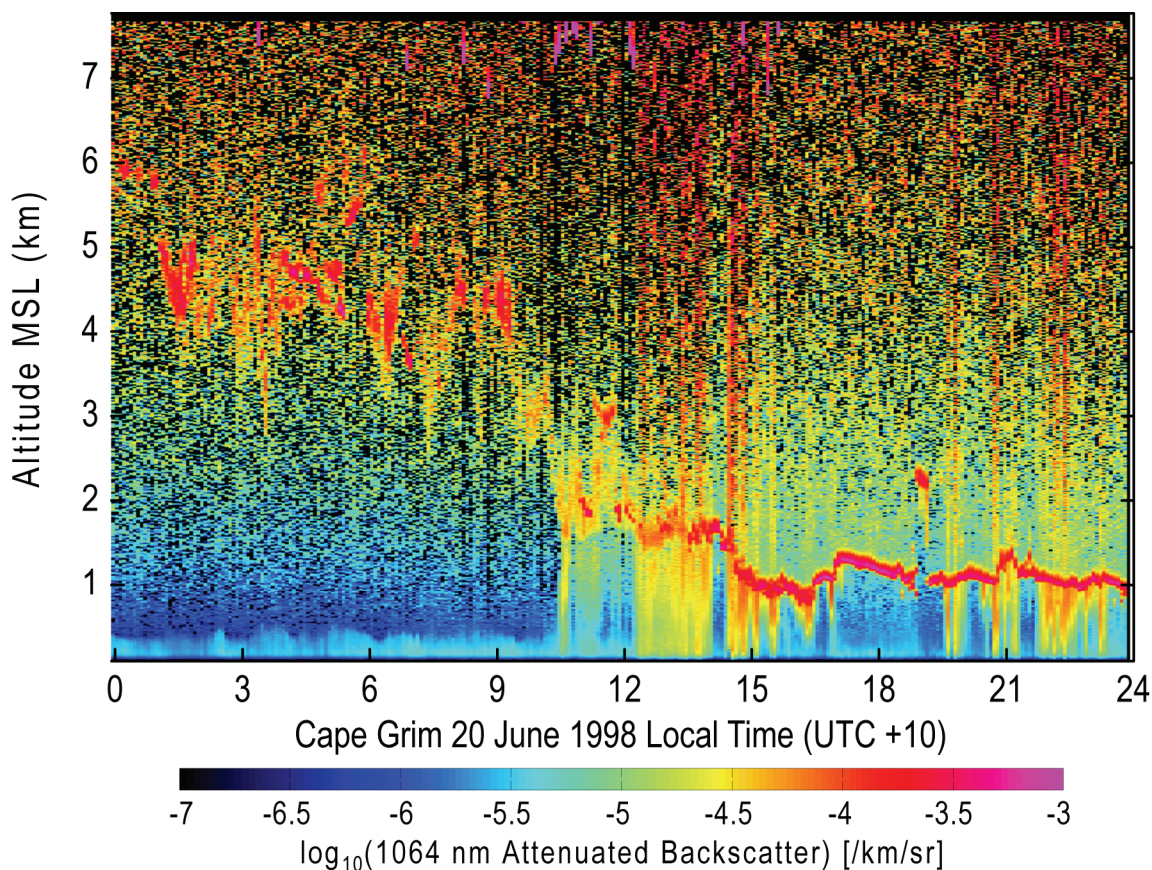


Figure 14. Atmospheric phenomena revealed by the MiniLidar during the passage of a cold front over Cape Grim on 20 June 1998. Attenuated backscatter is plotted on a logarithmic scale indicated by the colour bar beneath the figure.

4.2.2. Clouds and Precipitation

Two, strongly contrasting, further examples of clouds are illustrated in the following figures. Figure 15 shows a fairly solid deck of stratiform cloud above a layer of broken cumulus. Both layers start at the same high at midnight but thereafter diverge with the upper layer climbing to 1800 m while the lower layer descends to 500 m. Light precipitation can be seen falling occasionally from both layers.

An occluded front was to the south of Tasmania with a high pressure region centred over Victoria on this day. Winds blew steadily from the west and varied from 30 to 50 km hr⁻¹. Baseline conditions existed throughout most of the day.

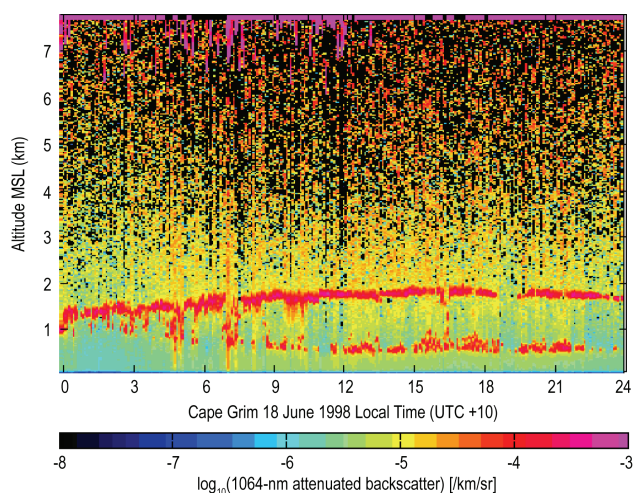


Figure 15. A layer of stratiform cloud overlying broken cumulus on 18 June 1998.

In contrast, Figure 16 illustrates a fairly common scene at CGBAPS, that of frequent short showers falling from small cumulus. It is interesting to note the variation in height in the bases of the clouds. The apparent extension of the vertical bands identifying the showers to heights above the clouds is explained by the overwhelming of the wiper system by the intensity of the showers and the attenuation and scattering of the laser beam by the water droplets on the window. This resulted in a reduction in SNR to levels similar to those experienced in conditions of fog.

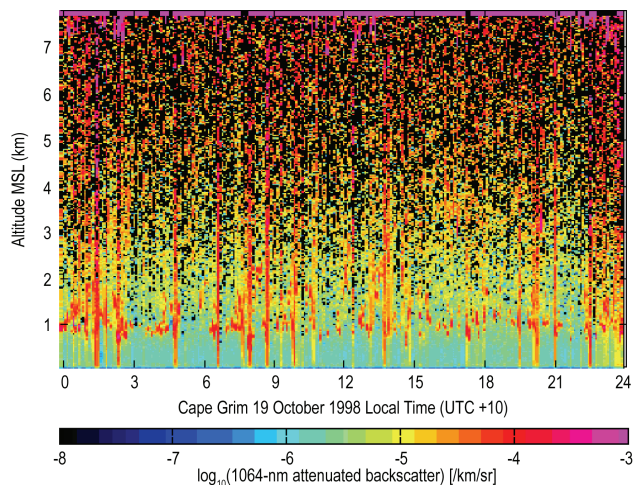


Figure 16. Short, intense showers from small cumulus. The apparent extension of the shower bands above the clouds is caused by rain on the window.

On this day winds were from the south west following the passage of a cold front two days earlier, and increased in strength from 40 km hr⁻¹ at midnight to over 70 km hr⁻¹ by the following evening. As indicated by the magenta band at the top of the figure, baseline conditions existed throughout most of the day.

4.2.3. Rain, Melting Level and the Lidar Dark Band

On 24 June 1998 an intense low was located to the east of Bass Strait. Winds were initially from 195 degrees but backed slightly to the south at around 1230. Wind speed varied between 40 and 60 km hr⁻¹ and the temperature between 7 and 9 degrees.

The lidar record in Figure 17 shows two distinct periods. In the morning, an aerosol layer extended to 1000 m was topped by thin stratiform cloud between 0200 and 0400. Several bands of cloud, varying in altitude between 1200 and 3500 m, began arriving after 0900. Following the passage of some initial rain bands at 1100 and 1200, an extended period of rain began at 1400 and continued for the remainder of the day. Cloud base varied between 1000 and 2000 m and isolated scud clouds can be seen in the figure at lower levels and immersed in the rain.

An interesting feature is the region of reduced backscatter (indicated by the yellow band) that can be seen to be consistently at around 1200 m despite the height variation of the cloud bases above this level. This is called the 'lidar dark band' and is related to the radar bright band. Both features are associated with the melting level [Sassen and Chen, 1995; Venema *et al.*, 2000]. Therefore it is likely that the clouds above 1200 m contained, or were composed of, ice.

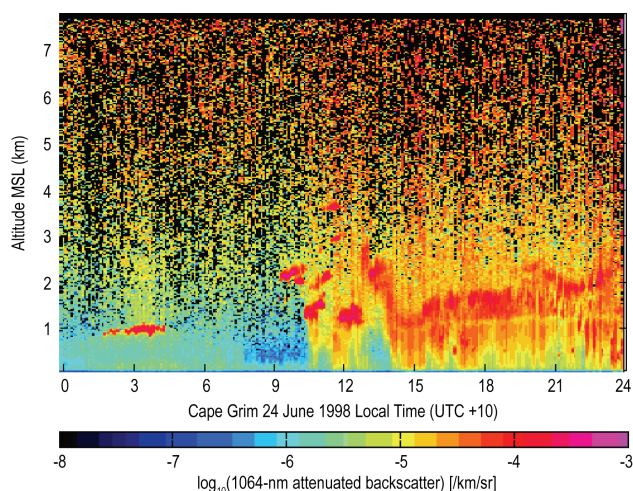


Figure 17. Afternoon rain on 24 June 1998. The lidar 'dark band' associated with the melting layer can be seen as the yellow band, indicating a region of reduced backscatter, at around 1200 m.

4.2.4. Fog

On 3 January 1999, a weak front passed CGBAPS at about 0100. Winds were initially less than 10 km hr⁻¹ from the south east and increased rapidly to greater than 40 km hr⁻¹ while veering to the south west.

The lidar record in Figure 18 indicates that fog was present until just after 0600. This can be seen by the thin red line along the surface with a weak backscatter region above. The marked increase in noise with altitude results from the lidar detector amplifier being set to maximum gain to accommodate the very weak signal detected in fog. See, for comparison, the profile in Figure 10.

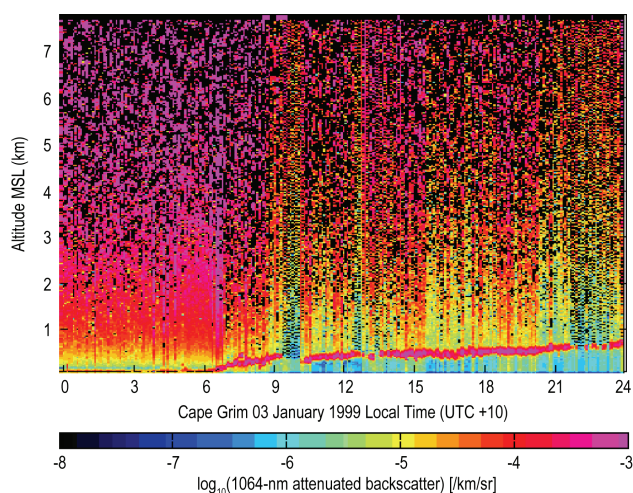


Figure 18. Morning fog, rising from the surface to become a layer of stratiform cloud overlying the ABL.

4.2.5. Atmospheric Boundary Layer

The variation in the structure of the boundary layer during 28 August 1999 is shown in Figure 15. A high pressure system was centred over Adelaide on this day and winds at CGBAPS were from the SW at 40 to 50 km hr⁻¹ until about 1900 when they dropped to below 20 km hr⁻¹ as the wind swung more to the south. Thin cloud can be seen capping the boundary layer until about 0400. Baseline conditions existed between 1050 and 1830. The detector amplifier gain was increased by a factor of more than three between 1130 and 1830 to accommodate the decrease in particulate backscatter (and signal strength) during this period.

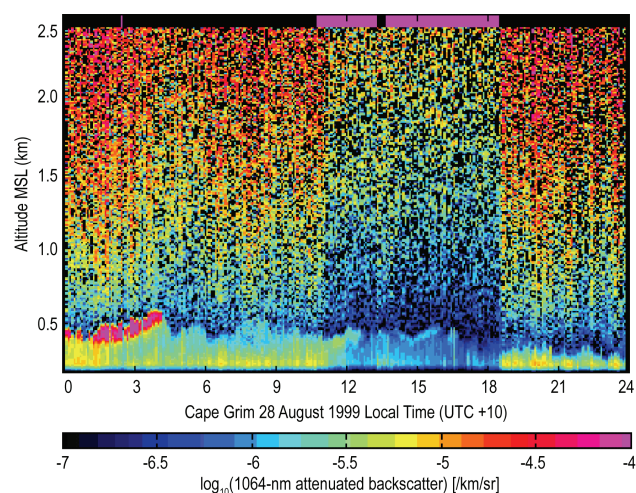


Figure 19. Variations in the boundary-layer aerosol during 28 August 1999. The magenta band at the top indicates the period during which baseline conditions existed at CGBAPS.

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The author gratefully acknowledges the assistance of some former members of CSIRO Atmospheric Research. Graeme Patterson designed some of the improved electronics and wrote the data acquisition software to drive the digitizer card and energy monitor. Reinout Boers modified some software, written by Denis O'Brien following discussions with the author, to enable remote control of the lidar system over the internet. The staff of the Electronics Development Laboratory at Aspendale, led by John Bennett, assembled, tested and calibrated various electronic circuits employed in the system.

Without the friendly, willing and extremely capable support of staff of the Cape Grim Baseline Air Pollution Station, the deployment of the system at Cape Grim and its control from Aspendale would have been impossible. The collaboration of Stuart Baly, Alan Gough, Laurie Porter and Brian Weymouth was particularly valuable.

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EFFECT OF TEMPERATURE ON THE CAPE GRIM UV-B RECORD

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Abstract

The detector dark current of the Cape Grim UV-spectrometer (SRAD), recorded before each spectrum, is clearly affected by spectrometer temperature, and correlates well with a change in the wavelength scale of the spectrometer. These two effects in combination provide a clear marker of spectrometer temperature change. This phenomenon is only apparent when the spectrometer temperature approaches the set-point of the spectrometer heater, and is delayed relative to changes in air temperature. The effect of temperature on spectral sensitivity is harder to quantify, as there are very few measurements made under the necessary conditions of clear skies and air temperatures high enough to cause variations in spectrometer sensitivity. A survey of 5 years of data has identified periods where an effect is observable, although difficult to quantify.

A method for identifying 'high temperature' spectra has been developed using the dark current, which flags 1.4% of all spectra as possibly temperature affected, and 0.6% flagged as probably temperature affected. Flagged spectra are mainly to be found in the late summer. As the magnitude of the effect has not been well estimated, no correction has been applied and the data have been retained within the processed dataset. An apparently unrelated increase in spectrometer dark current is observed early and late in the day on most days, but no cause has been identified.

1. Introduction

To quantify any long-term changes in ultraviolet radiation, and to understand the effects of short-term UV changes on atmospheric chemistry, it is important that factors that affect the accuracy of the measurement are well understood. Especially important are factors that effect the measurement but are not necessarily detected during the calibration process. One example of this is the recently identified change in performance of the input optics of the spectral radiometers (the diffuser) with temperature [McKenzie *et al.*, 2005; Ylianttila and Schreder, 2005]. In operation the temperature of the diffuser changes due to environmental conditions, such as the air temperature and solar exposure. During calibration, however, the diffuser is often at a constant temperature that may not be related to the normal operating conditions. Uncorrected, such effects can produce a bias in the measurement record.

In early studies of the Cape Grim UV-B spectrometer SRAD, a significant temperature dependence was observed, with a wavelength shift (0.07nm/°C) and a sensitivity change (up to -6% per °C at 368 nm) [Wilson, 2006]. Such large changes in sensitivity would seriously decrease the usefulness of the measurements. As a result, the temperature of the spectrometer is regulated. However, due to the location of the instrument, it is not simple to record the temperature of the spectrometer, and so it has not been recorded. It would be useful to identify a proxy for spectrometer temperature so that the effect of temperature can be assessed and periods where spectrometer temperature is variable identified. Such periods could then be excluded from analysis.

The wavelength shift is measured for each spectrum as part of the calibration process. However, temperature is not the only variable that can cause changes in the measured wavelength scale, as instrumental wear and tear, spectrometer realignment and transient cloud effects can all cause a variation in the retrieved wavelength shift. The spectrometer sensitivity is also determined when there are clear sun conditions. However, these conditions are not common at Cape Grim and so only a small fraction of the data could be used to identify temperature effects.

In a report characterising the performance of a UV spectrometer, [Gröbner, 2003] a close correlation was reported between the dark current determined for the photomultiplier and the temperature of the spectrometer as a whole. In the same study the sensitivity of the spectrometer was found to change by -4 ± 1 % per 10°C. The dark current sensitivity to temperature is well understood, as the signal level is determined primarily by the number of electrons emitted (thermally) from the photocathode and the magnitude of the accelerating voltage applied.

In the work presented here the use of the spectrometer dark current as a proxy for spectrometer temperature will be investigated, as this is measured at the start of every spectrum. Once periods of 'high' temperature spectra are identified, the effect on spectrometer sensitivity will be considered. This will then be used to flag periods where significant temperature effects exist in the Cape Grim UV-B record.

2. Methods

The measurements analysed here were made with the Cape Grim UV-spectrometer system (SRAD) which is documented elsewhere [Wilson, 2006]. In brief a scanning double monochromators (spectral resolution 0.9 nm Full Width at Half Maximum) is mounted on top of a sun-tracker. Spectral scans are made with either no shading (global irradiance) or with a shading disk between the input diffuser and the sun (diffuse irradiance). The spectrometer is calibrated by comparison of the SRAD direct beam irradiance (calculated from the difference between the global and diffuse irradiance) and the direct beam irradiance, measured with a co-located sun-photometer. Further details of the calibration process are presented elsewhere [Wilson, 2006; Wilson and Forgan, 1995]. Such a comparison is only possible when there is a clear view of the sun, and the diffuse irradiance is constant (i.e., ideally cloud free viewing conditions). Changes in irradiance over the time period of the measurements (~10 mins) can lead to significant variability in the derived sensitivity.

The spectrometer dark current is measured by blocking the radiation entering the Optronics Inc. OL-752 spectrometer housing. The signal measured (in amps) under those conditions, measured with the spectrometer set at 298 nm, is recorded just before each spectral scan. This measurement is subtracted from all measurements made during the spectral scan.

The Cape Grim site is not exposed to significant variations in daily temperature. As a result, the instrument temperature is stabilised by a resistive heater, controlled by a thermocouple sensor attached to the outside of the spectrometer case. For the 5-year period investigated here (2000-2004) the controller was set to 25°C.

As part of the data assessment presented here two methods of wavelength correction have been tested, both based on a comparison between the observed and a reference spectrum [Wilson, 2006]. The methods of Slaper *et al.*, [1995] and Bernhard *et al.*, [2004] were applied to >2600 measurements made in March 2004. The spectral shifts calculated by the two methods were very similar, with a median difference of less than 0.01 nm, implying no significant bias.

A second test was used to assess the wavelength scale reproducibility. The wavelength scale of the spectrometer is expected to change only slowly with time due to thermal effects. Therefore the following scatter estimate (d_i) was calculated.

$$d_i = \lambda_i^s - 0.5 \times (\lambda_{i+1}^s + \lambda_{i-1}^s)$$

Here λ_i^s is the wavelength shift at 395 nm for the i^{th} spectrum of the day. The variation in d_i will reflect both the reproducibility of the wavelength scale from the spectrometer, and the scatter in the wavelength correction method. The average \bar{d} should be (and is) not significantly different from zero. The standard deviation of d was found to be 0.013 nm for both methods. As no difference was found, the method of Slaper *et al.* has been used as it was computationally simpler.

The primary focus of this work is measurements made at solar zenith angles less than 70°. The data for solar zenith angles greater than 70° will be discussed separately.

3. Results and Discussion

3.1. Lauder measurements

In 1996/1997 the spectrometer was moved to Lauder, New Zealand for a period of comparison with the NIWA operated UV instrument. Lauder experiences significant diurnal temperature changes, with summer daytime temperatures well above 25°C. There was clear evidence in the data of the effect of temperature on the wavelength shift and sensitivity of the instrument.

As shown in Figure 1, the data for 15 February 1997 show large positive changes in the wavelength shift in the middle of the day, accompanied by a decrease in the spectrometer sensitivity measured at 368 nm. The dark current also increased significantly. By March the ambient temperature did not get as high and the spectrometer temperature controller managed to stabilize the spectrometer temperature, as is clearly visible in the right hand panel. There are none of the large changes observed in February. However, the derived sensitivity is clearly quite variable in the morning. This is due to the presence of broken cloud, which has not been filtered out by the simple cloud filter that has been used as clearly demonstrated in Figure 2.

The spectrometer sensitivity and wavelength shift are plotted as a function of the measured dark current for the period 15-18 February 1997 in Figure 3. Clearly the dark current is significantly correlated to both wavelength and spectrometer sensitivity, and by inference to the spectrometer temperature.

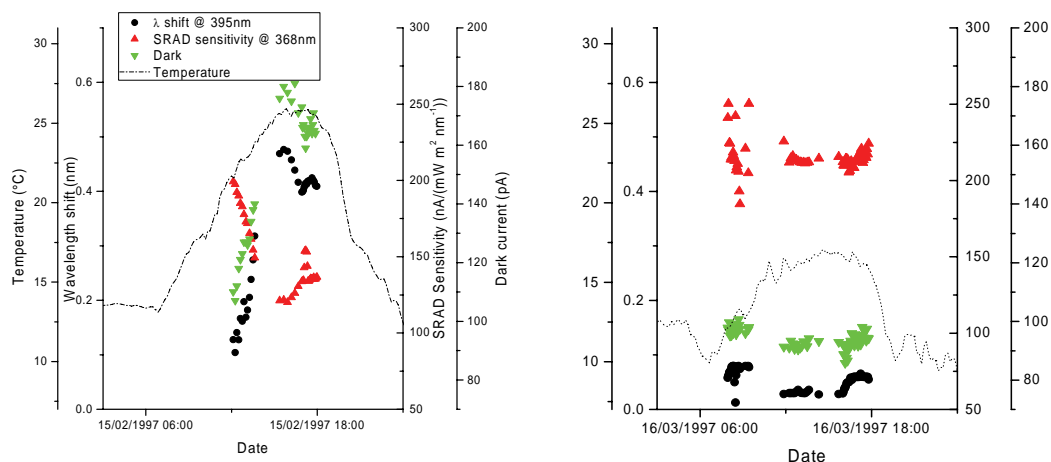


Figure 1. Indicators of SRAD spectrometer performance at Lauder, New Zealand. Axes and scales are the same for both plots. The left hand plot shows data for February 15 1997 and the right hand panel shows the same parameters for 16 March 1997. For the data on 16 March the early record is disturbed by cloud, causing a variation in the derived SRAD sensitivity. The temperature data was kindly supplied by Andrew Harper (NIWA).

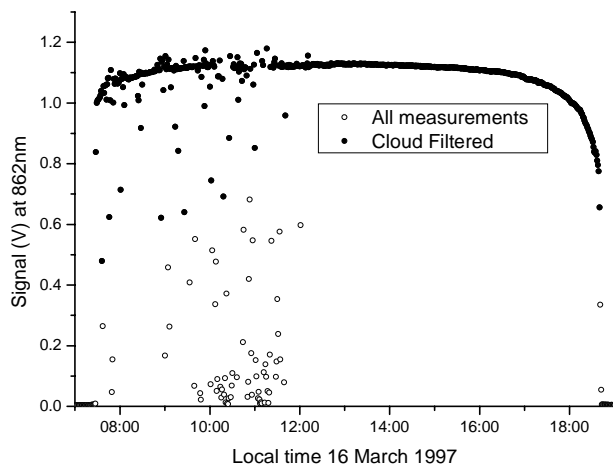


Figure 2. SPO1-A sunphotometer signal at 862 nm for 16 March 1997 (data supplied by B. Forgan). The figure shows that many measurements in the morning were accepted by the simple cloud filter used (solid symbols). However, a comparison with the afternoon demonstrates that the morning measurements have been significantly affected by cloud which leads to the large changes in observed signal.

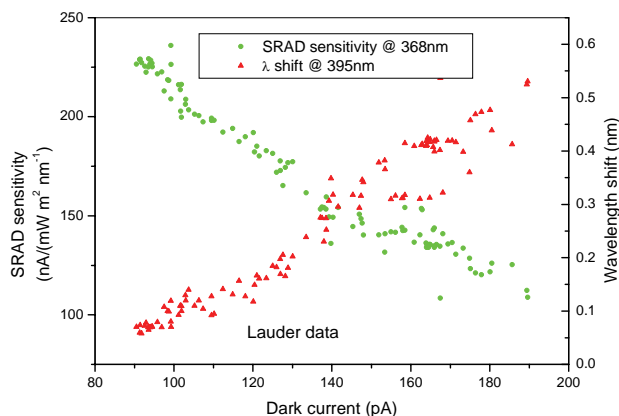


Figure 3. Sensitivity and shift as a function of dark current. Data from 15-8 February 1997.

3.2. Cape Grim Measurements

The measured dark current for the two year period 2003-2004 is shown in Figure 4. The data shown are all spectra collected during this two year period under clear sun conditions and solar zenith angle less than 70° (2070 spectra). The period has been chosen as the conditions under which the spectrometer ran were reasonably constant throughout. The dark current shows a slight increase in the second half of 2003 and a more substantial increase following the return of the instrument from repair in the second half of 2004. In general these changes are much smaller than those observed when the instrument was operating in Lauder. This is partly due to the photomultiplier operating at a lower voltage (resulting in a lower overall dark current) and also because of the more stable instrumental temperatures.

There is considerable variability in the derived SRAD sensitivity, at least partially due to the effect of clouds on the derivation of the direct beam irradiance (as noted earlier). Similarly, the wavelength shift goes through a number of step changes due to the instrument being powered down and also when the wavelength scale has been re-calibrated. It is not simple to identify within the two datasets periods where there has been a temperature effect. In contrast, the dark current record shows clear periods in the summer months when the dark current rises significantly, as indicated in the middle panel of Figure 4 by boxes.

A clearer picture emerges when a small portion of this record is investigated, looking at just the dark current and shift. In this case it is possible to use all the measurements, rather than just those made during clear sun periods. A period in March 2003 is shown in Figure 5 to illustrate the observed behaviour. In the last three days, when the air temperature climbs above 20°C there is a (positively) correlated change in both the dark current and wavelength shift, and based on the evidence presented previously it is reasonable to assume that this is due to

an increase in the temperature of the spectrometer. Below 20°C the temperature regulation system is functioning, decoupling the spectrometer's temperature from the air temperature. SRAD's temperature response appears delayed relative to the air temperature measurement, presumably due to the inherent thermal inertia in the system, as has been observed elsewhere [Gröbner, 2003]. If the spectrometer temperature change follows the change in external temperature but with a time lag, the wavelength shift dependence upon temperature is similar to that reported earlier (i.e. 0.07 nm/°C).

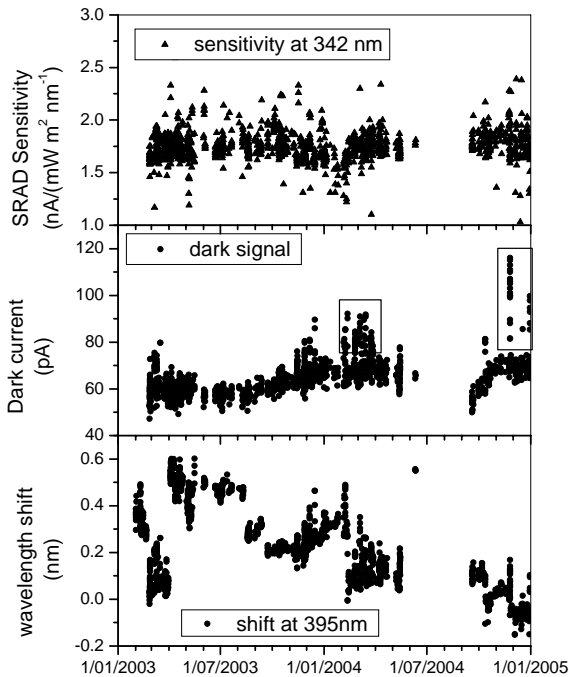


Figure 4. SRAD wavelength shift, measured dark current and sensitivity 2003-2004. Only data where clear sun conditions prevail are shown, as this is a prerequisite for the sensitivity determination. Note that the sensitivity is lower in this data relative to the New Zealand data due to changes in both the photomultiplier voltage and input optics. Periods of increased dark current are indicated by boxes.

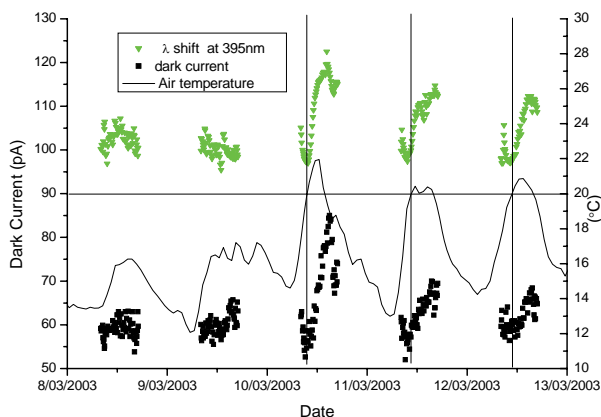


Figure 5. Air temperature, shift and dark current for 4 days in March 2003. The horizontal line is at 20°C and the vertical lines indicate when the atmospheric temperature reached 20°C.

An inspection of the data from early 2000 finds a similar behaviour, although the point at which the spectrometer responds to external temperatures appears to be closer to 23°C. This could be due to changes in the heating system for the spectrometer, as the system was dismantled when the spectrometer was sent back for repair in 2001.

The hourly average temperature record for Cape Grim has been inspected for the years 2000-2004 to assess the frequency of warm periods. Treating the years individually it was found that there was a maximum of 240 hrs per year when the hourly average temperature was greater than 20°C, and between 11 and 50 hours with $T > 22^\circ\text{C}$. It can be concluded that while there is a clear effect of temperature on the record, the number of days where the impact is significant is likely to be small.

3.3. Temperature effects on sensitivity

For the assessment of the effect of temperature on sensitivity it needs to be warm (above 20°C) and cloud free (to permit a reliable estimate of the direct beam irradiance). Unfortunately, nearly all days where the temperature was above 20°C there is significant cloud cover evident in the sunphotometer data. There is one clear day (17 February 2000) which provides some insight into the effect of temperature. The relevant data from this period are presented in Figure 6. There are other warm days with partial sunny records (1-4 hours), which support the general observations made below.

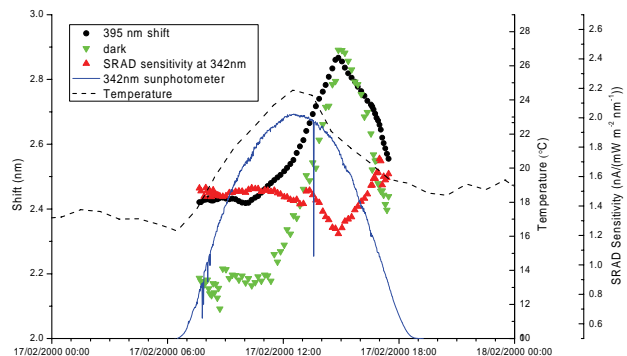


Figure 6. Temperature and SRAD quality control data for 17 February 2000. Included is the measurements made with the 342nm channel of the SPO1-A sunphotometer.

There is clear evidence of the effect of temperature on the shift, dark current and sensitivity. Throughout the day there are changes in dark current and wavelength shift. These changes significantly lag the changes in temperature, as noted before. In this case the maximum hourly temperature is reported for 12:00, and the maximum variation in spectrometer response (wavelength shift, dark current and sensitivity) is seen at 15:00. The wavelength shift is linearly correlated to the dark current ($r^2 = 0.97$). The relationship between dark current and spectrometer sensitivity is more complex, as demonstrated in Figure 7, which shows the variation in sensitivity as a function of dark current. It can be

seen that the dark current increases from around 60 pA to near 100pA without a clear trend in sensitivity (region A). Above this point the sensitivity starts to decrease markedly (region B). From the figure there is also evidence of the sensitivity lagging the dark current. This is illustrated by delaying the sensitivity by 2 scans (approximately 20 mins), whereby the correlation between the two parameters is clearly improved.

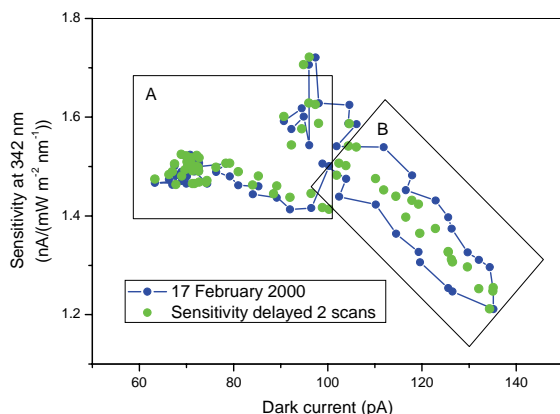


Figure 7. Relationship between observed sensitivity of SRAD and the measured dark current. For the green points the sensitivity measurements have been offset (delayed) by two scans. Region A displays an unclear dependence of sensitivity on dark current. In region B there is a clear decrease in sensitivity with increasing dark current.

For the data above 100pA (region B) there is a change in sensitivity of 6-7%/ °C. This has been derived by converting the observed wavelength shift into a temperature change as estimated earlier. Using the wavelength shift as a proxy for instrument temperature also implies that the onset of significant change in spectral sensitivity is some 3°C above the point at which the dark current begins to show temperature dependence. In region A the dependence of spectrometer sensitivity on temperature is harder to gauge. Based on several different days throughout the 5 year period the temperature driven change in sensitivity in this intermediate temperature range appears to be significantly less than 1%/°C.

In summary, there spectrometer sensitivity begins to change 3°C above the temperature at which the dark current does. Beyond this temperature there is a marked temperature dependence on sensitivity as well. The difference in behaviour of the sensitivity and dark current presumably arises from the differences in the physical processes underlying the two effects.

3.4. Identification of spectra affected by temperature

While there has been a clear indication that temperature does affect the data recorded at Cape Grim, the impact is small as there are few measurements that are made when air temperatures are sufficiently high. Further, as shown in section 3.3 air temperature alone is a poor indicator of a change in

sensitivity. The dark current is a better indicator of spectrometer temperature, as it is dependent upon the temperature of the detector. There are variations in the dark current with time due to instrument set-up and the aging of componentry, as shown in Figure 8 (a), which prohibits the use of a simple 'trigger level' to identify temperature affected spectra. A filter has therefore been devised to identify measurements where temperature is likely to have affected results. On a monthly basis the median dark current and Median Absolute Deviation (MAD) [Rousseeuw, 1990] is determined. Scans where the dark current is greater than 3.5 times the MAD from the monthly median are flagged as possibly affected by temperature. A second level of flag is set when, in addition, the dark current increases 30 pA above the monthly median dark current, and the data are flagged as probably affected by temperature, in an attempt to identify the significant sensitivity changes highlighted in Figure 7. The spectra flagged by this process as a function of date are shown in Figure 8. In total, 1.4% of the spectra (1723) have been flagged as being possibly affected by temperature and 0.6% flagged as probably affected by temperature. As can be seen from Figure 8(b) the filter identifies no spectra during the winter months, suggesting that the filter is not overly aggressive. The maximum temperature effects lie in late summer.

Daily median sensitivities have been calculated excluding all temperature flagged data. When these results are compared with an identical analysis using all data there are 8 days in the 5 years 2000-2004 when there is greater than 0.2% difference in median. In all cases the difference is less than the 95% confidence interval on the daily value. So while calibrations will be based on only those days not flagged by the procedure outlined above, it does not make a difference to the calibration of the data used in the period 2000-2004.

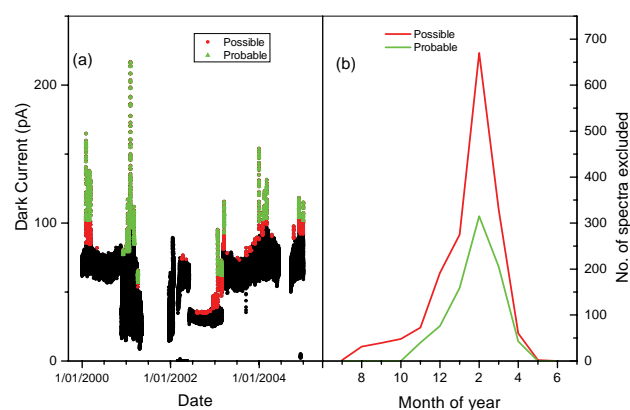


Figure 8. Filtering of SRAD spectra based on the recorded dark current. Panel (a) shows the 125,000 dark current measurements recorded from all spectra 2000-2004. Those marked in red have been marked as possibly affected by temperature. Those marked in green have been flagged as probably affected by temperature. Panel (b) shows the monthly distribution of the filtered spectra for both categories, showing the expected distribution for a temperature based filter.

3.5. Solar zenith angles > 70 degrees

The previous analysis has been limited to measurements made at solar zenith angles less than 70° . At solar zenith angles greater than 70° there is marked change in behaviour, with the dark current increasing, and the shift remaining constant or decreasing. To remove the effects of high temperature, only data collected when the atmospheric temperature is below 20°C are considered.

An example of measurements made under these conditions is presented in Figure 9. Both early and late in the day, the dark current is higher. Presumably this is driven by environmental factors, although the lack of a clear pattern in the wavelength shift implies that the mechanism is not a variant of the simple temperature effect mentioned above.

These variations in dark current could be due to changes in stray light within the spectrometer. However these would be expected to be greatest in the middle of the day, as this is the time of greatest solar irradiance. It is also possible that this is due to a change in temperature gradients within the spectrometer. During the bulk of the day solar radiation will warm the top surface of the spectrometer housing. Outside these times the system will be warmed only by the spectrometer heater, mounted on the central section of the spectrometer. It is plausible that this could preferentially change the temperature of the detector, and hence the dark current. The change in dark current is consistent with a change in spectrometer temperature of less than 1°C . If this were source of the effect, some dependence on the amount of cloud might then be expected, but there are no clear differences between the mornings and afternoons in the two days shown in Figure 9. It may be that the difference in solar heating is not that significant.

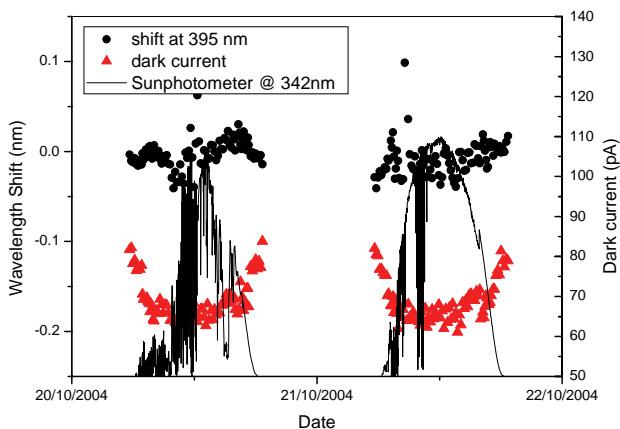


Figure 9. Wavelength shift and dark current for 2 days in October 2004, showing data from all zenith angles. The sunphotometer record of direct beam irradiance at 342 nm is also shown to highlight periods of cloud.

4. Conclusions

In this work criteria for identifying periods where air temperature may affect the UV measurements made at Cape Grim have been developed. Using these criteria the data has been flagged as either possibly or probably temperature affected. The flagged data have been retained within the dataset, allowing users to decide whether they wish to remove the data from consideration. The spectra identified as temperature affected do not have a significant impact on estimates of the instrument calibration.

Acknowledgements

I would like to acknowledge the ongoing efforts of the Cape Grim staff to keep the equipment running. The meteorological data used in this work was kindly provided by the Meteorology program of Cape Grim led by Arthur Downey and John Gorman. The temperature data for the New Zealand measurements were made by NIWA, and kindly supplied by Andrew Harper. While the instrument was in New Zealand Dr. Richard McKenzie and Mike Kotkamp provided much needed assistance in keeping the system running. I would also like to thank Don Anderson for his thoughtful comments and suggestions in reviewing this work.

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AEROSOL COMPOSITION AT CAPE GRIM: AN EVALUATION OF THE PM10 SAMPLING PROGRAM AND BASELINE EVENT SWITCHES

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Abstract

This work reports the results of an investigation into the effect of baseline event switches (criteria that define clean air, based upon wind direction and particle number) on aerosol mass and chemical composition measurements made on samples collected at Cape Grim. Aerosol mass and chemical composition of was determined for samples collected by a high volume aerosol sampler operated on a new baseline event switch that utilises the well-recognised seasonal cycle in particle number concentration to determine the maximum threshold for clean air. These were compared with mass and concentrations determined on samples collected using the traditional baseline event switch that relies on a single threshold value of particle number concentration. The new baseline event switch results in fewer samples with soil contamination and higher concentrations of non sea-salt species than the traditional baseline event switch so that we recommend permanently switching all aerosol sampling over to the new baseline event switch.

1. Background

During the lifetime of the Cape Grim program a number of general criteria have evolved to define clean air for collected samples and to operate a 'baseline switch'. The main baseline event switches (BEVS1 and BEVS2¹) are activated when winds are between 190° and 280° (measured at the 10-m level) and condensation nuclei (CN) is less than 600 cm⁻³. These conditions are encountered approximately 30% of the time. Use of this fixed CN limit has persisted to maintain consistent records, however the marked seasonal cycle in CN, with median concentrations of around 100 cm⁻³ in winter and 700 cm⁻³ in summer [Gras, 1995], as well as significant inter-annual variation, clearly indicate that a fixed CN level is less than ideal. Hence, a supplementary baseline criterion (and baseline switch) that utilises the previous five year's CN data for the current month selected for a 50-m level wind direction between 190° and 280° has been developed. The CN threshold is based on the 90th percentile of CN hourly medians for this period, interpolated using cubic splines to give daily values. Early in 2001, the Cape Grim Working Group recommended changes in the criteria used for operating the baseline switch for samplers making sample collections. This is in the form of a new switch (BEVS3) that operates in parallel with BEVS1 and BEVS2. BEVS3 was implemented in 2001.

The purpose of this work is to report the results of a comparison of aerosol mass and chemical composition measured on samples collected on instruments operated on BEVS2 and BEVS3, to ensure that switching permanently to BEVS3 sampling will not adversely impact on the long term aerosol mass and composition record collected at Cape Grim.

2. Methodology

2.1. Sampling

The composition of aerosols collected under baseline conditions at Cape Grim has been determined since 1981 using various high volume (HiVol) aerosol samplers with PM10 size selective inlets. Keywood [2003] summarised the history of aerosol composition measurements at Cape Grim until 2000, focusing on samples collected using the GoldTop HiVol, that was decommissioned in 2003 after one year of comparison with the replacement Ecotech 2000 HiVol sampler (HVA). A third HiVol, Ecotech 3000 (HVB) was introduced to the program in 2003. The times the samplers were operated on the different BEVS are listed in Table 1. Comparison 1 is the comparison between the GoldTop HiVol and HVA on BEVS2 and BEVS3 respectively before the GoldTop HiVol was decommissioned. Comparison 2 is the comparison between BEVS2 and BEVS3 using HVB and HVA.

Table 1. Details of comparison programs including times, samplers and baseline event switches.

Sampler	Period		Baseline Event Switch	Comparison
	From	To		
GoldTop	Mar 02	May 03	BEVS2	1
HVA	Mar 02	May 03	BEVS3	1
HVA	Aug 03	Aug 06	BEVS3	2
HVB	Aug 03	Aug 06	BEVS2	2

¹ BEVS2 is the same as BEVS1 except with a manual override.

Adjustments for seasonally averaged temperature and pressure were performed on the sample volumes for HVA so that data are reported at standard temperature and pressure. HVB measures ambient temperature and pressure so that a seasonal correction to the flow rate was not required. No seasonal adjustments were performed on the GoldTop flow rates, so that the volumes reported are for ambient temperature and pressure. This means that for Comparison 1 sample volumes are for ambient temperature and pressure, while for Comparisons 2 the sample volumes are for standard temperature and pressure. During Comparisons 2 the flow rates of each sampler were audited and calibrated every three months, and the inlets cleaned and re-greased every two months.

In addition a cascade impactor, the Micro-Orifice Uniform Deposit Impactor (MOUDI) was operated on BEVS3 during summer 2000/2001 to determine the size-resolved distribution of the mass and chemical 0.056 μm and 10 μm and has been described in detail elsewhere [Keywood *et al.*, 1999].

3. Analysis

HiVol samples were collected on EMFAB² filters (Pallflex Membrane filters EMFAB TX40H120-WW, P/N 7224) except for HVA between September 2002 to August 2003, when 250 mm x 200 mm tissue quartz filters (Pallflex Membrane Filters Tissuequartz 2500QAT-UP, P/N 7204) were used. Samples were collected weekly and a sample handling blank filter was collected every month on one of HVA or HVB.

Gravimetric mass measurements were performed on the GoldTop, HVA and HVB filters using a Sartorius Master Pro LA130S-F balance at relative humidity of approximately 50%. The resolution of the balance was 0.0001 g. Each 250 mm x 200 mm filter was weighed before and after sampling until three weights within 0.0010 g. Tissue quartz filters (both 250 mm x 200 mm and 47 mm) were baked at 400 °C for approximately 8 hours before use to remove organic carbon material from the unexposed filters.

MOUDI samples were collected on 47 mm polycarbonate substrates. Gravimetric mass measurements were performed on the substrates using a Mettler UMT-2 microbalance at < 20% relative humidity. Electrostatic charging is reduced by the presence of radioactive static discharge sources within the balance chamber. The resolution of the balance is 0.0001 mg (0.1 μg). Each substrate was weighed repeatedly, both before and after sampling, until three weights within 0.001 mg are obtained.

After mass determination, a 6.25 cm² section of the HVA, HVB and GoldTop filters were wetted with methanol before being extracted in 10 ml of MQ-grade³ water. The sample was then preserved using 100 μl of chloroform. Anion and cation concentrations were determined by suppressed ion chromatography (IC) using a Dionex DX500 gradient ion

chromatograph. Anions are determined using an AS11 column and an ASRS ultra-suppressor and a gradient eluent of sodium hydroxide. Cations were determined using a CS12 column and a CSRS ultra-suppressor and a methanesulfonate acid eluent. Data quality assurance was achieved with the application of strict criteria for ion balances.

4. Results

4.1. Run Times

Figure 1a compares hours run (or the time the BEVS was activated) for BEVS2 and BEVS3 over Comparison 1 and Comparison 2. In general, BEVS3 displays greater run hours than BEVS2, particularly during summer (Figure 1b).

Table 2 summarises this with average summer and winter hours run for each year of the comparison (summer is December, January and February and winter is June, July and August). Table 2 also shows that differences in hours run between the two BEVS for each season of the comparisons are statistically significant.

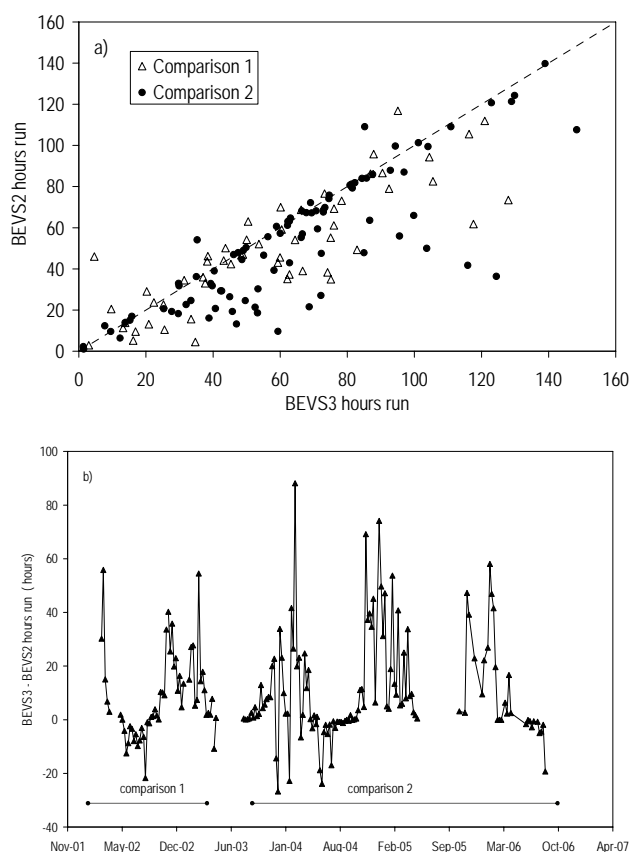


Figure 1. (a). Relationship between hours run for each BEVS. The dashed line is the 1:1 line. (b) time series of difference in hours run for each BEVS for Comparisons 1 and 2.

² EMFAB is borosilicate glass fibres reinforced with woven glass and bonded with PTFE.

³ MQ-grade water is 18 m Ω de-ionized water

Table 2. Average, standard deviation and number of samples (n) for hours run for summer and winter of each year and statistical significance of the differences between the averages (summer is December, January and February, winter is June, July and August).

Period	BEVS2		BEVS3		P(T<=t) two-tail*
	Average±sd hours	n	Average±sd hours	n	
Winter 2002	58.6±26.9	13	51.6±22.6	13	0.001
Summer 2002/2003	57.7±28.0	11	76.3±33.2	11	0.002
Winter 2003	61.5±36.9	13	40.0±27.3	13	0.07
Summer 2003/2004	50.4±31.0	13	66.2±40.7	13	0.08
Winter 2004	57.9±35.4	13	55.0±34.8	13	0.04
Summer 2004/2005	36.4±20.9	11	64.9±27.6	11	0.003
Winter 2006	61.4±23.8	10	57.7±22.7	10	0.07

* If P is < 0.05 data are significantly different (p=0.05 represents 95% of data fall outside to the overlap between the two means and their standard deviations).

4.2. Masses

Figure 2 shows the relationships between the mass of samples collected BEVS2 and BEVS3 for both comparison and the statistical significance of the difference between the means is shown in Table 3. While masses measured on samples collected on each BEVS for Comparison 2 are not significantly different, the masses collected during Comparison 1 are significantly different with masses sampled with the GoldTop on BEVS2 being greater than masses sampled with HVA on BEVS3. PM10 collected on BEVS2 is greater than PM10 collected on BEVS3 78% of the time.

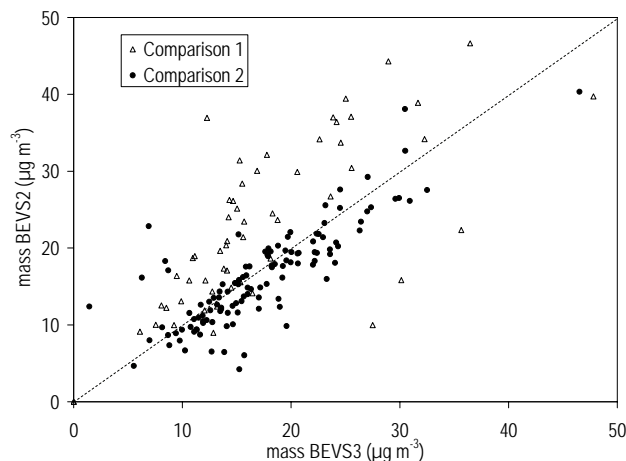


Figure 2. Relationship between mass for each BEVS over Comparison 1 and Comparison 2. The dashed line is the 1:1 line.

Table 3. Average, standard deviation and number of samples for mass for Comparison 1 and Comparison 2 and statistical significance of the differences between the averages.

Period	BEVS2		BEVS3		P(T<=t) two-tail
	Average±sd N µg m ⁻³	n	Average±sd N µg m ⁻³	n	
Comparison 1 GoldTop/HVA	26.3±12.9	57	17.6±9.0	57	0.005
Comparison 2 HVB/HVA	16.5±7.8	90	17.4±6.9	91	0.374

Since this difference is not observed in Comparison 2 we can infer that the difference observed between the masses in Comparison 1 may result from differences in the samplers rather than the BEVS. Further investigation revealed that the GoldTop was operated at a lower flow rate than required for the size-selective inlet to sample PM10 (54 m³ hr⁻¹ compared with 68 m³ hr⁻¹). Based on the theoretical relationship between flow rate and d50 summarised by Chow [1995], the cut-size of the PM10 inlet on the GoldTop was actually 11 – 12 µm. Whether this increased cut-size is sufficient to explain the greater masses determined from the GoldTop samples can be determined using size-resolved mass distributions collected during summer 2000/2001 using the MOUDI. The average of 13 size distributions is shown in Figure 3. The distribution is dominated by a coarse mode at 6 µm. Increasing the cut-point from 10 µm to 12 µm for the averaged size distribution increases the mass of aerosol by 15% and the GoldTop during this period (summer 2000/2001) returned masses that were on average 16% greater than the HVA masses. This indicates that the increase in cut-size caused by the lower flow rate of the GoldTop is responsible for the greater mass measured by the GoldTop during Comparison 1. For this reason, the effect of the BEVS on the chemical composition of PM10 measured at Cape Grim will be restricted to Comparison 2 and the HVA and HVB samplers.

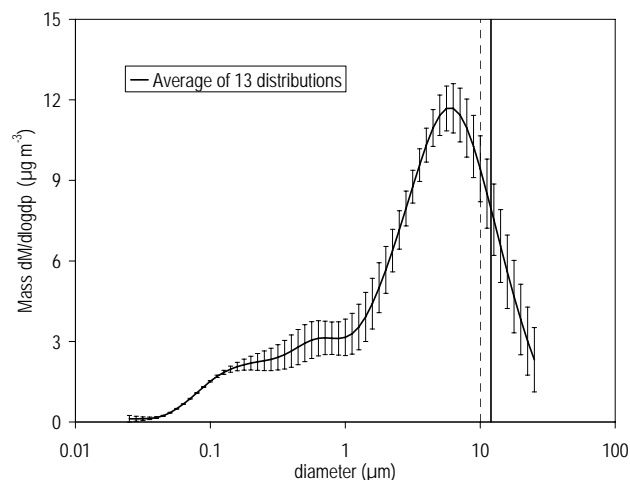


Figure 3. Average of 13 mass size distributions collected during summer 2000 (December 2000 to March 2001).

4.3. Chemical Composition

The Cape Grim aerosol composition under Baseline conditions can be broadly grouped into being derived from three sources; sea-salt (and species produced by heterogeneous reactions on the surface of sea-salt particles), soil-dust and non sea-salt related processes [Keywood, 2003]. The following section discusses the effect of the different BEVS on these sources as reflected in the aerosol composition.

The main contributor to the aerosol composition, or mass, at Cape Grim is sea-salt. A soil correction to the sea-salt contribution is required since the observatory buildings at Cape Grim are located 20 m

back from the cliff edge. As a result of the considerable mechanical turbulence of air passing over the cliff top and buildings, particle samples are contaminated by local soil eroded from the cliff. Using the unique chemical signatures for the cliff soils, Ayers (2001) devised a method based on the ratio of magnesium to sodium (Mg^{2+}/Na^+ ratios, where Mg^{2+} is used as the tracer for sea-salt after Caaney *et al.*, 1999) to quantify the effect of the soil on aerosol samples and suggested the soil sodium (soil Na^+) to sea-salt sodium ($ssNa^+$) ratio (soil $Na^+/ssNa^+$) of less than 0.2 as the limit for soil correction. This takes into considerations of analytical uncertainties in that Na^+ soil loadings of greater than 20% of the sea-salt Na^+ would be detectable. Of the 119 samples collected during the Comparison 2, 51 samples collected on BEVS2 and 30 samples collected on BEVS3 exceeded the soil $Na^+/ssNa^+$ limit for soil correction and so were removed from the data set. Note however that MSA (methansulfonic acid) is not present in soil on the cliff at Cape Grim so a soil correction is not required for this species.

Table 4 shows the average and standard deviation of $ssNa^+$, soil Na^+ , non-sea-salt sulfate ($nssSO_4^{2-}$) and methansulfonic acid (MSA) for Comparison 2, as well as the significance of the differences of the means for each BEVS. There is no significant difference between the average $ssNa^+$ or soil Na^+ concentration measured on samples collected on the BEVS2 or BEVS3, although, as mentioned above, the number of samples with soil $Na^+/ssNa^+$ exceeding 0.2 is greater for samples collected on BEVS2 than BEVS3. Most importantly however, there are significant difference between $nssSO_4^{2-}$ and MSA measured on samples collected on the different BEVS, with both species being greater on the samples collected on BEVS3.

Table 4. Average concentrations (and standard deviation and number of samples) for sea-salt sodium ($ssNa^+$), soil sodium (soil Na^+), non sea-salt sulfate ($nssSO_4^{2-}$) and methansulfonic acid (MSA) for samples collected on BEVS2 and BEVS3 with soil $Na^+/ssNa^+$ less than 0.2. Note that no soil correction is required for MSA (since MSA is not measured in the soil on the cliff at Cape Grim). Of the 119 samples collected during the sample period, 68 samples had ratios less than 0.2 on BEVS2 and 89 had ratios less than 0.2 on BEVS3.

Period	BEVS2		BEVS3		P(T<=t) two-tail
	Average±sd μg^{-3}	n	Average±sd μg^{-3}	n	
$ssNa^+$	167±54	68	159±55	89	0.369
soil Na^+	16±8	68	16±8	89	0.646
$nssSO_4^{2-}$	1.12±0.89	68	1.69±1.24	89	0.001
MSA	0.30±0.36	119	0.51±0.89	119	0.017
MSA/ $nssSO_4^{2-}$	0.17±0.26	68	0.19±0.17	89	0.630

Figure 4 shows that most of the difference between MSA measured on samples collected on BEVS2 and BEVS3 is seen in the summer, with the BEVS3 samples returning on average four times more MSA than BEVS2 over summer. During the winter months, MSA concentrations measured on the BEVS2 samples are similar to samples collected

on BEVS3, however as shown in Figure 5, the winter time concentrations are very low. While there are differences in $nssSO_4^{2-}$ and MSA concentrations in samples collected on BEVS2 and BEVS3, the ratio of the species is not significantly different (Table 4).

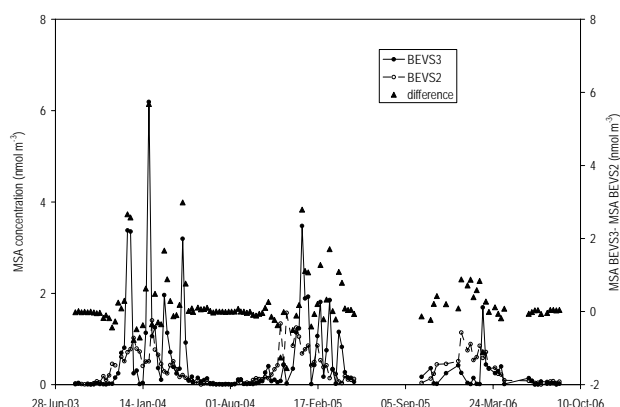


Figure 4. Time series of MSA concentration and the difference in MSA concentration for samples collected on BEVS2 and BEVS3 for Comparison 2.

5. Implications for aerosol composition measurements at Cape Grim

5.1. Gold top HiVol record

The GoldTop HiVol with PM10 size selective inlet extends from 1988 to 2000, making it one of the longest records of remote marine soluble ion composition in the world. This work has shown that the size selective inlet on the GoldTop was sampling PM11-12 rather than PM10. In the marine atmosphere, where aerosol is dominated by coarse sea-salt particles, an increase in 1-2 μm cut point of the size selective inlet, results in a significant increase in the mass of aerosol sampled, in this case up to 15%. Similarly, the concentration of sea-salt ionic species such as Na^+ and Cl^- , and species associated with the coarse alkaline sea-salt such as nitrate and weak organic acids will also be elevated relative to samples collected with a PM10 inlet. While the increase in the cut-point of the size selective inlet from 10 μm to 11-12 μm does not diminish the value of the GoldTop HiVol record at Cape Grim, users of the record should be aware of the change in cut-point, particularly if comparing the record to other stations in the Global Atmospheric Watch network of observatories.

5.2. MSA and $nssSO_4^{2-}$ record

The MSA and $nssSO_4^{2-}$ records obtained from samples on BEVS2 extend from 1981 to 2005, have been reported in a number of publications discussing the role of oceanic emissions of dimethyl sulfide (DMS) as a source of cloud condensation nuclei (CCN) [e.g. Ayers and Gras, 1991; Ayers *et al.*, 1997; Ayers and Gillett, 2000]. DMS emissions from biological activity in ocean surface waters are believed to be the major source of reactive sulfur to the global atmosphere [Bates *et al.*, 1992]. Once in the atmosphere DMS undergoes a number of photo-

chemical reactions, with the major endpoints being MSA and nssSO_4^{2-} . This work suggests that the MSA and nssSO_4^{2-} concentrations were influenced by the BEVS on which the HiVol sampler was operating, since the BEVS2 cuts out samples associated with $\text{CN} > 600 \text{ cm}^{-3}$. The BEVS3 on the other hand, allows sampling of air masses associated with CN number of $\sim 1200 \text{ cm}^{-3}$ for 80 days of the year (during the summer⁴). The association between MSA and CN previously noted in Ayers and Gras [1991] suggests that the higher concentrations of MSA on BEVS3 result because the switch is on during periods of higher CN concentration. For Comparison 2 data presented here, this has resulted in a 50%, 30% and 60% reduction in MSA concentrations measured on samples collected on BEVS2 compared with the BEVS3 samples for summer 2003/2004, summer 2004/2005, and summer 2005/2006 respectively. The nssSO_4^{2-} record has been similarly impacted, with BEVS2 resulting in 30% less nssSO_4^{2-} than the BEVS3 sample concentrations over each summer period. During the winter months the BEVS3 allowed sampling of air masses associated with CN number of 400 cm^{-3} for 100 days (over winter). However, the BEVS2 samples displayed 20% lower concentrations for MSA than the BEVS3 samples for each winter period. Hence, using the BEVS3 results in an enhancement of the seasonal cycle in MSA and nssSO_4^{2-} compared with BEVS2 (Figure 5). This means that the relationship between CN and MSA previously reported [e.g. Ayers and Gras 1991] remains valid.

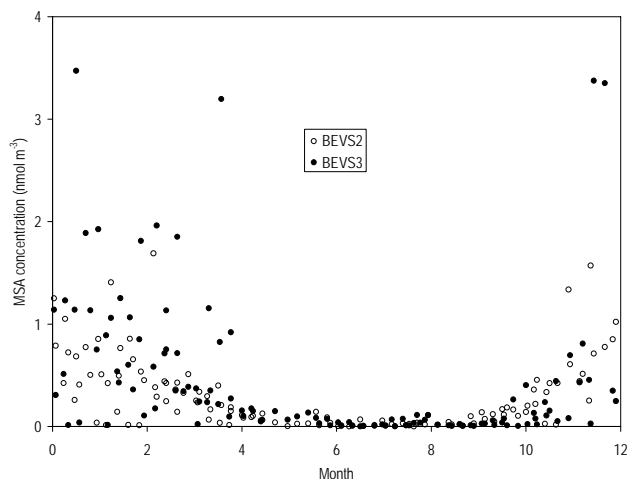


Figure 5. MSA concentrations for samples collected on BEVS2 and BEVS3 during Comparison 2, plotted on one annual cycle.

The Cape Grim MSA and nssSO_4^{2-} record has also been used to investigate the oxidation of DMS, with Ayers *et al.* [1995a] and Ayers *et al.* [1996] using a simplified box model to simulate the oxidation of DMS in low NO_x marine boundary layer. The ratio of $\text{MSA}/\text{nssSO}_4^{2-}$ was used as a marker for DMS-derived CCN. This work has shown that while the absolute concentrations of MSA and nssSO_4^{2-} are

affected by the BEVS, the ratio of these species remains unchanged (Table 4). While numerous uncertainties still remain concerning the mechanisms for the oxidation of DMS and its definitive role in CCN production, the verification of the simple DMS modelling carried out for the remote marine boundary layer using the $\text{MSA}/\text{nssSO}_4^{2-}$ ratio remains valid.

5.3. Soil Contamination

This work has shown that the number of exceedences of the soil $\text{Na}^+/\text{ssNa}^+$ of 0.2 limit for soil correction is significantly greater for samples collected on BEVS2. It is unclear why this is the case. Despite this however, once these samples are removed from the dataset, there is no significant difference between the mean Na soil concentrations measured on samples collected using each BEVS.

6. Conclusions

The effect of the BEVS on the mass and chemical composition of PM_{10} aerosol collected at Cape Grim has been evaluated in two comparisons spanning March 2002 to August 2006. Comparison 1 has revealed that the GoldTop HiVol, operating at Cape Grim on BEVS2 between 1998 and 2000 was sampling PM_{11-12} , resulting in a 15% increase in aerosol mass. Comparison 2 has revealed that samples collected on BEVS2 showed a significantly greater number of exceedences of the soil $\text{Na}^+/\text{ssNa}^+$ of less than 0.2 recommended as the limit for soil correction, although the mean soil Na concentration was not significantly different for samples on each BEVS once the samples exceeding the soil correction ratio limit were removed from the data set. Comparison 2 has also revealed significantly different concentrations of MSA and nssSO_4^{2-} concentrations measured on samples collected on BEVS3, with higher concentrations resulting in summer and, resulting in an enhancement of the seasonal cycle of MSA and nssSO_4^{2-} .

Hence, we recommend permanently switching all aerosol sampling to the BEVS3. This will result in a reduction of the number of soil contamination events and a more accurate picture of the seasonal variation in non-sea-salt species.

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⁴ based on the BEVS3 CN threshold values calculated for 2004.

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4. PROGRAM REPORTS

4.1. INTRODUCTION

The Program Reports section documents the status and preliminary results of the scientific experiments and measurements at Cape Grim during the years 2005 and 2006. There are essentially three types of measurement programs at Cape Grim.

The first and main group are the Cape Grim Programs which are long-term and provide the core measurements of compounds monitored in the atmosphere at Cape Grim. The Lead Scientists for these programs collectively form the Cape Grim 'Working Group', essentially the scientific steering committee, and are responsible for maintaining the continuity and quality of the core data from Cape Grim.

The second group of scientific programs are the short-term, more research orientated, studies labelled as 'Pilot Projects'. Generally these studies only last from one to three years and are designed to develop and test new sampling techniques and/or equipment, or for short-term intensive measurements of compounds that are difficult to measure routinely.

The final group of programs includes all the Collaborative Programs, primarily the longer-term international collaborations where samples and data are collected and shared with international colleagues. Some of these collaborative studies form part of global surveys and Cape Grim provides assistance and samples to outside researchers. Sometimes included in the collaborative program reports are the short-term intensive studies made by scientists and research students who are visiting Cape Grim to take advantage of the sampling facilities and support at the Cape Grim station.

Cape Grim reports

The Program, Pilot Project and Collaborative reports included in this edition of *Baseline* are categorised into four groupings:

General (including climatology and transport tracers, and the report on the Cape Grim database and data management)

Trace Gases (radiatively or chemically active gases)

Multi-phase (including precipitation, particles and multi-phase studies and

Radiation (electromagnetic radiation monitoring).

Missing reports

A brief summary is included below of the Cape Grim and collaborative programs that have not submitted reports for 2005-2006, but were in operation during at least some of this period.

Oxygen isotopes in precipitation; approximately 1500 daily samples were collected from the manual rain gauge (since 1998) and sent to the University of Tasmania for ^{18}O analysis, as a proxy for temperature.

Aerosol radionuclides; Weekly hi-volume aerosol filter samples are collected and counted for radionuclide radiation. Data are then directly transmitted by satellite to the Department of Energy (DOE), USA. Filters and data backups are sent approximately every month. This program ceased operation in October 2005.

Elemental carbon; Weekly low-volume aerosol filters are collected and sent to the University of Stockholm, Sweden, for the analysis of particulate elemental carbon.

Passive Dioxin Sampling; Quarterly and annual passive dioxin samples are collected and sent to Environment Canada for analysis.

4.2. DATA MANAGEMENT REPORT

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[Supported by CGBAPS research funds.]

Introduction

Data is collected at CGBAPS from 2 broad sources: the analog Data Acquisition System (DAS) and instrument control PCs.

The DAS consists of two 60-channel digital voltmeters running in parallel. A HP3497A ('DAS1') controlled over a HP-IB interface by custom software on a HP9000/715 HP workstation ('Jacob') and a HP34970A ('DAS2') connected by HP-IB to a Linux-based Dell workstation. The DAS1 system was retired in March 2006 when the system disk on Jacob failed. The DAS samples voltages from each channel 10 times per minute and reduces these 10 raw readings to mean, maximum, minimum, standard deviation and first reading for each minute. The resulting data is stored in a daily binary-format file. All 60 channels are sampled although not all are in use at any given time.

Newer experiments at CGBAPS have tended to use a decentralised approach in which an instrument is controlled by a dedicated PC. The controlling PC typically accesses a central file server over the network to archive its data. Instrument control software and hardware are developed elsewhere by the responsible scientist.

In 2006 a 16 port Cyclades Console Server was installed in an attempt to centralise the control and data collection process of several instruments. Instruments that only require an RS232 serial connection can connect to the Cyclades and a process running on a server can collect the data over the network via the Cyclades. This removes the need to have a dedicated PC for each instrument. Up to 16 instruments can be concentrated onto a single reliable and maintained device.

System Operation

The DAS lost 44 minutes in 2005 (a success rate of 99.992%) and 38 minutes in 2006 (99.993%). 7 minutes on 21 January 2005 due to a reboot of Gretel, 12 minutes on 2 May 2005 due to electrical testing, 1 minute on 18 July due to a data transfer failure, 17 minutes on 5 December 2005 due to updating the DAS software to support changing the baseline wind instrument, 6 minutes on 20 January 2006 due to accidentally disconnecting power while decommissioning old HP1000 computer racks, 11 minutes on 17 March 2006 due to Jacob failing and the switch to the DAS2 system as the primary DAS source and 12 minutes on 6 April 2006 due to moving the DAS hardware into a new rack.

In August 2005 the old HP workstation/server, Wilhelm, was switched off. All services that it was providing had been running to newer Linux servers for some time.

In September 2005 the PC that runs the SF6 GC failed. A replacement PC was installed but the old DOS software that controlled the GC would not run in a DOS window under Windows 98. The PC was booted into DOS mode and the software run there without network support while replacement software was written in Perl to run under Windows. This was completed by the end of September.

On 23 February 2006 the TSI 3010 and 3025 PC, Eps, was replaced with a new Dell computer running Windows XP and new software to collect data from the TSIs. This was after over a year of regular crashes and "hangs" on the old computer resulting in data loss (and associated lack of baseline switching) sometimes spanning whole weekends.

In March 2006 the system disk in Jacob, the DAS1 controlling computer, failed. As the new DAS2 system had been running since 2004 and Hewlett Packard had announced the end of life of Jacob's hardware it was decided to not try recovering from the failure and to switch to DAS2 as the primary data source. It was then discovered that some data channels and actuators hadn't been replicated on DAS2. Most notably the baseline switching and ozone zero actuators and the tipping bucket rain gauge counter. Once these were connected normal DAS operations recommenced.

On 21 August 2006 the system disk in the AGAGE PC failed. A new disk was sourced locally and the latest version of Fedora Linux was installed on it. The AGAGE software and data was then restored remotely by Peter Salameh and sampling was affected for less than 48 hours.

On 18 September 2006 Virazon, the database server located in Smithton, failed. This was also an end of life HP workstation. The major service this server provided was the Oracle database storing the hourly means of the 1 minute DAS data. Because it had already been decided to retire the Oracle database and move to a MySQL database a recovery was not attempted. No data acquisition was impacted but access to the hourly data was affected

for several months while the data was reloaded and scripts were updated.

During 2005 and half of 2006 the tape drive on the file server Mauka would occasionally fail and not eject the backup tape. In order to ensure regular backups could continue Mauka would need to be rebooted to reset the tape drive. Because instruments on the particle bench, ozone and radon all wrote their data to Mauka they would sometimes also need to be rebooted and this would occasionally result in a small amount of lost data. With the installation of the new file server, Boab1, in July 2006 backups were migrated to using a removable hard disk rather than tape.

In July 2005 the imminent construction of the new gas store was likely to cause the disconnection of the temperature probes connected to the DAS as the data cables entered the building exactly where the gas store was to be built. Since the Almos Automatic Weather Station was providing 'official' temperature data it was decided it was no longer necessary to reconnect the probes to the DAS. However many scripts, programs and web pages used the temperature data from the DAS so, rather than change every program to use the AWS, a script was written to copy the AWS temperature data into the DAS binary files thus making the move transparent.

Problems with the network hub in Smithton continued into 2005. On April 14 the spare network switch from the Station was relocated to Smithton to replace the hub. No data acquisition was affected. In October 2005 new switches and routers were supplied by the Network Group. This coincided with a major upgrade of the wide area network. The link from Smithton to the rest of the Bureau network was originally a 64kb/s link to Hobart. This was upgraded to a 512kb/s DSL link direct to Head Office in Melbourne. In August 2006 the network link between Smithton and the Station was upgraded from 128kb/s to 256kb/s.

The network changes necessitated a complete renumbering of all computer equipment in Smithton and at the Station. This resulted in some brief interruptions to data acquisition as equipment was configured with new addresses. At this time the Cape Grim domain 'baps.bom.gov.au' was discontinued in favour of a 'baps-' prefix in front of the names. For example: pampero.baps.bom.gov.au became baps-pampero.bom.gov.au. A large number of scripts with hard-coded hostnames had to be changed to work with the new names so some data processing was delayed by a day or two while the scripts were located and updated.

Finally, in July 2006 two new servers were purchased to replace the aging (and in some cases failing) Mauka, Pampero, Wilhelm, Virazon and Shamal. The new servers are rack mountable and each have 2 AMD Opteron 2.6GHz processors, 4GB RAM and 500GB RAID-5 disk space. These servers are called Boab1 and Boab2. Boab2 will act as a standby for Boab1. In the event of a Boab1 failure Boab2 will be able to automatically take over.

Data Processing

An audit of Cape Grim's data holdings, begun in 2004, continued by restoring all data archived to CD onto the new servers. The hope is to provide a definitive list of all data that Cape Grim should have and compare that to what we actually have and then attempt to locate what is missing.

A new MySQL database system was installed on the new servers to replace the old Oracle database. A project was initiated to import all Cape Grim data holdings into this database, beginning with the raw minute DAS data. Along with the data import a new web based front end will be created to access these data holdings and provide lead scientists access to their raw data and the ability to upload quality assured data directly into the database.

2005 and 2006 processed data were received from the MAC program (Melita Keywood), GASLAB Flasks (Paul Krummel), SRAD (Stephen Wilson), CCN (John Gras), CG Air Archive (Paul Steele/Paul Krummel), Lidar (Paul Krummel) and ALE/GAGE/AGAGE and insitu CO₂ (Paul Krummel).

Software Development

An advanced service monitoring system was implemented in early 2005. This system, called Nagios, monitors all aspects of the computer systems, network and data acquisition. Alerts are sent via E-Mail to staff members and availability statistics are recorded and reported in Cape Grim's Monthly Reports.

In April 2005 a documentation Wiki was installed to facilitate the documentation of equipment and procedures at Cape Grim. Initial progress was slow but increased in 2006.

A wish to sample aerosols from a northerly wind direction in early 2005 necessitated the development of an additional baseline criteria called 'Northern Exposure'. This was a useful exercise as we are now able to create customised baseline switching based on arbitrary criteria.

In late 2005 a web site interface and database backend were developed for tracking the movements of various flasks in and out of Cape Grim's possession. All flasks are now checked into the system when they arrive and given a unique identifying number. When they are filled they are checked out of the system just before shipping them for analysis.

A major rewrite of the Ozone data acquisition system was undertaken in late 2006. The Ozone instruments were connected to the new Cyclades terminal server rather than a PC and software was written to gather data from the instruments and store it in the MySQL database.

4.3. METEOROLOGY/CLIMATOLOGY 2005-2006

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Introduction

Tables 1 to 10 present a summary of the Cape Grim meteorological conditions for 2005 and 2006.

Tables 1, 2 and 3 show monthly means for dry bulb temperatures, relative humidity and barometric pressure respectively. They contain mean values for 0000, 0300, 0600, 0900, 1200, 1500, 1800, 2100 (AEST) which are computed using, for example, the mean of hours 2, 3 and 4 to represent 0300. The monthly means for dry bulb temperatures are represented in Figures 1 to 4 and barometric pressure is shown in Figures 5 and 6

In Table 4, extreme max is the highest of all the minute means for the month. Mean daily max is the mean of the daily maxima for the month. Similarly for mean daily min and extreme min.

Table 5 and Figures 7 and 8 show the monthly rainfall in millimetres (mm) for 2005 and 2006.

Table 6 contains 'baseline' time data derived from month-to-date and year-to-date counts of the number of minutes during which the 'baseline switch' was on. Baseline conditions are said to exist if the wind direction is between 190° and 280° and the count of condensation nuclei is less than 600 cm⁻³.

Tables 7 to 10 are derived from the hourly mean vector wind speed and direction from the 10-m and 50-m levels.

Figure 9 is derived from (raw) minute data recorded at the 50-m level. These are wind run roses showing the total wind run for the month (wind speed multiplied by time) for each of 128 directional bins. The seasons are represented by their middle months; January, April, July and October.

Much of the overview description below is drawn from the excellent monthly climate summaries prepared by the Climate and Consultancy Section of the Tasmanian Regional office of the Bureau [Australian Bureau of Meteorology 2005 and 2006].

The overviews and discussion below generally relate to the entire Tasmanian state; trying to paint a picture of the regional weather influences. Where available, interesting information (weather records, for example) is presented for sites near to Cape Grim, though the station's relative isolation makes these points of interest a little sparse.

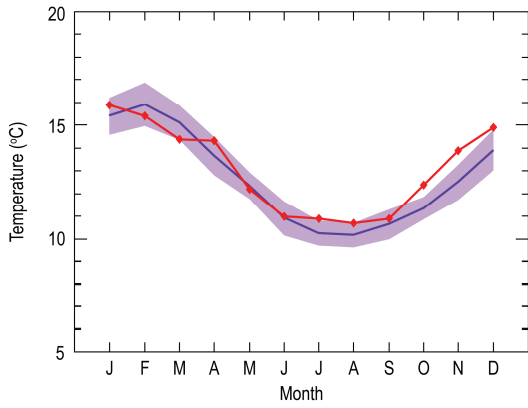


Figure 1. Monthly mean temperature for 2005. The blue line shows long term (1986-2004) mean and the shaded area one standard deviation from the mean.

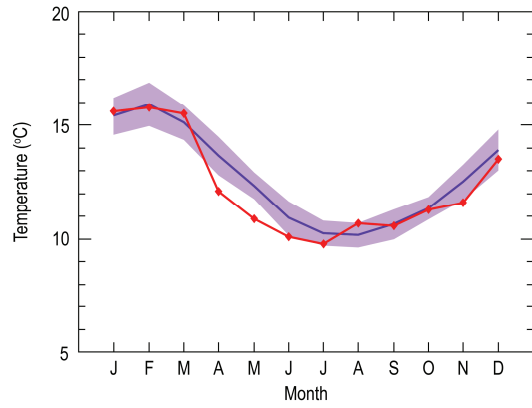


Figure 2. Monthly mean temperature for 2006. The blue line shows long term (1986-2004) mean and the shaded area one standard deviation from the mean.

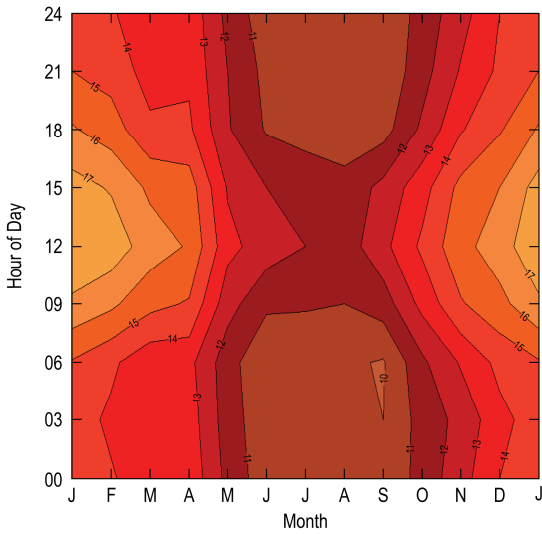


Figure 3. Monthly mean temperature for 2005 by hour of the day with contours at 1°C intervals.

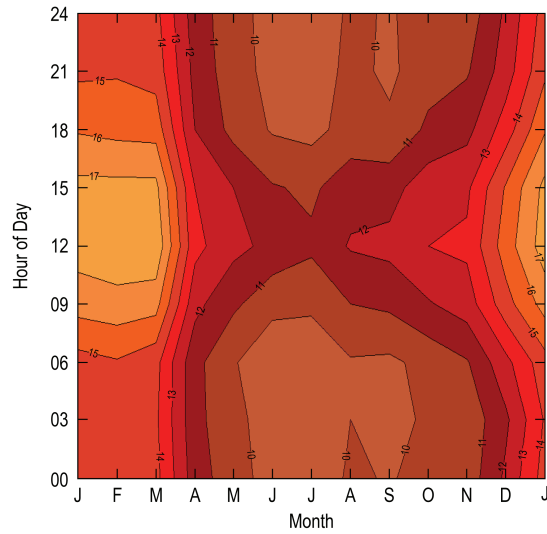


Figure 4. Monthly mean temperature for 2006 by hour of the day with contours at 1°C intervals.

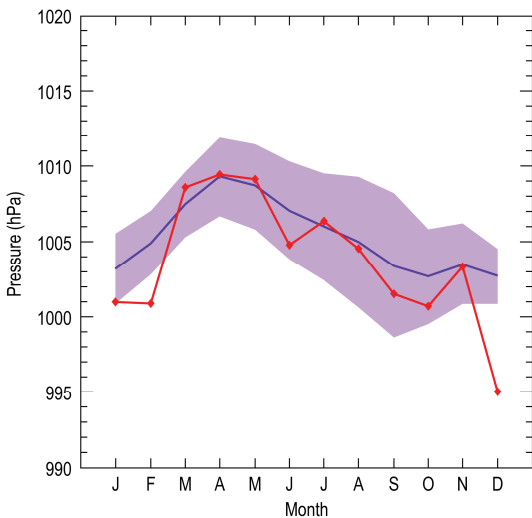


Figure 5. Monthly mean barometric pressure for 2005. The blue line shows long term (1986-2004) mean and the shaded area one standard deviation from the mean.

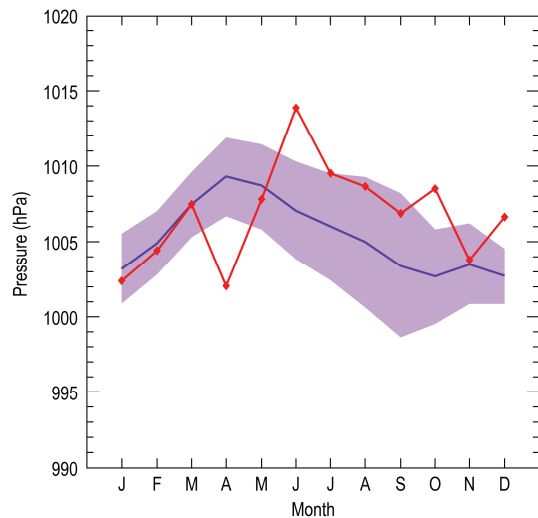


Figure 6. Monthly mean barometric pressure for 2006. The blue line shows long term (1986-2004) mean and the shaded area one standard deviation from the mean.

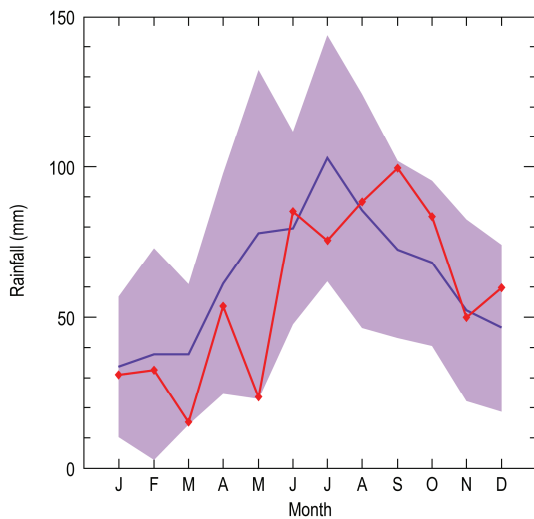


Figure 7. Monthly mean rainfall for 2005. The blue line shows long term (1986-2004) mean and the shaded area one standard deviation from the mean.

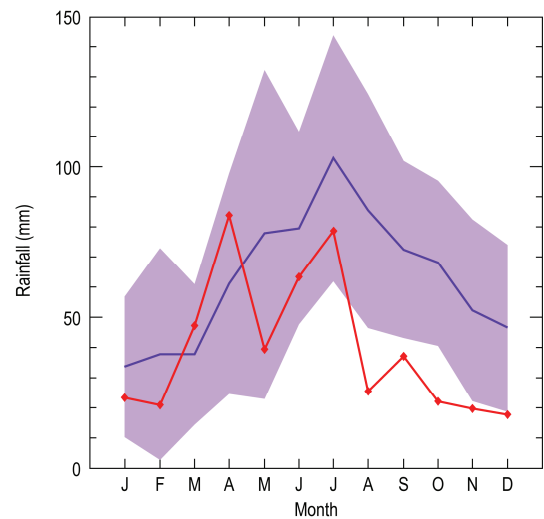


Figure 8. Monthly mean rainfall for 2006. The blue line shows long term (1986-2004) mean and the shaded area one standard deviation from the mean.

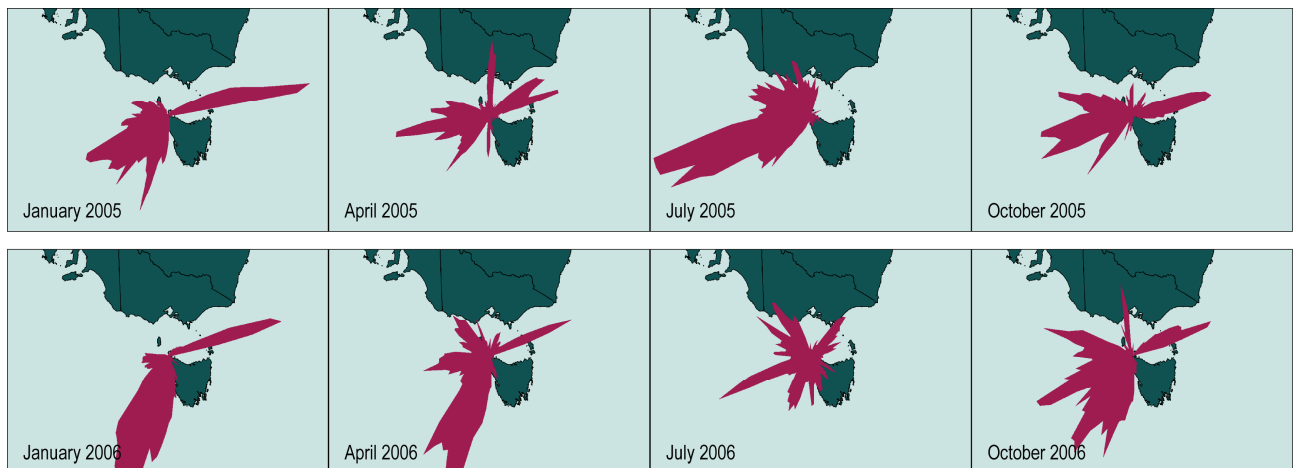


Figure 9. Seasonal wind run roses for 2005 and 2006 derived from (raw) minute data recorded at the 50-m level. The seasons are represented by their middle months; January, April, July and October.

Overview 2005

January synoptic conditions are associated with lighter wind circulations associated with the west to east migration of high pressure systems. January temperatures were near average and rainfall across Tasmania was below average. February is generally the driest month of the year, with synoptic patterns close to those in January. In early February, northern Tasmania experienced some strong winds, forcing the Spirit of Tasmania to return to Melbourne (on its trip to Davenport in the northeast) due to 20 m seas. Generally, in March there is a weakening of the summer patterns and some cold fronts bring higher rainfalls. Rainfall at Cape Grim however, remained well below average. By April, the high pressure systems have normally begun to migrate north, exposing Tasmania to a more persistent westerly flow and bringing more reliable rainfalls and lower temperatures. However, April 2005 was one of the warmest recorded. This was a broad-scale phenomenon, with Australia as a whole, experiencing its

warmest April since 1950. The warmer weather and lower rainfalls contributed to an ongoing dry period with sites in the northwest (including Burnie and Wynyard) having their driest September-to-April on record. In May, temperatures are again normally lower and increased frontal passages bring greater rainfalls, especially across the north. This May, rainfalls in the northeast (and Cape Grim) were well below average with some sites recording their lowest ever rainfalls. Along the west coast however, there were some very heavy rains, with Mount Read in the southwest recording nearly 500 mm for the month. By June, winter is setting in and the temperatures are generally lower and rainfalls higher, with the return of persistent westerly winds and frontal systems. In June, rainfall at Cape Grim reached the monthly average for the first time in 2005. Westerly weather becomes very well established and persistent during July. This July, while the westerly winds did become well established, it was also warmer than average with some sites setting records. Temperatures were higher than average at Cape Grim

and remained above average for the rest of the year. Westerly winds and cold fronts normally dominate during August as was the case this year. September showed similar patterns to that of August. By October, Tasmania is usually beginning to be influenced by high pressure systems and the temperatures begin to rise significantly. In October, Tasmanian rainfall was higher than average with Penguin, on the north coast near Burnie (about 120 km east of Cape Grim) recording its highest ever October rainfall of 250.6 mm. Marrawah (about 30 km south of Cape Grim) recorded its highest daily rainfall of 50.2 mm (in 34 years of records) and not to be left out, Wynyard also recorded its highest monthly rainfall of 195.4 mm (in 22 years of records). Both September and October were wetter than usual at Cape Grim. By November the subtropical ridge has moved southward over Bass Strait and Tasmania is increasingly under the influence of high pressure systems. In December the weather patterns can be quite variable, influenced by westerly winds and high pressure systems which migrate west to east along the subtropical ridge which continues to migrate slowly southward. At Cape Grim, apparently no rainfall at all was recorded for the month of December.

Overview 2006

January synoptic conditions are characterised by weak circulations associated with the migration of high pressure systems in Tasmanian latitudes. The rain during this month is usually lower than December and, with February, represents the driest period of the year. Temperatures and rainfall this January were close to average. In February, rainfall is the lowest for the year in southern Tasmania and for the north it is a little higher than for January. During February a large fire on Robbins Island (15 km east of Cape Grim) burned out 4000 ha (about half the island). By March, Tasmania begins to be influenced by westerly winds, temperatures drop and rainfall increases. This was a drier than normal March, although close to average at Cape Grim. In April, westerly changes become more common and the rainfall is more reliable. By May, there is usually an increase in rainfall in the north, and Tasmania becomes increasingly under the influence of westerly winds. Rainfall was close to normal and temperatures in the north were a little below average with some sites setting long-term records. Temperature was well below average at Cape Grim in both April and May. In June, rainfall across Tasmania usually increases and the westerly winds become more persistent. This June, high pressure systems north of, or close to Tasmania, meant that there was much less rain, and many more cold nights than is normal. Pressure was well above average at Cape Grim (Figure 6) and the effect of night time temperatures is evident in Figure 2. Many sites set records for their lowest ever June rainfall. In July, the westerly winds become more persistent, in August they remain well established and Tasmania experiences the passage of numerous cold fronts. This August

had significantly below average rainfall, with many sites setting long-term records, and slightly above normal temperatures across the state. Cape Grim was both warmer and much drier than average, and rainfall remained very low for the rest of 2006. September conditions are usually similar to those of August with Tasmania still predominantly under the influence of westerly winds. This September, rainfalls returned to near normal but the state remained drier due to the prolonged period of below average rainfall over much of it. During October, Tasmania begins to come under the influence of high pressure systems and begins to experience more easterly winds as cut-off lows develop. This October was quite variable with records for both high and low temperatures being set. Burnie set a new record for the lowest October rainfall of 13 mm (in 62 years of records).

Temperature 2005

In April, Wynyard had its highest mean maximum temperature for the month of 19°C (the same as the value in 2005) and it also reported its highest daily temperature of 26.5°C (also the same as the record observed in 2005). Wynyard, whose appetite for records is apparently insatiable, recorded its highest mean maximum for June of 14.1°C (equal to the record set in 2001) and its highest daily minimum of 13.7°C (in 20 years of records). In July, Wynyard set yet another record with its highest mean daily maximum of 13.9°C demolishing the 13.6°C set in 2001. Marrawah, some 30 km south of Cape Grim had its highest mean daily minimum July temperature of 8.1°C (equal to that recorded in 2001) and its highest daily minimum of 12.7°C (in 65 years of records). In August, Burnie recorded its highest daily maximum temperature in 56 years of records of 18.9°C, with ever reliable Wynyard recording its lowest daily maximum of 8.0°C. Burnie, Wynyard and Marrawah recorded their highest daily minima of 12.7°C, 12.4°C and 12.5°C respectively. Marrawah recorded its highest mean maximum and its highest mean daily minimum for October of 15.9°C and 9.6°C (both in 33 years of records). In November Wynyard recorded its highest daily minimum temperature of 16.4°C (in 20 years of records).

Temperature 2006

In April, Wynyard recorded its lowest daily maximum temperature of 15.8°C (in 22 years of records). In May, Wynyard set records for the lowest mean daily minimum of 2.8°C (in 22 years of records) and lowest daily minimum temperature of -2.7°C (in 22 years of records). In June, Wynyard set a new record for its lowest mean daily minimum for the month of 1.4°C (21 years of record) and its lowest daily minimum in the month of -3.5°C (in 21 years of records). Marrawah and Wynyard both set July records for the highest daily maximum temperature of 17°C and 17.7°C (in 36 and 21 years of records) respectively. Marrawah set a new October record for

the highest daily minimum temperature of 16.3°C (in 34 years of records). Wynyard set a record for the lowest October temperature of -1.6°C (in 20 years of records).

Acknowledgements

The author would like to thank L. Porter, S. Baly, R. Parr, C. Rickard, S. McEwan and other Cape Grim staff for their dedicated efforts in maintaining instrumentation and records, providing data and being thoroughly pleasant to deal with.

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Bureau of Meteorology, Monthly Weather Review Tasmania (January to December 2005). Commonwealth of Australia, 2005.

Bureau of Meteorology, Monthly Weather Review Tasmania (January to December 2006). Commonwealth of Australia, 2006.

Table 1. Monthly mean dry bulb temperature (°C) for 2005 and 2006.

2005	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
0000	14.7	14.1	13.4	13.7	11.7	10.4	10.6	10.3	10.1	11.4	12.6	14.0	12.3
0300	14.5	13.8	13.1	13.5	11.5	10.3	10.4	10.2	10.0	11.4	12.3	13.7	12.1
0600	14.9	14.2	13.3	13.3	11.4	10.1	10.3	10.2	9.9	11.8	13.1	14.3	12.2
0900	16.8	16.2	15.3	14.9	12.4	11.2	11.1	11.0	11.5	13.3	14.9	15.7	13.7
1200	17.9	17.6	16.5	15.9	13.3	12.5	12.0	11.5	12.7	14.2	15.7	16.5	14.7
1500	17.4	16.9	15.8	15.5	12.9	12.0	11.5	11.3	12.3	13.6	15.3	16.0	14.2
1800	16.1	15.5	14.2	14.2	12.1	10.9	10.7	10.5	10.6	12.2	13.9	14.9	13.0
2100	15.0	14.6	13.6	13.8	12.0	10.7	10.6	10.3	10.2	11.6	13.1	14.2	12.4
Mean	15.9	15.4	14.4	14.3	12.2	11.0	10.9	10.7	10.9	12.4	13.9	14.9	13.1
2006	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
0000	14.4	14.6	14.3	11.5	10.4	9.6	9.2	10.2	9.9	10.4	10.4	12.2	11.4
0300	14.1	14.5	14.2	11.3	10.3	9.5	9.0	10.0	9.8	10.1	10.3	11.8	11.2
0600	14.6	14.9	14.3	11.3	10.1	9.2	9.2	9.9	9.8	10.3	10.9	12.7	11.4
0900	16.4	16.6	16.4	12.3	11.2	10.3	10.2	11.0	11.2	11.9	12.5	14.6	12.9
1200	17.5	17.8	17.8	13.3	12.3	11.7	11.2	12.1	12.3	13.0	13.2	15.5	13.9
1500	17.3	17.3	17.3	13.0	12.0	11.1	10.8	11.6	11.6	12.6	12.8	15.1	13.5
1800	15.9	15.7	15.6	12.0	10.7	9.9	9.7	10.4	10.2	11.2	11.7	13.5	12.2
2100	14.8	14.9	14.6	11.7	10.4	9.7	9.4	10.3	9.8	10.6	10.9	12.5	11.6
Mean	15.6	15.8	15.5	12.1	10.9	10.1	9.8	10.7	10.6	11.3	11.6	13.5	12.3

Table 2. Monthly mean relative humidity (%) for 2005 and 2006.

2005	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
0000	83.1	82.7	82.7	83.3	81.4	90.3	82.0	80.2	83.6	85.9	86.0	83.2	83.7
0300	82.9	82.8	83.3	85.0	80.3	89.9	82.5	80.4	84.5	86.7	86.5	82.2	83.9
0600	80.3	82.0	83.2	86.5	81.4	91.0	83.1	79.8	85.3	84.4	84.0	79.9	83.4
0900	74.0	74.8	75.2	81.2	79.3	86.6	79.7	77.4	81.8	78.1	78.0	75.4	78.5
1200	69.2	69.0	71.5	74.9	75.5	83.0	77.6	75.9	76.4	74.8	75.4	73.2	74.7
1500	71.5	72.4	73.4	76.3	76.0	85.9	77.9	77.2	76.3	76.3	75.9	74.6	76.2
1800	76.7	77.9	80.1	83.2	80.3	90.5	80.2	80.4	82.7	81.8	80.4	80.1	81.2
2100	80.9	80.6	82.8	83.8	81.6	90.7	80.4	80.7	83.8	84.6	84.2	83.2	83.1
Mean	77.3	77.8	79.0	81.8	79.5	88.5	80.4	79.0	81.8	81.6	81.3	79.0	80.6
2006	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
0000	82.0	80.8	82.2	78.6	80.1	83.5	82.2	82.5	80.6	78.9	81.6	79.3	81.0
0300	81.8	81.2	83.6	79.0	79.3	83.0	85.1	83.4	81.7	80.4	82.8	79.8	81.8
0600	79.8	79.1	83.9	79.3	80.3	84.4	84.1	82.3	81.4	78.0	80.9	75.4	80.8
0900	73.5	72.7	74.5	76.7	77.4	82.9	81.9	78.5	75.7	71.3	74.7	67.7	75.6
1200	70.3	67.8	67.8	71.4	73.6	76.5	78.3	74.0	70.4	66.4	71.7	65.6	71.2
1500	70.3	68.7	69.7	73.3	72.4	77.5	77.7	75.7	73.3	67.0	72.9	67.2	72.2
1800	76.5	75.1	76.9	78.3	77.0	81.6	81.4	80.7	79.7	73.4	76.5	74.6	77.7
2100	81.2	79.4	81.8	78.9	79.5	82.3	81.3	82.0	81.6	77.4	80.0	78.2	80.3
Mean	76.9	75.6	77.6	76.9	77.5	81.4	81.5	79.9	78.1	74.1	77.7	73.5	77.6

Table 3. Monthly mean barometric pressure (hPa) for 2005 and 2006.

2005	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
0000	1001.1	1000.9	1008.5	1009.4	1008.8	1004.9	1006.5	1004.8	1001.7	1000.8	1003.2	994.6	1003.8
0300	1000.3	1000.0	1007.9	1008.9	1008.3	1004.7	1006.0	1004.2	1001.1	0999.8	1002.8	994.1	1003.2
0600	1001.1	1000.6	1008.6	1009.4	1008.9	1004.9	1006.2	1004.4	1001.4	1000.3	1003.7	995.0	1003.7
0900	1001.6	1001.4	1009.3	1010.1	1009.9	1005.6	1006.9	1005.1	1002.0	1000.9	1004.0	995.5	1004.4
1200	1001.3	1001.2	1008.9	1009.5	1009.3	1004.8	1006.2	1004.5	1001.4	1000.7	1003.5	995.7	1004.0
1500	1000.7	1000.7	1008.2	1008.8	1008.7	1004.1	1005.7	1003.8	1001.0	1000.5	1002.9	995.0	1003.4
1800	1000.6	1000.9	1008.5	1009.2	1009.2	1004.5	1006.3	1004.3	1001.5	1001.1	1003.1	994.8	1003.7
2100	1001.4	1001.6	1009.0	1009.6	1009.6	1004.9	1006.9	1004.9	1002.1	1001.7	1003.6	995.0	1004.2
Mean	1001.0	1000.9	1008.6	1009.4	1009.1	1004.8	1006.3	1004.5	1001.5	1000.7	1003.3	995.0	1003.8
2006	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
0000	1002.4	1004.4	1007.7	1001.9	1007.9	1014.0	1009.5	1008.7	1006.8	1008.4	1003.8	1006.4	1006.9
0300	1001.5	1003.6	1007.1	1001.4	1007.4	1013.7	1009.0	1008.1	1006.0	1007.9	1003.2	1005.6	1006.2
0600	1002.3	1004.0	1007.5	1002.0	1007.7	1013.9	1009.3	1008.4	1006.6	1008.6	1003.8	1006.5	1006.7
0900	1002.9	1004.8	1008.3	1002.9	1008.4	1014.6	1010.0	1009.3	1007.6	1009.2	1004.4	1007.2	1007.5
1200	1002.7	1004.7	1007.8	1002.4	1007.6	1014.0	1009.5	1008.8	1007.2	1008.7	1004.0	1007.0	1007.1
1500	1002.2	1004.2	1006.9	1001.6	1007.0	1013.2	1009.0	1008.3	1006.5	1008.1	1003.4	1006.4	1006.4
1800	1002.2	1004.4	1007.1	1002.1	1007.8	1013.7	1009.5	1008.8	1007.0	1008.4	1003.6	1006.7	1006.8
2100	1003.1	1005.3	1007.9	1002.6	1008.2	1014.1	1010.0	1009.1	1007.4	1009.0	1004.4	1007.3	1007.4
Mean	1002.4	1004.4	1007.5	1002.1	1007.8	1013.9	1009.5	1008.7	1006.9	1008.5	1003.8	1006.7	1006.9

Table 4. Monthly extreme temperature (°C) for 2005 and 2006.

2005	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Extreme max	24.7	23.6	20.3	23.3	17.4	15.2	15.3	16.4	18.7	19.1	21.4	22.1
Mean daily max	19.1	19.0	17.6	17.6	14.4	13.4	13.1	12.8	14.0	15.4	17.0	17.9
Mean daily min	13.4	12.5	11.8	11.5	10.1	8.9	8.9	8.4	8.4	10.2	11.2	12.4
Extreme min	10.5	10.1	7.0	6.4	6.6	4.9	2.8	3.0	4.9	7.2	8.2	10.5
2006	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Extreme max	28.5	23.4	23.0	18.0	16.4	14.2	15.4	15.8	18.0	21.7	20.8	23.4
Mean daily max	19.4	19.1	19.0	14.5	13.5	12.7	12.4	13.1	13.6	14.1	14.6	16.8
Mean daily min	12.8	13.2	12.8	9.6	8.2	7.9	7.5	8.6	7.8	8.4	9.0	10.6
Extreme min	9.6	9.3	6.4	6.3	4.1	3.1	2.9	4.9	4.4	4.1	5.5	7.1

Table 5. Monthly rainfall (mm) for 2005 and 2006.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
2005	31.0	32.6	15.2	53.6	23.6	85.2	75.4	88.4	99.6	83.8	50.0	0.0	638.4
2006	23.0	25.2	47.0	84.0	39.4	63.4	78.6	25.6	37.2	22.0	19.8	17.6	482.8

Table 6. Monthly baseline time (%) 2005 and 2006.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
2005	24.7	21.4	27.9	24.3	40.4	21.4	41.8	47.8	28.3	22.4	15.8	12.1	27.5
2006	21.9	43.4	28.2	37.2	38.2	31.6	22.0	40.6	30.0	27.4	26.4	28.1	31.2

Table 7. 10-m vector wind summary 2005 (%).

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
Wind speed (km hr ⁻¹), Range [a,b) meaning less than b and equal to or greater than a.													
[0,10)	4.0	3.9	7.7	12.2	4.8	9.0	6.0	0.8	7.9	8.7	5.7	2.8	6.1
[10,20)	14.7	17.3	17.2	21.1	14.0	25.8	16.5	6.7	28.1	16.5	15.7	12.4	17.1
[20,30)	23.8	24.0	20.8	23.6	22.2	33.9	21.8	14.8	24.7	15.7	15.7	18.4	21.6
[30,40)	20.1	21.1	27.3	17.8	21.8	20.6	23.7	25.1	16.2	18.5	19.6	21.2	21.1
[40,50)	16.7	21.1	17.5	11.7	17.2	9.3	16.5	25.4	12.4	22.8	22.1	21.8	17.9
[50,60)	15.6	8.9	5.9	5.7	8.5	1.4	8.1	18.5	4.7	11.3	14.0	13.5	9.7
[60,70)	4.3	3.0	2.8	5.7	6.7	0.0	5.2	5.5	3.1	4.0	5.4	7.8	4.5
[70,...)	0.8	0.7	0.8	2.2	4.8	0.0	2.2	3.1	2.9	2.3	1.8	2.1	2.0
Wind direction (°), Range [a,b) meaning less than b and equal to or greater than a.													
[0,45)	0.9	5.2	0.8	11.8	8.6	17.2	5.5	13.3	15.7	7.3	4.0	4.2	7.9
[45,90)	16.4	16.7	21.6	19.0	3.5	17.5	1.9	1.3	16.4	12.4	14.0	15.1	12.9
[90,135)	10.2	8.0	8.2	9.0	8.7	16.8	9.0	0.0	3.3	20.2	23.5	7.7	10.4
[135,180)	2.4	6.2	8.2	2.6	3.8	4.6	4.3	0.4	2.5	1.7	2.4	0.7	3.3
[18,225)	19.5	22.9	20.0	6.2	12.5	4.9	5.4	15.6	14.3	5.4	16.8	1.3	12.0
[225,270)	31.9	29.8	32.1	26.7	40.2	18.2	32.7	32.0	19.7	20.7	23.5	33.2	28.4
[270,315)	13.6	9.1	7.1	17.2	15.2	9.6	27.4	19.6	19.0	23.7	13.3	34.0	17.5
[315,360)	5.0	2.1	1.9	7.4	7.5	11.2	13.8	17.7	9.0	8.7	2.5	3.9	7.6

Table 8. 50-m vector wind summary 2005 (%).

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
Wind speed (km hr ⁻¹), Range [a,b] meaning less than b and equal to or greater than a.													
[0,10)	3.6	4.3	7.0	10.4	8.7	11.7	7.3	0.8	7.5	7.5	4.0	3.4	6.4
[10,20)	15.9	14.9	20.3	21.2	14.0	29.9	12.0	3.9	23.2	24.6	21.9	17.6	18.2
[20,30)	29.6	22.8	22.6	20.5	15.2	28.0	16.7	13.0	23.3	19.9	28.5	20.8	21.7
[30,40)	23.7	28.1	26.2	21.3	21.8	14.2	24.5	22.4	16.0	15.9	23.2	20.2	21.5
[40,50)	17.9	21.0	16.3	11.8	20.2	14.0	19.2	21.6	16.0	16.5	12.6	16.0	17.0
[50,60)	8.1	7.1	5.4	6.0	10.9	2.0	13.4	21.0	8.9	9.5	4.2	14.4	9.2
[60,70)	1.1	1.8	2.2	6.1	5.5	0.1	4.2	12.5	3.6	3.9	3.8	6.5	4.3
[70,...)	0.1	0.0	0.1	2.7	3.6	0.0	2.8	4.7	1.5	2.2	1.8	1.2	1.8
Wind direction (°), Range [a,b] meaning less than b and equal to or greater than a.													
[0, 45)	1.1	5.4	1.2	10.5	8.3	15.8	5.6	13.6	17.1	7.3	4.2	4.0	7.9
[45, 90)	24.2	20.4	24.7	22.8	8.3	27.7	3.1	0.9	16.8	25.1	29.4	23.1	18.7
[90,135)	2.4	4.2	5.1	5.1	3.1	5.1	7.8	0.0	1.4	7.3	8.1	1.8	4.3
[135,180)	5.2	11.0	12.2	3.3	5.0	5.8	6.0	0.5	5.8	3.1	5.4	1.2	5.5
[180,225)	23.0	28.9	21.8	11.1	20.2	10.4	7.9	25.5	14.3	7.7	16.9	8.5	16.5
[225,270)	26.8	20.1	26.2	25.2	32.6	15.0	36.3	23.1	21.9	22.3	23.8	29.8	25.3
[270,315)	11.7	8.0	6.5	12.7	13.9	8.2	18.7	17.7	13.3	18.0	9.4	27.3	13.5
[315,360)	5.5	2.1	2.3	9.4	8.6	12.0	14.5	18.5	9.3	9.3	2.8	4.3	8.4

Table 9. 10-m vector wind summary 2006 (%).

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
Wind speed (km hr ⁻¹), Range [a,b] meaning less than b and equal to or greater than a.													
[0,10)	6.5	4.3	6.0	7.4	8.1	20.6	5.9	6.2	4.3	1.1	1.9	2.2	6.2
[10,20)	14.2	12.1	18.7	12.9	21.0	20.0	22.3	21.9	17.1	10.5	9.0	11.2	15.9
[20,30)	21.0	26.9	24.6	22.1	23.7	17.8	20.6	27.2	25.0	23.7	18.9	16.1	22.3
[30,40)	20.7	30.7	15.9	18.3	19.6	21.1	18.0	21.0	22.5	21.5	25.4	17.1	20.9
[40,50)	18.1	13.8	15.6	13.8	10.9	11.9	15.3	15.3	15.0	17.3	17.8	19.2	15.4
[50,60)	13.3	8.8	14.8	9.4	10.6	5.8	12.9	6.6	9.3	14.1	14.4	16.7	11.4
[60,70)	4.4	2.5	4.3	7.9	4.8	2.5	4.6	1.1	4.9	7.0	8.1	14.2	5.5
[70,...)	1.7	0.9	0.1	8.2	1.3	0.3	0.4	0.8	1.9	4.8	4.4	3.4	2.4
Wind direction (°), Range [a,b] meaning less than b and equal to or greater than a.													
[0,45)	1.7	1.3	0.8	6.2	5.2	13.8	5.4	14.9	12.8	7.0	4.4	6.5	6.7
[45,90)	14.9	7.3	26.6	14.4	6.6	12.1	12.5	3.1	4.4	10.6	8.6	22.6	12.0
[90,135)	12.8	11.6	16.4	6.8	11.2	8.1	19.1	0.7	4.0	2.4	6.8	2.6	8.5
[135,180)	6.2	2.5	5.5	5.4	10.1	9.2	10.9	3.4	3.9	4.0	5.6	2.4	5.8
[180,225)	34.9	22.9	18.0	22.8	12.0	15.3	15.6	7.8	14.0	20.7	39.4	26.7	20.8
[225,270)	26.1	44.2	27.2	21.1	34.3	20.4	13.8	28.2	25.8	32.7	26.9	33.6	27.8
[270,315)	3.0	8.0	5.0	14.6	13.3	12.1	12.8	26.7	25.7	15.9	7.9	4.8	12.5
[315,360)	0.4	2.1	0.5	8.6	7.4	9.2	9.9	15.2	9.3	6.7	0.3	0.8	5.9

Table 10. 50-m Vector Wind Summary 2006 (%).

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
Wind speed (km hr ⁻¹), Range [a,b] meaning less than b and equal to or greater than a.													
[0,10)	6.5	6.5	8.3	8.2	8.3	21.4	7.0	4.8	5.4	0.9	2.2	2.3	6.8
[10,20)	22.0	17.4	22.2	12.8	18.8	17.2	20.9	14.5	13.1	9.4	12.9	11.6	16.1
[20,30)	26.6	33.8	27.4	15.6	25.0	13.2	18.2	27.7	19.7	23.3	23.1	26.2	23.3
[30,40)	22.6	25.6	18.5	18.8	18.8	25.9	15.0	25.4	21.9	24.9	27.9	28.1	22.7
[40,50)	14.5	12.6	12.8	15.4	10.8	15.6	16.0	14.7	18.6	16.4	17.2	14.1	14.9
[50,60)	4.2	2.2	8.5	15.3	11.0	4.7	17.9	8.9	12.1	13.7	10.3	13.3	10.2
[60,70)	3.5	1.8	2.2	11.5	5.1	1.8	5.0	3.4	5.8	7.8	4.6	3.8	4.7
[70,...)	0.1	0.0	0.1	2.5	2.2	0.1	0.0	0.7	3.3	3.6	1.8	0.7	1.3
Wind direction (°), Range [a,b] meaning less than b and equal to or greater than a.													
[0,45)	1.9	1.3	1.2	6.9	5.9	14.6	7.3	14.1	12.9	2.7	1.2	1.9	6.0
[45,90)	23.8	17.1	34.7	15.3	9.9	12.0	19.3	1.5	5.8	15.3	16.0	29.2	16.7
[90,135)	5.0	2.4	8.5	3.8	7.5	4.5	11.9	0.3	1.9	0.4	2.1	0.5	4.1
[135,180)	12.1	2.2	8.2	7.8	15.2	11.7	14.2	6.0	7.9	8.3	13.3	4.4	9.3
[180,225)	42.9	43.0	28.1	30.7	15.2	19.9	13.2	10.9	13.8	26.9	37.8	36.7	26.5
[225,270)	11.7	25.4	15.2	15.8	28.6	17.5	12.4	30.2	25.0	23.7	21.8	21.4	20.7
[270,315)	2.3	6.1	3.5	11.2	9.9	9.0	11.5	19.6	22.8	15.6	7.6	5.1	10.4
[315,360)	0.4	2.4	0.7	8.5	7.7	10.8	10.4	17.3	9.9	7.1	0.1	0.8	6.4

4.4. RADON AND RADON DAUGHTERS

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Introduction

The focus in the reporting period was on improving the precision of the radon detection system for the lower range of radon concentrations characteristic of the least perturbed oceanic air. The work started at the end of 2004 with a change of the main radon detector at Cape Grim from the two- to a four- sensing head system, followed by a thorough evaluation of the new setup in 2005. The next development involved the construction and testing of an eight head sensing unit to achieve even higher instrument sensitivity. The system was built and tested at ANSTO in 2006 and was ready for deployment in early 2007. Progress was also made in developing software for real-time processing of the recorded data.

Hardware and software development

The following points detail the developments and achievements of 2005-2006:

- A four head sensing unit installed in the primary radon detector (HURD2) was comprehensively tested by the end of 2005. Positive results led to further work on the feasibility of doubling the number of sensing heads and thus further improving the lower limit of detection of the primary radon instrument at CGBAPS from the current 10 mBq m⁻³ down to 3 mBq m⁻³;
- A method was developed, and a prototype unit constructed and tested in late 2006. It was ready to be deployed at Cape Grim in 2007;
- Other improvements of HURD2 included (a) replacing remaining PVC sections of the HURD2 inlet with copper tubing (December 2005); (b) installing an external isolation switch for the small external HURD2 blower (December 2005, February/March 2006); (c) upgrading the power supply for HURD2 to meet current electrical regulations (March 2006);
- Improvements made to the background radon detector (BHURD) included: (a) re-furbishing the sensing head (February 2006) and (b) installing a sensor for continuous monitoring of the velocity of air flow passing the sensing head (November 2006).

A summary of the development of the software controlling the dual (main and background) radon detector system is as follows:

- Outputs from the main and backup instruments were integrated to provide hourly radon concentrations in real time. New software was developed at ANSTO and installed on HURD2 and BHURD computers (July 2005). As a result, hourly radon concentrations have been estimated in real time and can be accessed remotely. The concentrations are calculated from raw data sourced either from HURD2 or BHURD depending on scheduled calibration and background measurements, as well as on any maintenance or upgrade activities which might affect the radon instruments. In this scheme calibration and background events are processed manually.
- Developed and tested a code for fully automated data processing (December 2006).

Data summary

The data recovery in 2005-2006 improved in comparison to 2003-2004. It was 99.4% with 100 hourly observations non valid in 2005 and only 4 non valid observations in 2006. The improvement was due to the fact that the dual radon detector system was operational throughout the period.

The tabulated data and figures shown in this report are in a format adopted in previous bi-annual reports and thus provide an easy comparison of the inter-annual variability of the reported quantities. Two new figures were added to further illustrate features in the baseline wind sector. Table 1 shows monthly radon means based on hourly radon observations for 2005 and 2006 in baseline and non-baseline sectors. Numbers of hourly radon observations in the baseline wind sector affected by recent land contact indicated by radon concentrations higher than 100 mBq m⁻³ are compared with the corresponding monthly totals. A subset of the baseline set observations characterised by ultra-fine particle concentrations lower than 600 cm⁻³ has lower radon means (by about 21%) and a lower number of hourly observations (by about 29%). The percentage of radon observations higher than 100 mBq m⁻³ (the commonly adopted radon threshold for baseline events) is similar in the two sets and is equal to 17% and 15.5% for the full baseline set and the subset defined by ultra-fine particle concentrations lower than 600 cm⁻³, respectively. The percentage figures are based on the 2005 dataset.

Radon annual medians as a function of local (i.e. at Cape Grim) wind direction are shown in Figures 1 and 2 for 2005 and 2006, respectively. The strongly anisotropic distribution validates categorizing the data into baseline and non-baseline, and oceanic and continental, groups.

Table 1. Monthly mean radon concentrations (mBq m^{-3}) in 2005 and 2006. The baseline criteria are wind speed $>2 \text{ m s}^{-1}$ and wind direction between 190° and 280° , with wind direction persisting in the sector for at least two hours.

Month	Non-baseline Rn	Baseline						Non-baseline Rn	Baseline					
		All ultra-fine particles			Ultra-fine particles				All ultra-fine particles			Ultra-fine particle		
		Rn	hours	hours	Rn	hours	hours		Rn	hours	hours	Rn	hours	hours
2005		Rn>100			Rn>100		2006		Rn>100			Rn>100		
Jan	470	81	316	35	67	173	16	555	131	301	56	49	129	16
Feb	496	104	281	57	84	141	32	724	70	418	47	45	232	20
Mar	636	109	307	50	70	209	20	610	136	268	46	47	171	11
Apr	1369	185	241	44	107	168	24	668	53	266	4	52	204	2
May	1667	85	389	41	65	308	20	684	168	291	81	120	251	54
Jun	2269	260	161	78	177	150	67	1200	127	224	70			
Jul	1164	188	315	118	143	296	101	1301	91	162	35			
Aug	1766	62	353	27	60	352	26	1305	96	287	62			
Sep	896	101	233	50	87	192	33	906	124	247	42			
Oct	450	80	209	25	43	164	7	712	108	322	29			
Nov	546	57	242	21	56	105	10	377	76	312	39	87	94	11
Dec	329	48	276	21	56	111	12	472	92	368	32	44	224	7
ALL	1030	107	3323	567	85	2369	368	827	104	3466	543	64	1305	121

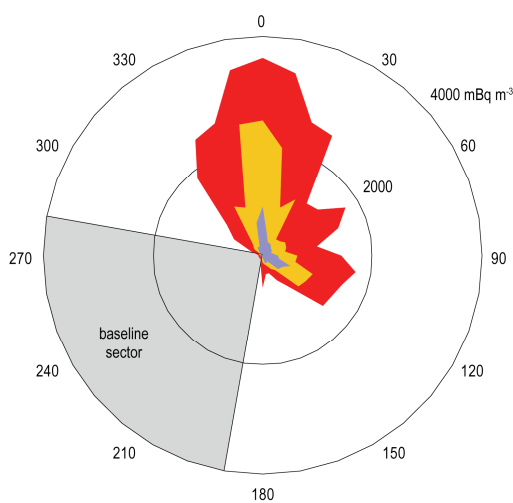


Figure 1. Angular radon concentration distribution in 2005 characterised by 25, 50, and 75 percentiles.

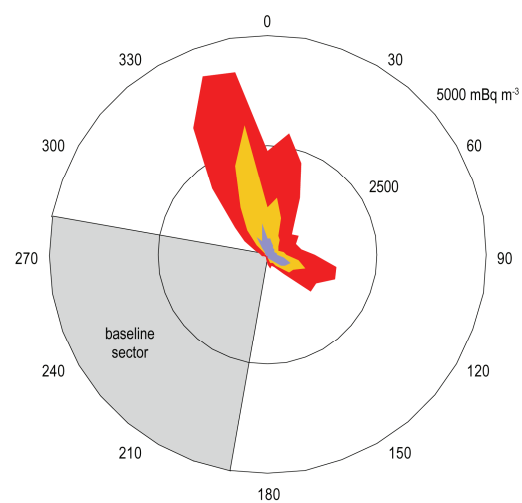


Figure 2. Angular radon concentration distributions in 2006 characterised by 25, 50, and 75 percentiles.

Oceanic fetch

Table 2 shows monthly radon concentration distributions in the baseline wind sector characterised by the 25, 50, and 75 percentiles for 2005 and 2006. Only for two Southern Hemisphere winter months in 2005 are the monthly medians significantly higher than 50 mBq m^{-3} . 75% of baseline events are below the 100 mBq m^{-3} baseline threshold for 20 months of the 24 month long period. A weak seasonal signal is evident, especially for 2005. On the other hand, the angular radon concentration distributions in the sector do not exhibit any distinctive pattern (Table 3). There is a significant decrease in the radon composite signal in the first 12 hours after change to the baseline sector. After the first 24 hours the signal reaches levels characteristic of the least perturbed oceanic air (Figure 3). This pattern is also documented in Table 4, which shows radon angular median concentrations in the baseline sector for the first 24 hours after change to the sector calculated for 10 deg wide sub-sectors.

Figure 4 shows the extent of the oceanic fetch corresponding to baseline events persisting in the sector for longer than 24 hours. The contrast is de-

rived from the back trajectory density for 2001-2005 spring events. The same events are shown in Figure 5 with the contrast representing the mean time required for the air parcels to reach Cape Grim.

Table 2. Monthly radon concentrations (mBq m^{-3}) in the baseline wind sector in 2005 and 2006, where wind speed $>2 \text{ m s}^{-1}$ and wind direction between 190° and 280° , persisting in the sector for at least two hours.

Month	2005			2006		
	25 th percentile	Median	75 th percentile	25 th percentile	Median	75 th percentile
Jan	27	34	47	24	34	67
Feb	33	41	57	19	26	34
Mar	34	41	67	30	40	67
Apr	41	49	67	43	53	59
May	41	49	65	33	43	137
Jun	41	94	228	41	51	155
Jul	42	70	236	44	61	88
Aug	35	42	52	36	48	81
Sep	35	45	75	36	51	76
Oct	27	34	44	17	28	47
Nov	18	28	39	26	37	57
Dec	22	30	39	21	34	45
ALL	32	42	65	28	40	61

Table 3. Angular radon concentration (mBq m^{-3}) distributions in the baseline wind sector in 2005 and 2006 characterised by the 25, 50, and 75 percentiles, where wind speed $>2\text{ms}^{-1}$ and wind direction between 190° and 280° , persisting in the sector for at least two hours.

Sub-sector in baseline Sector ($^\circ$)	2005			2006		
	25 th percentile	Median	75 th percentile	25 th percentile	Median	75 th percentile
190-200	38	52	129	28	41	60
200-210	34	43	62	26	40	60
210-220	33	41	54	26	38	58
220-230	35	44	64	26	35	53
230-240	33	42	63	25	38	59
240-250	32	41	68	29	42	75
250-260	30	40	65	29	41	64
260-270	30	41	57	33	47	76
270-280	32	41	57	31	47	83
ALL	32	42	65	28	40	61

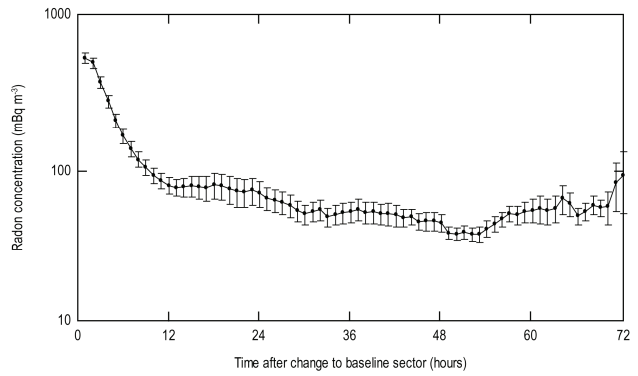


Figure 3. Radon concentration means in consecutive composite periods of 1 hour after the sector change to baseline. Based on the 2005-2006 radon data set.

Table 4. Angular radon concentration (mBq m^{-3}) distribution in the baseline wind sector in 2005 and 2006 characterised by their median values, where wind speed $> 2\text{m s}^{-1}$, wind direction between 190° and 280° .

Hour after change to baseline sector	Sub-sectors in the baseline sector ($^\circ$)									
	190-200	200-210	210-220	220-230	230-240	240-250	250-260	260-270	270-280	190-280
1	79	234	290	254	1388	67	1003	187	58	93
2	66	221	378	256	159	169	196	73	56	105
3	65	62	236	221	76	186	67	67	45	72
4	76	68	56	96	129	70	51	52	42	61
5	68	128	43	61	82	51	61	44	52	60
6	48	73	50	66	48	54	44	43	54	49
7	65	51	40	67	40	51	38	45	61	48
8	45	43	40	46	50	44	39	50	51	45
9	52	40	43	45	44	40	32	51	50	41
10	47	34	35	47	50	37	37	42	72	41
11	41	45	34	44	39	69	32	35	60	41
12	42	42	36	43	39	43	40	39	28	40
13	47	41	40	41	35	42	47	34	42	40
14	50	34	39	39	40	34	47	40	40	40
15	42	38	37	41	45	38	39	43	28	39
16	44	42	42	36	33	38	36	38	37	39
17	37	48	44	32	28	38	41	41	31	37
18	39	38	40	35	35	34	41	40	36	38
19	44	37	42	37	39	40	31	36	29	38
20	38	35	39	29	34	42	35	43	32	37
21	43	29	31	31	37	41	39	34	34	37
22	47	34	31	36	35	37	39	39	41	36
23	36	29	39	40	49	38	44	26	38	37
24	31	33	30	35	45	38	37	34	39	35

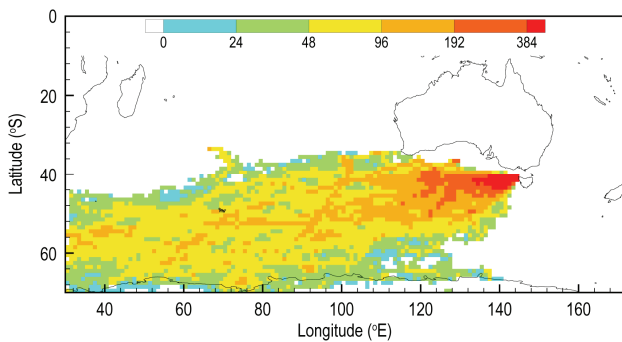


Figure 4. Back trajectory density function for baseline sector observations at Cape Grim. The contour map indicates the number of times a $1^\circ \times 1^\circ$ grid cell has been traversed by a baseline sector event trajectory. Composite spring events persisting in the baseline wind sector for longer than 24 hours (2001-2005)

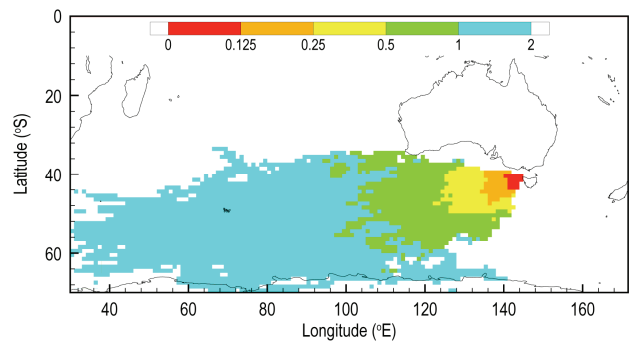


Figure 5. Mean time required for the least perturbed air parcels to reach Cape Grim (in units of $R_n \tau_{1/2} = 3.84$ days). Composite spring events persisting in the baseline wind sector for longer than 24 hours (2001-2005).

Continental fetch

Table 5 shows monthly radon concentration distributions in the mainland wind sector characterised by the 25, 50, and 75 percentiles for 2005 and 2006. A broad maximum centred in June/July is typical for the sector and is caused by a seasonal change in the geographic extent of the fetch over mainland. The angular radon concentration distributions showed in Table 6 exhibit a strong angular anisotropy of the radon signal in the sector. Figure 6 shows mean radon concentrations as a function of time after change to the mainland sector. There is a period of steady increase in radon concentrations in the first 24 hours after change to the mainland sector. The increase is a typical annual feature for mainland sector observations (cf. Figure 4 in the 2001-2002 and 2003-2004 reports). However, only a fraction of all mainland observations correspond to air masses over mainland. For instance, analysis of back trajectories for mainland events in 2001-2005 has demonstrated that only 45% of the trajectories were over mainland, with the remaining trajectories over ocean (34%), over Tasmania (13%) and of mixed origin (8%). Hence, these individual fetch areas are likely to have different time dependence and/or radon means to those shown in Figure 6.

Table 5. Monthly radon concentrations (mBq m^{-3}) in the mainland wind sector in 2005 and 2006, where wind speed $>2\text{m s}^{-1}$ and wind direction between 280° and 90° , persisting in the sector for at least two hours.

Month	2005			2006		
	25 th percentile	Median	75 th percentile	25 th percentile	Median	75 th percentile
Jan	62	184	389	192	290	1131
Feb	174	334	588	79	248	1497
Mar	101	205	1119	194	263	775
Apr	274	684	2874	138	275	609
May	195	1303	3306	84	358	893
Jun	734	1682	3384	175	589	2036
Jul	124	999	2739	201	689	2920
Aug	111	1399	3538	209	609	2324
Sep	181	457	1886	115	435	1906
Oct	53	215	922	117	216	946
Nov	93	341	1254	259	464	935
Dec	35	63	114	170	279	501
ALL	104	421	1842	168	369	1318

Table 6. Angular radon concentration (mBq m^{-3}) distributions in the mainland wind sector in 2003 and 2004 characterised by the 25, 50, and 75 percentiles, where wind speed $>2\text{ms}^{-1}$ and wind direction between 280° and 90° , persisting in the sector for at least two hours.

Sub-sector in mainland Sector ($^\circ$)	2005			2006		
	25 th percentile	Median	75 th percentile	25 th percentile	Median	75 th percentile
280-290	35	53	127	51	97	349
290-300	36	65	372	40	83	395
300-310	42	90	661	47	115	591
310-320	66	180	861	104	315	904
320-330	94	321	1854	190	706	1979
330-340	158	1077	2531	475	1261	3443
340-350	197	1097	2722	298	1558	4186
350-360	595	2411	3437	639	2669	4225
0-10	917	2574	3710	389	1768	3122
10-20	560	2189	3415	552	1618	2951
20-30	265	991	2730	295	989	2511
30-40	266	1234	2524	238	490	1767
40-50	217	378	1300	222	422	954
50-60	212	401	1345	213	307	643
60-70	185	450	1710	186	265	740
70-80	142	414	1517	170	244	590
80-90	154	325	821	199	354	705
ALL	104	421	1842	168	369	1318

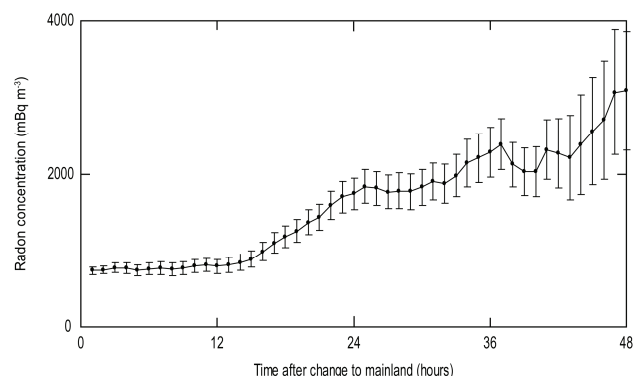


Figure 6. Radon concentration means in consecutive composite periods of 1 hour after the sector change to mainland. Based on the 2005-2006 radon dataset.

Acknowledgements

The author would like to thank the Cape Grim staff for their support in the running of the radon program at CGBAPS and John Gras of CSIRO for making available an edited version of the ultra-fine particle 2005-2006 dataset.

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4.5. BASELINE CARBON DIOXIDE MONITORING

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The continuous monitoring of atmospheric carbon dioxide (CO₂) continued at Cape Grim during 2005–2006, with the LoFlo Mk 2 CO₂ analyser system (designated as LoFlo2A). The operation of the system was relatively trouble-free during this period. An internal power supply failed on 24 January 2005, and was quickly replaced. The drying reagent and CO₂-absorbing reagent in the Li-Cor optical bench were changed on 4 May 2005, and again on 14 December 2006.

After testing that there would be no loss of performance of the LoFlo2A system, the flow rate of the reference gas through the reference cell was reduced from 15 ml min⁻¹ to 10 ml min⁻¹ on 22 September 2006, to further increase the lifetime of the reference gas cylinders. Also, the software of LoFlo2A was modified slightly on 6 September 2006 so that the ambient air CO₂ value could be provided directly (via a serial port) to a system installed at Cape Grim to make continuous measurements of atmospheric oxygen.

There were three changes of air intake pumps during this period (on 11 July 2005, 29 November 2005, and again on 16 March 2006). A leak in the 70-meter inlet line was found and repaired on 31 October 2006.

The LoFlo2A system continued to be calibrated with the suite of 7 CO₂-in-dry (natural) air standards, contained in 29.5 L high-pressure aluminium cylinders (Luxfer Gas Cylinders, Riverside, California, USA) – see Table 1. CO₂ values are assigned to these standards in CSIRO GASLAB, using the gas chromatographic technique described elsewhere [Francey *et al.* 1996]. Each standard cylinder is fitted with its own dedicated, pressure reducing regulator (high purity, single stage, stainless steel, 74-2400 series, Tescom Corporation, Elk River, Minnesota, USA). The regulators have not been removed from their cylinders since the time of installation of the prototype LoFlo in May 2000. The reference gases are also CO₂-in-dry (natural) air contained in similar high-pressure cylinders. Due to the higher usage rate of the reference gas (compared to the calibration gases), the reference gas cylinders require to be changed every few months. Details of all of the reference gases used so far are also shown in Table 1.

As described previously, the response function of the LoFlo system is evaluated approximately once per month, using a classical ‘calibration pyramid’ approach, flowing gas from each calibration stan-

dard through the sample cell in turn. Multiple pyramids were run on each occasion. A ‘zero’ determination (reference gas passing through both cells simultaneously) is made each alternate sample, so that the measurement of each calibration sample is bracketed by the measurement of a ‘zero’. The occasions of these response function determinations during 2005–2006 are given in Table 2. In each such calibration experiment, the response function (a shallow quadratic) of the analyser system is determined, as well as the CO₂ value of the reference gas (see last column of Table 2), relative to the suite of seven calibration standards. These are then deemed to define the response of the analyser during ambient air measurements, until the time of the next calibration experiment.

All of the instrumentally valid, hourly-average CO₂ data from the LoFlo system during 2005–2006 are shown in Figure 1. The top panel shows all of the instrumentally valid hourly values. The second panel of Figure 1 shows only those hourly values which are selected as baseline (see Steele *et al.* 2003 for the explanation of the baseline selection technique). The blue curve shown in the second panel is the 80-day smooth curve fit, and the green curve is the 650-day trend curve fit, calculated using the filtering techniques of Thoning *et al.* [1989].

Monthly average, and annual average baseline CO₂ values from the LoFlo system during 2005–2006 are given in Table 3. The CO₂ data are reported in units of $\mu\text{mol mol}^{-1}$ of dry air as recommended in Schwartz and Warneck [1995].

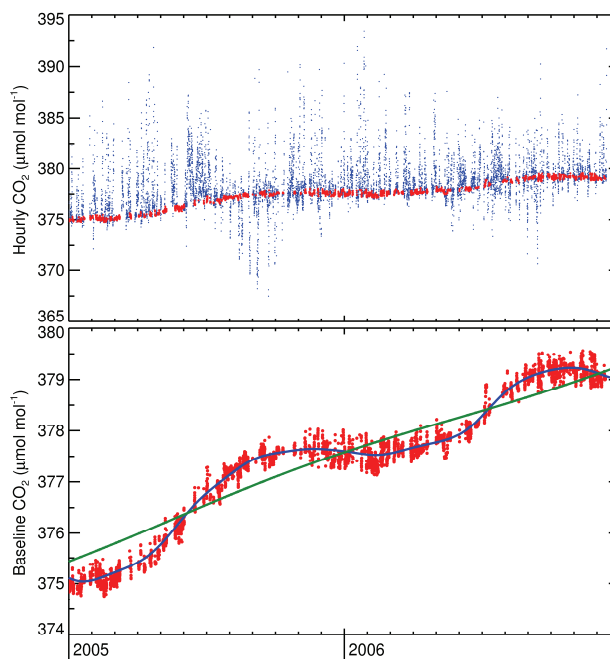


Figure 1. Cape Grim LoFlo Mk 2 *in situ* carbon dioxide (CO₂) record for 2005 to 2006 inclusive. First panel: all instrumentally valid hourly CO₂ values, with baseline data shown in red and non-baseline shown in blue. Second panel: hourly baseline data only, with 80-day smooth curve (blue) and 650-day long-term trend curve (green).

The long term *in situ* record of baseline CO₂ at Cape Grim has been updated with the results presented here for 2005 and 2006, and is shown in the top panel of Figure 2. The variation of the growth rate of CO₂ over the period 1976-2006 is shown in the bottom panel of Figure 2.

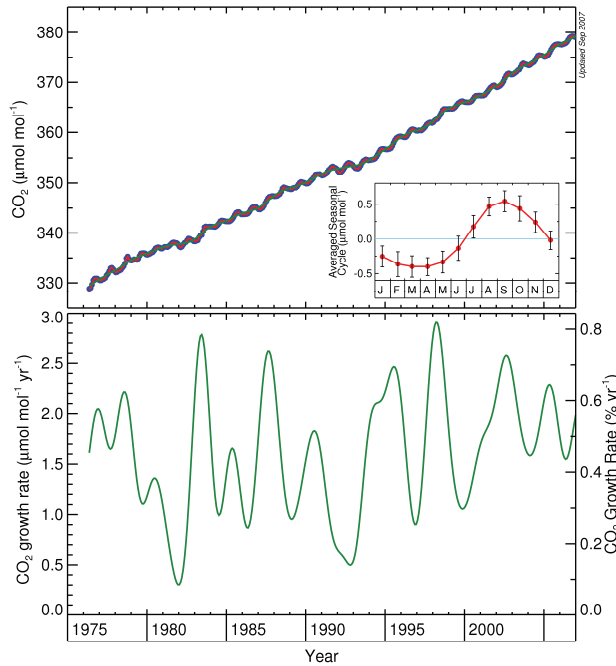


Figure 2. The Cape Grim *in situ* record of atmospheric CO₂, showing monthly average baseline values for 1976 to 2006 inclusive (top panel). Inset to the top panel shows the average seasonal cycle of CO₂ at Cape Grim. The bottom panel shows the instantaneous growth rate.

Table 1. Details of the CO₂-in-air calibration suite used on the LoFlo CO₂ analyser systems, as well as those of all of the CO₂-in-air reference gases to the end of 2006.

ID	Installation Date	Cyl. #	UAN	Starting Pressure (psig)	CO ₂ GASLAB (μmol mol ⁻¹)	CO ₂ LoFlo (μmol mol ⁻¹)
Cal1	20000510	CA01666	980773	1870	338.96	
Cal2	20000510	CA01687	980772	1950	350.24	
Cal3	20000510	CA01647	970830	1750	360.68	
Cal4	20000510	CA01688	980771	1890	369.99	
Cal5	20000510	CA01634	970337	1790	380.37	
Cal6	20000510	CA01640	970338	1780	388.47	
Cal7	20000510	CA01622	970339	1740	400.15	
Ref1	20000510	CA01686	991782	1400	367.39	
Ref2	20000607	CA01605	991071	1860	365.23	
Ref3	20001011	CA01698	992447	1880	366.59	
Ref4	20010214	CA03130	993362	1880	367.64	
Ref _{Temp}	20010622	CA01605	993363		367.06	
Ref5	20010625	CA03122	993756	1910	367.47	
Ref6	20011024	CA03130	993943	1860	368.41	
Ref7	20020222	CA03122	994363	1980	369.52	
Ref8	20020823	CA03130	994746	1960	369.42	
Ref9	20030321	CA04934	994225	1900	368.63	
Ref10	20030814	CA03130	995659	1920	372.31	
Ref11	20040109	CA01698	995477	1980	371.78	
LoFlo changed to LoFlo Mk 2						
Ref12	20040615	CA04934	995805	1820	373.66	373.523
Ref _{Temp}	20041126	CA01620	995982	800	368.36	368.351
Ref13	20041203	CA04936	996662	1920	-	375.622
Ref14	20050512	CA06058	996755	1880	-	374.195
Ref15	20051013	CA05644	997348	1940	-	379.901
Ref16	20060314	CA05433	997517	1890	-	374.936
Ref17	20060821	CA04934	998024	1870	-	379.115

Table 2. Basic details of the calibration experiments conducted on the LoFlo CO₂ analyser system, during 2005-2006. Dates (yyyymmdd) and times (hhmm) are in AEST. The reference gas is assigned a CO₂ value (last column) on the basis of each calibration experiment. *A failure of an internal power supply occurred on 24 January 2005. The calibration run #67, run after the replacement of the power supply, was not acceptable, due to instrument instability. The Ref CO₂ value from the previous calibration run (#66) was used until the time of the next calibration run (#68).

CAL #	Start Date	Start Time	Finish Date	Finish Time	Ref CO ₂ (μmol mol ⁻¹)
Ref13 (cont.)					
66	20050107	1240	20050110	1400	375.624
67	20050125	1515	20050128	1325	n/a*
68	20050324	1447	20050328	0240	375.627
69	20050510	1202	20050512	1611	375.642
Ref14					
70	20050512	1616	20050516	0410	374.195
71	20050708	1701	20050711	1221	374.194
72	20050829	1036	20050901	0832	374.191
73	20051006	1330	20051010	0123	374.201
Ref15					
74	20051013	1305	20051017	0058	379.901
75	20051111	1208	20051115	0001	379.907
76	20051220	1513	20051223	1308	379.904
77	20060112	1021	20060115	2222	379.907
78	20060303	1014	20060306	1252	379.916
Ref16					
79	20060314	0952	20060317	1227	374.936
80	20060421	1258	20060425	0052	374.939
81	20060526	1521	20060530	0315	374.934
82	20060630	1211	20060704	0004	374.941
83	20060811	1008	20060814	0220	374.951
Ref17					
84	20060821	1327	20060825	0120	379.115
85	20060922	1645	20060925	1551	379.116
86	20061027	1340	20061030	1136	379.114
87	20061215	1459	20061219	0253	379.117

Table 3. Monthly mean baseline atmospheric carbon dioxide mixing ratios measured by the LoFlo Mk 2 *in situ* monitoring system at Cape Grim during 2005-2006. The monthly mean values have been calculated from smooth curve fits to the hourly baseline data (see text for details). The mixing ratios are expressed in the WMO mole fraction calibration scale, as micro-mole (μmol) of CO₂ per mole of dry air (μmol mol⁻¹). Also shown is the number of CO₂ baseline hours, the number of instrumentally valid CO₂ hours, the total possible hours for each month, and a summary for each year.

Month	2005		2006	
	CO ₂ (μmol mol ⁻¹)	bl hrs	CO ₂ (μmol mol ⁻¹)	bl hrs
Jan	375.058	217	377.555	180
Feb	375.135	246	377.524	375
Mar	375.295	158	377.605	169
Apr	375.548	193	377.712	229
May	376.012	284	377.826	238
Jun	376.548	61	378.073	216
Jul	376.959	257	378.508	125
Aug	377.289	355	378.910	195
Sep	377.502	167	379.127	179
Oct	377.596	101	379.219	295
Nov	377.638	127	379.182	310
Dec	377.618	277	379.050	257
Year	376.517	2443	378.358	2768

Overlap experiment

A second LoFlo Mk 2 CO₂ analyser system (known as LoFlo2B) was installed at Cape Grim in March 2005, to run alongside the existing LoFlo2A system. The LoFlo2B system was installed to operate with its own suite of seven CO₂-in-air standards. Both LoFlo systems shared the air intake pump during the period when both systems operated. The LoFlo2B system was removed from Cape Grim and returned to CMAR, Aspendale in late November 2005.

Part of the purpose in operating two LoFlo CO₂ systems in this way was to determine the level of agreement between the analysers when measuring the same ambient air over a suitably long period of time. An essential part of this experiment was to determine precisely the relationship between the two calibration suites. During 10-16 March 2005, the calibration standards of LoFlo2B were measured on LoFlo2A. Then during 14-16 March 2005, and 13-21 April 2005, the calibration standards of LoFlo2A were measured on LoFlo2B.

The results of these experiments will be presented elsewhere.

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4.6. $\delta^{13}\text{C}$ AND $\delta^{18}\text{O}$ OF CO₂ IN BASELINE CAPE GRIM AIR: 2005-2006

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[Supported by CGBAPS and CSIRO research funds.]

CSIRO Marine and Atmospheric Research (CMAR) measures the stable isotopic composition of atmospheric carbon dioxide ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) at Cape Grim using two programs; the *in situ* program (CIA), where CO₂ is extracted from baseline air at Cape Grim and sent to the Global Atmospheric Sampling Laboratory (GASLAB) in Aspendale (CMAR) for stable isotope analysis; and the flask program (CGA), where samples of air are collected in 0.5 litre glass flasks and returned to CMAR for analysis as part of the global flask network operated by CSIRO GASLAB. Both of these programs have been previously described in detail [Allison *et al.*, 1994; Francey *et al.*, 1995]. Results from these two programs for 2005 and 2006 are summarised here with the data from both programs available through the Cape Grim data archive.

Sample collection

Sample collection for both programs is initiated when air originates from the marine sector, 190° to 280°, the *in situ* CO₂ concentration has been steady (variation < 0.2 $\mu\text{mol mol}^{-1} \text{h}^{-1}$) for 2 hours before sampling, and the Baseline Events Switch 3 indicates that the condensation nuclei (CN) count is less than a seasonally variable threshold based on the 90th percentile of CN hourly medians for this day-of-year over the previous five years. All three criteria are re-assessed during data processing and if a sample fails any of the three criteria, e.g. if the wind direction moves outside the baseline sector during sample collection, the sample is identified as non-baseline.

No problems with sample collection for the CIA or CGA programs were recorded in the logbooks; however, in October 2006 the 70 metre 'polypipe' intake line was replaced due to severe leakage. Both CIA and CGA samples are collected through this intake line and so samples collected in September and October have been flagged as suspect. Several periods of mass spectrometer failure in GASLAB lead to increased sample storage times, i.e. the time between sample collection at Cape Grim and analysis at CMAR, for both the CIA and CGA programs. For 2005-2006, storage times are 68±46 days and 68±30 days for CIA and CGA respectively. Previous storage times were 39±22 days and 66±32 days in 2003-2004, and 25±17 days and 55±43 days in 2001-2002 for CIA and CGA respectively. While no discernable impact on the stable isotopic composition of samples from increased sample storage time has been observed [Allison and Francey, 2007], the delay in mass spectrometric analysis caused a shortage of sample flasks for the *in situ* program (but

not for the flask program) resulting in fewer CIA samples being collected and fewer extractions from the air standard (see below) being performed.

Sample analysis and data processing

CO₂ samples extracted at Cape Grim are measured directly against a calibrated pure CO₂ standard. CO₂ samples are extracted from the CGA samples and measured against the same calibrated pure CO₂ gas but are then calibrated using bracketing measurements of a CO₂-in-air standard to maintain an independent scale. We use the CSIRO2005 assignment [Allison and Francey, 2007] to report data on the VPDB-CO₂ scale [Coplen, 1995]. The CSIRO2005 assignment supersedes previous measurement assignments [Francey and Goodman, 1988; Allison and Francey, 1999]. The CSIRO2005 assignment corrects for systematic instrument effects and provides a consistent traceable assignment to the VPDB-CO₂ reference scale that includes a comprehensive assessment of measurement and calibration uncertainties.

Measurements made on all CO₂ samples must be corrected for the presence of nitrous oxide (N₂O) in the trapped CO₂ samples [Francey and Goodman, 1985]. The CO₂ and N₂O concentrations of all CGA samples are measured in GASLAB [Steele *et al.*, 2007]; any missing data are estimated using a procedure described previously [Allison *et al.*, 2001] that applies the fitting procedure of Thoning *et al.* [1989] to the 0.5 L flask data from 1992 onwards. For CIA samples, the average CO₂ concentration during the CO₂ trap is obtained from the *in situ* CO₂ program [Steele *et al.*, 2004] and the N₂O concentration is estimated using the 'missing data' procedure mentioned above.

The resulting data ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO₂) are then subjected to a quality control process that includes assessment of the analytical procedures and a statistical filtering procedure as described by Steele *et al.* [1996]. In the statistical filtering procedure, retained data are fitted with a curve consisting of a quadratic and four harmonics, using the procedure of Thoning *et al.* [1985], to capture the seasonal cycle and any data further than 2.5 standard deviations away from the fitted curve are flagged.

In situ program (CIA)

Fifty-three CO₂ samples were extracted at Cape Grim; forty-seven samples were extracted from baseline air and six samples were extracted from a high-pressure cylinder of air used to monitor performance of the extraction process (see below). No samples were collected outside the baseline sector but subsequent data processing indicated that two samples were collected under conditions of high CN (> 10% above the 90th percentile criteria). One baseline air sample (CGIS#1179) was not analysed due to air contamination (leaking valve). Two significant disruptions to sample collection resulted from the shortage of sample flasks; no samples were collected between 15 March 2005 and 27 May 2005 or

between 10 February 2006 and 13 June 2006. Omitting these two periods the average sampling interval was 12±8 days.

Ten samples were flagged as 'suspect'; four samples were analysed during a period of mass spectrometer instability and six were collected during the period immediately prior to the leaking polypipe being replaced.

The CIA $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data are presented in Figures 1 and 2. Individual points are shown as filled blue circles. The high CN samples are identified separately in Figures 1 and 2 using open squares and other flagged data are identified with + symbols. Also shown in the figures is the curve (quadratic plus four harmonic functions) derived from the statistical filtering procedure fitted to all available CIA data from 1990 onwards (see Figure caption for details). In 2005-2006, no $\delta^{13}\text{C}$ data were flagged from the quality control procedure but five $\delta^{18}\text{O}$ data were. A summary of the collection and storage details for the CIA samples is presented in Table 1.

Table 1. Sample collection and storage details for samples collected at Cape Grim during 2005-2006. The forty-four analyses of the cylinder CA04606 were made in 2001 before the cylinder was transported to Cape Grim.

	CIA	CGA
Intake mast height (m)	70	70
No. of collected samples	47	140
No. of retained $\delta^{13}\text{C}$ samples	34	99
No. of retained $\delta^{18}\text{O}$ samples	29	92
Average sampling frequency (days)	12±8	10±7
Average storage time prior to analysis	68±46	68±30
Average wind direction (°N)	246±22	247±24
Average wind speed (m s ⁻¹)	12±4	12±5
No. of samples with CN above 90 th percentile	2	10
No. of CO ₂ samples extracted from CA04606	6	44

Flask program (CGA)

One hundred and forty 0.5 litre flasks of air were collected, usually two per sampling day, at an average sampling interval of (10±7) days; six were not analysed due to leakage. The periods of mass spectrometer instability that affected the CIA samples did not affect CGA samples due to the different analysis protocols but fifteen samples collected during the period immediately prior to the leaking polypipe replacement were flagged as suspect. Of the one hundred and nineteen remaining samples, thirteen were collected under marginal baseline conditions, as indicated by CN counts or wind outside marine sector.

The CGA $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data are presented in Figures 1 and 2; individual points are shown as filled red circles. Samples with high CN or other flags are identified separately in Figures 1 and 2 as for the CIA samples. Also shown is the curve from the statistical filtering procedure fitted to all available CGA 0.5 litre flask data from 1990 onwards. In 2005-2006, seven $\delta^{13}\text{C}$ data and fourteen $\delta^{18}\text{O}$ data were flagged from the quality control. A summary of the sample collection and storage details for all CGA samples are presented in Table 1.

For CGA $\delta^{18}\text{O}$, we have previously observed increased scatter to more negative values [Allison *et al.*, 2006] that is consistent with moisture in the flasks exchanging ^{18}O with the CO_2 . The occurrence of these events has decreased in 2005-2006.

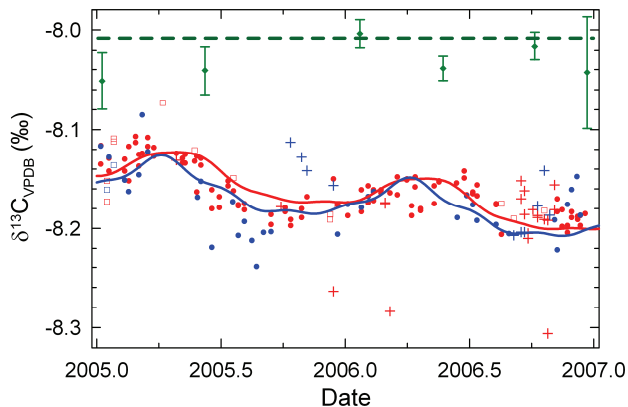


Figure 1. Cape Grim $\delta^{13}\text{C}$ of CO_2 for 2005-2006: CIA (\bullet), CGA (\bullet), and CJA (\bullet). Samples collected when CN exceeded the 90th percentile threshold are shown as (\square) for CIA and (\square) for CGA. Samples identified as outliers from the statistical filter or from other flagging procedures are identified as (+) for CIA and (+) for CGA. The generated CIA and CGA curves are shown as (—) and (—) respectively. The CO_2 samples extracted from the air standard at Cape Grim (CJA) are shown as filled green circles (\bullet) and the assigned value is indicated by the dashed green line (---). The measurement uncertainties for the “air standard” samples are indicated by the vertical bars, for all other samples the average measurement uncertainty is less than 0.03 ‰.

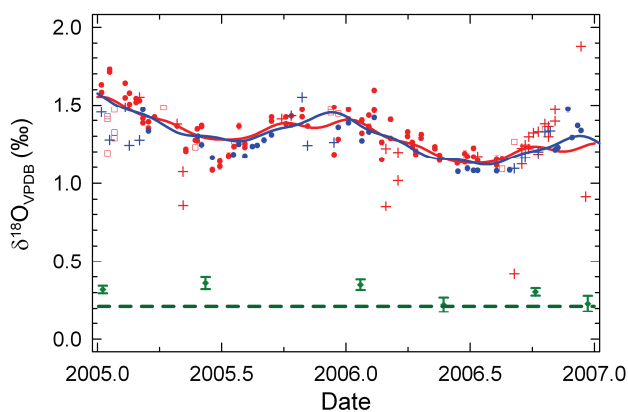


Figure 2. Cape Grim $\delta^{18}\text{O}$ of CO_2 for 2005-2006: Symbols are as for Figure 1. The average measurement uncertainty for each data point, other than the CJA samples, in the period is less than 0.06 ‰.

Cape Grim *in situ* air standard (CJA)

At Cape Grim, samples of CO_2 are extracted from a high-pressure cylinder of air to monitor the *in situ* extraction system [Allison *et al.*, 2004]; these samples are identified using the CJA site code. The current cylinder (ID CA04606, UAN993888) was sent to Cape Grim in February 2002 and six extractions were made during 2005-2006. The measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for these extractions are shown in Figures 1 and 2 respectively. Also shown in the figures is a

line representing the value assigned to the air standard at CMAR before the cylinder was shipped to Cape Grim. Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ show variations over the two year period but the Cape Grim extractions are consistently about +0.025 ‰ lower for $\delta^{13}\text{C}$ and about 0.1 ‰ greater for $\delta^{18}\text{O}$, consistent with previous measurements. The $\delta^{18}\text{O}$ difference is slightly larger than in previous years but the small number of samples collected in 2005-2006 may be affecting this comparison. A replacement air standard is being prepared to enable the present air standard to be returned to CMAR for re-analysis. No adjustments are made to the CIA or CGA data based on the analysis of the air standard.

Comparison of the records: $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

There is good agreement between both the CIA and CGA records. While there appears to be a small offset between the two $\delta^{13}\text{C}$ records, the average difference between the two records over 2005-2006 is 0.01 ‰ +/- 0.01 ‰; within the uncertainty estimates for the measurements. This small difference is consistent with a previously observed offset between these two records which we assigned to uncertainty in the assignment of the $\delta^{13}\text{C}$ value of the primary reference CO_2 gas used for the CIA measurement (designated ST06) that is not used for the CGA measurements. This is discussed further in Allison and Francey [2007] and the assignment of values to ST06 is under further investigation. For $\delta^{18}\text{O}$ there is no indication of an offset.

During 2005-2006, both CGA and CIA $\delta^{13}\text{C}$ decreased at a rate of -0.03 ‰ per year, very close to the long term (25-year) decrease of -0.024 ‰ per year, with peak-to-peak amplitude of about 0.05 ‰. For the same period, $\delta^{18}\text{O}$ remained consistent with the long-term (25-year) average value of 1.3 ‰ with peak-to-peak amplitude of 0.3 ‰.

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We would like to thank the Cape Grim staff (Laurie Porter, Chris Rickard, Stuart Baly, and Jill Cainey) for their expertise in maintaining both the CIA and CGA programs. We also thank GASLAB staff (Ray Langenfelds, Marcel van der Schoot, Darren Spencer and Paul Krummel) for providing the CO_2 and N_2O concentration data and Nada Derek and John Gras for providing the CN data.

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4.7. ARCHIVING OF CAPE GRIM AIR

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Regular collection of Cape Grim air in high pressure metal cylinders for the purpose of maintaining an archive of atmospheric composition has continued since 1978. A history of sampling events, protocols, techniques and reconstruction of atmospheric trace gas records through 1995 has been given previously [Langenfelds *et al.*, 1996 and references therein] and updated through 2004 [Langenfelds *et al.*, 2006 and references therein]. Since 2004, Cape Grim Air Archive data have been used to investigate the long-term trends of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) [Beer *et al.* 2006; MacFarling Meure *et al.* 2006] and $\delta^{13}\text{C}$ in CH_4 [Ferretti *et al.* 2005]. Vollmer *et al.* [2006] used measurements from four Cape Grim Air Archive subsamples taken from 2004-2006, to aid in the detection of the first appearance of HFC-245fa ($\text{CHF}_2\text{CH}_2\text{CF}_3$) in the Southern Hemisphere atmosphere. Velders *et al.* [2006] have published global records of HCFC-22 (CHClF_2), HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$), HCFC-142b (CH_3CClF_2), HFC-134a (CH_2FCCF_3) and HFC-23 (CHF_3) based on AGAGE *in situ* measurements and SIO/UEA measurements on the Cape Grim Air Archive and Cape Grim flasks. Porter *et al.* [2006] have published the Cape Grim methyl bromide (CH_3Br) record based on *in situ* and Cape Grim Air Archive data.

In late 2006, an AGAGE GC-MS Medusa system (Medusa9) was commissioned at CMAR-Aspendale. The majority of samples remaining in the Cape Grim Air Archive were subsequently measured on this system during the first half of 2007, and a summary of results will be presented in a future issue of *Baseline*.

Primary sampling

Fifteen cylinders were filled during 2005/06 (Table 1), including seven filled specifically to be used as calibration standards at CGBAPS for measurement programs maintained by the Advanced Global Atmospheric Gases Experiment (AGAGE).

The AGAGE calibration standards are included here because they are filled with the same techniques used for the majority of the dedicated air archive samples and measurements of their composition may be included in air archive datasets for some applications.

Subsampling

A total of four archive subsamples were prepared during 2005/06 (Table 2), for collaborative projects where the trace gas measurements were performed at laboratories other than Cape Grim and CMAR. Specifically a suite of four subsamples taken from four individual primary air archive samples spanning the years 2004-2006, was prepared for analysis of HFC-245fa at the Swiss Federal Laboratories for Materials Testing and Research (Empa), Dübendorf, Switzerland.

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Table 1. Collection and status details for primary archive samples filled at Cape Grim. Samples are listed against UAN (a number unique to each sample, assigned at CMAR), Tank ID (a label unique to each individual sample container), Archive ID (a sample identifier commonly used before 1992) and AGAGE ID (a sample identifier used in the AGAGE program). Wind data represent estimated averages over the period of collection. They are calculated either from collection records or from Cape Grim hourly average data.

UAN	Tank ID	Archive ID	AGAGE ID	Collection Date (GMT)	Sampling Method ^a	Drying Method ^b	Wind Speed (m s ⁻¹)	Wind Direction (°)	Pressure Fill (kPa abs)	Current Status ^{c,d}	
997090	S34L-H19	CG010205	G-113	1 Feb 05	cryo	wet	12.8	245	6340	2510	CMAR
	S34L-H24	CG160205	G-114	16 Feb 05	cryo	wet	16.8	236	5170	-	exhausted
	S34L-H23	CG120405	G-115	12 Apr 05	cryo	wet	2.2	234	3820	-	exhausted
	S34L-H20	CG290405	G-116	29 Apr 05	cryo	wet	17.5	250	6310	-	exhausted
	S34L-H23	CG170605	G-117	17 Jun 05	cryo	wet	9.3	258	5620	-	exhausted
998005	S34L-H23	CG280605	G-118	28 Jun 05	cryo	wet	6.9	262	6440	5920	CMAR
997424	S34L-H21	CG070705	G-119	7 Jul 05	cryo	wet	9.3	261	6720	-	exhausted
998006	S34L-J04	CG051005	G-120	5 Oct 05	cryo	wet	14.2	267	6030	5615	CMAR
	S34L-H24	CG011105	G-121	1 Nov 05	cryo	wet	14.4	94	3960	-	exhausted
	S34L-H20	CG091205	G-122	9 Dec 05	cryo	wet	8.0	282	5690	-	exhausted
997724	S34L-H28	CG120106	G-127	12 Jan 06	cryo	wet	9.3	266	6030	5825	AGAGE
998195	S34L-H24	CG100206	G-128	10 Feb 06	cryo	wet	13.9	222	6030	5270	CMAR
998197	S34L-H20	CG060706	G-134	6 Jul 06	cryo	wet	15.1	264	5760	150	CMAR
998897	S34L-J02	CG220806	G-135	23 Aug 06	cryo	wet	10.7	254	6100	3685	CMAR
998852	S34L-F06	CG111206	G-144	11 Dec 06	cryo	wet	18.7	246	4890	4720	CMAR

^acryo immersion in liquid nitrogen
^cCMAR managed and stored at CMAR

^bwet no drying
^dAGAGE used as a standard in the AGAGE program

Table 2. Preparation and status details for subsamples of primary archive samples. Current status entries denote the institute managing the sample.

UAN	Subsample Tank ID	Parent UAN	Archive Date	Subsample Preparation Date	Fill Pressure kPa abs	Current Pressure kPa abs	Current Status
997725	V-001	997724	12-Jan-06	25-Jan-06	280	-	Empa
997726	V-004	997723	11-Jan-06	25-Jan-06	280	-	Empa
997727	V-007	997424	7-Jul-05	25-Jan-06	280	-	Empa
997732	RL-002	997089	1-Dec-04	7-Feb-06	280	-	Empa

4.8. CONTINUOUS MEASUREMENTS OF ^{14}C IN ATMOSPHERIC CO_2 AT CAPE GRIM, 1997-2006

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[Cooperative Research report.]

The collection of atmospheric carbon dioxide at Cape Grim for analysis of its $^{14}\text{CO}_2$ started in April 1987 as part of a world wide network [Levin *et al.*, 1992; Levin and Hesshaimer, 2000]. During 2005-2006, two-week integrated atmospheric CO_2 sampling for this project continued.

The atmospheric CO_2 is collected from about 15 m^3 of air by quantitative absorption in sodium hydroxide solution. After shipping of the bottles of exposed sodium hydroxide solution to the Heidelberg laboratory, CO_2 is extracted from the solution in a vacuum system by adding hydrochloric acid [Levin *et al.*, 1980]. For ^{14}C analysis, the CO_2 gas is purified over activated charcoal and counted in a high-precision proportional counter system [Krome and Münnich, 1992]. The $^{13}\text{C}/^{12}\text{C}$ ratio is measured, as $\delta^{13}\text{C}$, by mass spectrometry from small aliquots of the pure CO_2 gas and is only used for the fractionation correction of the ^{14}C data; the $\delta^{13}\text{C}$ values (‰) are given relative to the international V-PDB scale. The ^{14}C activity is expressed as per mil deviation ($\Delta^{14}\text{C}$ (‰)) from the US National Institute of Standards and Technology (formerly National Bureau of Standards) oxalic acid, activity corrected for decay [Stuiver and Polach, 1977]. The recent precision (1 σ of a single analysis) is typically $\Delta^{14}\text{C} = \pm 2$ ‰.

All samples collected in 1997-2006 are listed in Table 1. Those samples analysed so far in the Heidelberg ^{14}C laboratory are listed in Table 1 and shown in Figure 1. Not all samples have been analysed yet due to restrictions on funding. The results from this program have been discussed in Levin *et al.* [1992] and Levin and Hesshaimer [2000].

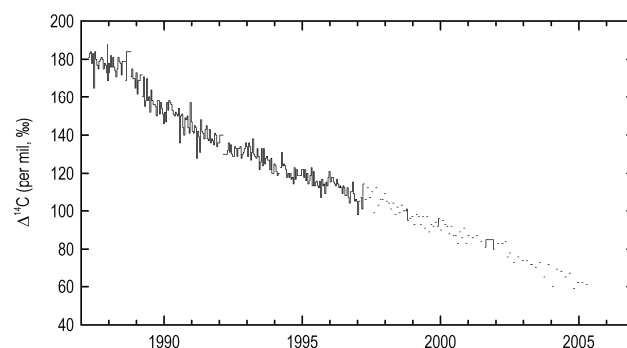


Figure 1. $\Delta^{14}\text{C}$ in atmospheric CO_2 measured with the CG-MAIN sampler for the period 1987-2005 at Cape Grim.

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Table 1. ^{14}C activity in atmospheric CO_2 at Cape Grim during 1997 - 2004. Missing data (-) indicate samples have not been analysed.

Sample No.	Sampling Period		$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	σ (‰)	Sample No.	Sampling Period		$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	σ (‰)
	Start	Stop					Start	Stop			
333	02 Jan 97	16 Jan 97	-8.20	98	3	461	21 Feb 02	07 Mar 02	-	-	-
334	16 Jan 97	30 Jan 97	-8.12	105	3	462	07 Mar 02	21 Mar 02	-	-	-
335	31 Jan 97	13 Feb 97	-	-	-	463	21 Mar 02	04 Apr 02	-8.71	83	2
336	13 Feb 97	27 Feb 97	-8.21	107	3	464	04 Apr 02	18 Apr 02	-	-	-
337	27 Feb 97	13 Mar 97	-8.09	101	3	465	18 Apr 02	02 May 02	-	-	-
338	13 Mar 97	27 Mar 97	-8.14	114	4	466	02 May 02	16 May 02	-8.30	84	2
339	27 Mar 97	10 Apr 97	-	-	-	467	16 May 02	30 May 02	-	-	-
340	10 Apr 97	24 Apr 97	-8.08	106	3	468	30 May 02	13 Jun 02	-8.40	76	2
341	24 Apr 97	08 May 97	-	-	-	469	13 Jun 02	27 Jun 02	-	-	-
342	08 May 97	22 May 97	-8.09	112	3	470	27 Jun 02	11 Jul 02	-8.27	78	2
343	22 May 97	05 Jun 97	-	-	-	471	11 Jul 02	25 Jul 02	-	-	-
344	05 Jun 97	19 Jun 97	-8.86	107	3	472	25 Jul 02	08 Aug 02	-	-	-
345	19 Jun 97	04 Jul 97	-	-	-	473	08 Aug 02	22 Aug 02	-	-	-
346	04 Jul 97	17 Jul 97	-8.80	110	3	474	22 Aug 02	05 Sep 02	-8.31	73	3
347	17 Jul 97	31 Jul 97	-	-	-	475	05 Sep 02	19 Sep 02	-	-	-
348	31 Jul 97	14 Aug 97	-8.12	99	2	476	19 Sep 02	03 Oct 02	-	-	-
349	14 Aug 97	28 Aug 97	-	-	-	477	03 Oct 02	17 Oct 02	-	-	-
350	28 Aug 97	11 Sep 97	-8.33	112	3	478	17 Oct 02	31 Oct 02	-8.77	76	2
351	11 Sep 97	25 Sep 97	-	-	-	479	31 Oct 02	14 Nov 02	-	-	-
352	25 Sep 97	09 Oct 97	-8.81	103	2	480	14 Nov 02	28 Nov 02	-	-	-
353	09 Oct 97	23 Oct 97	-	-	-	481	28 Nov 02	12 Dec 02	-	-	-
354	23 Oct 97	06 Nov 97	-9.05	106	3	482	12 Dec 02	30 Dec 02	-9.03	74	2
355	06 Nov 97	20 Nov 97	-	-	-	483	30 Dec 02	10 Jan 03	-	-	-
356	20 Nov 97	04 Dec 97	-8.93	106	3	484	10 Jan 03	23 Jan 03	-	-	-
357	04 Dec 97	18 Dec 97	-	-	-	485	23 Jan 03	06 Feb 03	-	-	-
358	18 Dec 97	02 Jan 98	-9.10	109	3	486	06 Feb 03	20 Feb 03	-8.49	74	2
359	02 Jan 98	15 Jan 98	-	-	-	487	20 Feb 03	06 Mar 03	-	-	-
360	15 Jan 98	29 Jan 98	-9.04	105	3	488	06 Mar 03	20 Mar 03	-	-	-
361	29 Jan 98	12 Feb 98	-	-	-	489	20 Mar 03	03 Apr 03	-	-	-
362	12 Feb 98	26 Feb 98	-8.90	104	2	490	03 Apr 03	28 Apr 03	-8.49	72	2
363	26 Feb 98	12 Mar 98	-	-	-	491	28 Apr 03	08 May 03	-	-	-
364	12 Mar 98	26 Mar 98	-8.91	101	3	492	08 May 03	22 May 03	-	-	-
365	26 Mar 98	09 Apr 98	-	-	-	493	22 May 03	05 Jun 03	-	-	-
366	09 Apr 98	23 Apr 98	-8.68	104	3	494	05 Jun 03	19 Jun 03	-8.41	70	2
367	23 Apr 98	07 May 98	-	-	-	495	19 Jun 03	03 Jul 03	-	-	-
368	07 May 98	21 May 98	-8.89	98	2	496	03 Jul 03	17 Jul 03	-	-	-
369	21 May 98	04 Jun 98	-	-	-	497	17 Jul 03	31 Jul 03	-	-	-
370	04 Jun 98	18 Jun 98	-9.16	102	3	498	31 Jul 03	14 Aug 03	-9.01	73	2
371	18 Jun 98	02 Jul 98	-	-	-	499	14 Aug 03	28 Aug 03	-	-	-
372	02 Jul 98	16 Jul 98	-8.68	99	3	500	28 Aug 03	11 Sep 03	-	-	-
373	16 Jul 98	30 Jul 98	-	-	-	501	11 Sep 03	25 Sep 03	-	-	-
374	30 Jul 98	13 Aug 98	-9.01	103	5	502	25 Sep 03	09 Oct 03	-8.29	65	3
375	13 Aug 98	28 Aug 98	-	-	-	503	09 Oct 03	23 Oct 03	-	-	-
376	28 Aug 98	10 Sep 98	-8.94	100	3	504	23 Oct 03	06 Nov 03	-	-	-
377	10 Sep 98	24 Sep 98	-	-	-	505	06 Nov 03	20 Nov 03	-	-	-
378	24 Sep 98	08 Oct 98	-8.95	100	3	506	20 Nov 03	04 Dec 03	-9.30	72	2
379	08 Oct 98	22 Oct 98	-8.62	101	3	507	04 Dec 03	18 Dec 03	-	-	-
380	22 Oct 98	06 Nov 98	-8.94	95	2	508	18 Dec 03	31 Dec 03	-	-	-
381	06 Nov 98	19 Nov 98	-	-	-	509	31 Dec 03	15 Jan 04	-	-	-
382	19 Nov 98	03 Dec 98	-8.95	96	2	510	15 Jan 04	30 Jan 04	-8.83	60	2
383	03 Dec 98	17 Dec 98	-	-	-	511	30 Jan 04	12 Feb 04	-	-	-
384	17 Dec 98	31 Dec 98	-9.03	97	2	512	12 Feb 04	26 Feb 04	-	-	-
385	31 Dec 98	14 Jan 99	-	-	-	513	26 Feb 04	11 Mar 04	-	-	-
386	14 Jan 99	28 Jan 99	-8.83	93	2	514	11 Mar 04	25 Mar 04	-9.17	69	2
387	28 Jan 99	11 Feb 99	-	-	-	515	25 Mar 04	08 Apr 04	-	-	-
388	11 Feb 99	25 Feb 99	-8.65	98	2	516	08 Apr 04	22 Apr 04	-	-	-
389	25 Feb 99	11 Mar 99	-	-	-	517	22 Apr 04	06 May 04	-	-	-
390	11 Mar 99	25 Mar 99	-8.86	97	2	518	06 May 04	20 May 04	-8.79	68	2
391	25 Mar 99	08 Apr 99	-	-	-	519	20 May 04	03 Jun 04	-	-	-
392	08 Apr 99	22 Apr 99	-8.27	93	2	520	03 Jun 04	17 Jun 04	-	-	-
393	22 Apr 99	06 May 99	-	-	-	521	17 Jun 04	01 Jul 04	-	-	-
394	06 May 99	20 May 99	-8.32	97	2	522	01 Jul 04	15 Jul 04	-8.73	65	2
395	20 May 99	03 Jun 99	-	-	-	523	15 Jul 04	29 Jul 04	-	-	-
396	03 Jun 99	17 Jun 99	-8.45	91	2	524	29 Jul 04	12 Aug 04	-	-	-
397	17 Jun 99	01 Jul 99	-	-	-	525	12 Aug 04	26 Aug 04	-	-	-
398	01 Jul 99	15 Jul 99	-8.69	97	2	526	26 Aug 04	09 Sep 04	-9.24	67	2
399	15 Jul 99	29 Jul 99	-	-	-	527	09 Sep 04	23 Sep 04	-	-	-
400	29 Jul 99	12 Aug 99	-8.31	89	2	528	23 Sep 04	07 Oct 04	-	-	-
401	12 Aug 99	26 Aug 99	-	-	-	529	07 Oct 04	21 Oct 04	-	-	-
402	26 Aug 99	09 Sep 99	-8.47	93	2	530	21 Oct 04	04 Nov 04	-9.42	59	2
403	09 Sep 99	23 Sep 99	-	-	-	531	04 Nov 04	18 Nov 04	-	-	-
404	23 Sep 99	07 Oct 99	-8.23	92	2	532	18 Nov 04	02 Dec 04	-	-	-

Table 1. continued.....

Sample No.	Sampling Period		$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	σ (‰)	Sample No.	Sampling Period		$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	σ (‰)
	Start	Stop					Start	Stop			
405	07 Oct 99	21 Oct 99	-	-	-	533	02 Dec 04	16 Dec 04	-	-	-
406	21 Oct 99	05 Nov 99	-8.19	94	2	534	16 Dec 04	30 Dec 04	-9.40	62	2
407	05 Nov 99	18 Nov 99	-	-	-	535	30 Dec 04	13 Jan 05	-	-	-
408	18 Nov 99	02 Dec 99	-8.64	92	2	536	13 Jan 05	27 Jan 05	-	-	-
409	02 Dec 99	16 Dec 99	-8.62	96	2	537	27 Jan 05	10 Feb 05	-	-	-
410	16 Dec 99	30 Dec 99	-	-	-	538	10 Feb 05	24 Feb 05	-8.94	62	2
411	30 Dec 99	13 Jan 00	-8.56	90	2	539	25 Feb 05	10 Mar 05	-	-	-
412	13 Jan 00	27 Jan 00	-	-	-	540	10 Mar 05	24 Mar 05	-	-	-
413	27 Jan 00	10 Feb 00	-8.17	95	3	541	24 Mar 05	07 Apr 05	-	-	-
414	10 Feb 00	24 Feb 00	-	-	-	542	07 Apr 05	21 Apr 05	-9.12	61	2
415	25 Feb 00	09 Mar 00	-8.69	93	2	543	21 Apr 05	05 May 05	-	-	-
416	09 Mar 00	23 Mar 00	-	-	-	544	05 May 05	19 May 05	-	-	-
417	23 Mar 00	06 Apr 00	-8.86	92	2	545	19 May 05	02 Jun 05	-	-	-
418	06 Apr 00	20 Apr 00	-	-	-	546	02 Jun 05	15 Jun 05	-	-	-
419	20 Apr 00	04 May 00	-8.69	88	2	547	15 Jun 05	30 Jun 05	-	-	-
420	04 May 00	18 May 00	-	-	-	548	30 Jun 05	14 Jul 05	-	-	-
421	18 May 00	01 Jun 00	-8.28	92	2	549	14 Jul 05	28 Jul 05	-	-	-
422	01 Jun 00	15 Jun 00	-	-	-	550	28 Jul 05	11 Aug 05	-	-	-
423	15 Jun 00	29 Jun 00	-8.59	87	2	551	11 Aug 05	25 Aug 05	-	-	-
424	29 Jun 00	13 Jul 00	-	-	-	552	25 Aug 05	09 Sep 05	-	-	-
425	13 Jul 00	27 Jul 00	-8.95	87	2	553	09 Sep 05	22 Sep 05	-	-	-
426	27 Jul 00	10 Aug 00	-	-	-	554	22 Sep 05	06 Oct 05	-	-	-
427	10 Aug 00	24 Aug 00	-8.29	83	2	555	06 Oct 05	20 Oct 05	-	-	-
428	24 Aug 00	07 Sep 00	-	-	-	556	20 Oct 05	03 Nov 05	-	-	-
429	07 Sep 00	21 Sep 00	-9.22	89	1	557	03 Nov 05	17 Nov 05	-	-	-
430	21 Sep 00	05 Oct 00	-	-	-	558	17 Nov 05	01 Dec 05	-	-	-
431	05 Oct 00	19 Oct 00	-9.28	86	2	559	01 Dec 05	15 Dec 05	-	-	-
432	19 Oct 00	02 Nov 00	-	-	-	560	15 Dec 05	29 Dec 05	-	-	-
433	02 Nov 00	16 Nov 00	-8.25	91	3	561	29 Dec 05	12 Jan 06	-	-	-
434	16 Nov 00	30 Nov 00	-	-	-	562	12 Jan 06	26 Jan 06	-	-	-
435	30 Nov 00	14 Dec 00	-8.61	83	2	563	26 Jan 06	09 Feb 06	-	-	-
436	14 Dec 00	28 Dec 00	-	-	-	564	09 Feb 06	17 Feb 06	-	-	-
437	28 Dec 00	11 Jan 01	-8.42	87	2	565	17 Feb 06	03 Mar 06	-	-	-
438	11 Jan 01	25 Jan 01	-	-	-	566	03 Mar 06	17 Mar 06	-	-	-
439	25 Jan 01	08 Feb 01	-	-	-	567	17 Mar 06	31 Mar 06	-	-	-
440	08 Feb 01	22 Feb 01	-	-	-	568	31 Mar 06	13 Apr 06	-	-	-
441	22 Feb 01	08 Mar 01	-8.34	86	2	569	13 Apr 06	27 Apr 06	-	-	-
442	08 Mar 01	22 Mar 01	-	-	-	570	27 Apr 06	11 May 06	-	-	-
443	22 Mar 01	05 Apr 01	-	-	-	571	11 May 06	25 May 06	-	-	-
444	05 Apr 01	19 Apr 01	-	-	-	572	25 May 06	08 Jun 06	-	-	-
445	19 Apr 01	03 May 01	-8.99	87	2	573	08 Jun 06	22 Jun 06	-	-	-
446	03 May 01	17 May 01	-	-	-	574	22 Jun 06	06 Jul 06	-	-	-
447	17 May 01	31 May 01	-	-	-	575	06 Jul 06	20 Jul 06	-	-	-
448	31 May 01	14 Jun 01	-	-	-	576	20 Jul 06	03 Aug 06	-	-	-
449	14 Jun 01	28 Jun 01	-8.92	84	2	577	03 Aug 06	17 Aug 06	-	-	-
450	28 Jun 01	12 Jul 01	-	-	-	578	17 Aug 06	31 Aug 06	-	-	-
451	12 Jul 01	26 Jul 01	-	-	-	579	31 Aug 06	14 Sep 06	-	-	-
452	26 Jul 01	09 Aug 01	-	-	-	580	14 Sep 06	28 Sep 06	-	-	-
453	09 Aug 01	23 Aug 01	-8.63	81	2	581	28 Sep 06	12 Oct 06	-	-	-
454	23 Aug 01	06 Sep 01	-8.15	85	3	582	12 Oct 06	26 Oct 06	-	-	-
455	29 Nov 01	13 Dec 01	-8.71	80	2	583	26 Oct 06	10 Nov 06	-	-	-
456	13 Dec 01	27 Dec 01	-	-	-	584	10 Nov 06	23 Nov 06	-	-	-
457	27 Dec 01	10 Jan 02	-	-	-	585	23 Nov 06	07 Dec 06	-	-	-
458	10 Jan 02	24 Jan 02	-	-	-	586	07 Dec 06	22 Dec 06	-	-	-
459	24 Jan 02	07 Feb 02	-8.76	83	2	587	22 Dec 06	04 Jan 07	-	-	-
460	07 Feb 02	21 Feb 02	-	-	-						

4.9. SF₆ FROM FLASK SAMPLING

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[Cooperative Research report.]

Sulfur hexafluoride (SF₆) is a man-made trace gas used predominantly in gas insulated switchgear. Because of its well known, largely northern hemispheric source distribution and long lifetime of over 3000 years, it is a useful tracer of atmospheric circulation and exchange between the atmosphere and linked reservoirs. It is also a strong greenhouse gas with radiative forcing 36000 times that of CO₂ on a per molecule basis.

A high precision record of its accumulation in the atmosphere between 1978 and 1994 was reconstructed from measurements made at University of Heidelberg- Institut für Umweltp Physik (UH-IUP) of subsamples of the Cape Grim Air Archive [Maiss *et al.*, 1996]. This record has subsequently been strengthened and extended by analysis of additional pre-1996 archived air and by regular, direct flask sampling of baseline air in 1.6 L, stainless steel flasks since November 1995 [Levin *et al.*, 2001; 2004; Fraser *et al.*, 2004]. The full Cape Grim record, now spanning 29 years, is shown in Figure 1.

Data are available on request, e-mail: Ingeborg.Levin@iup.uni-heidelberg.de

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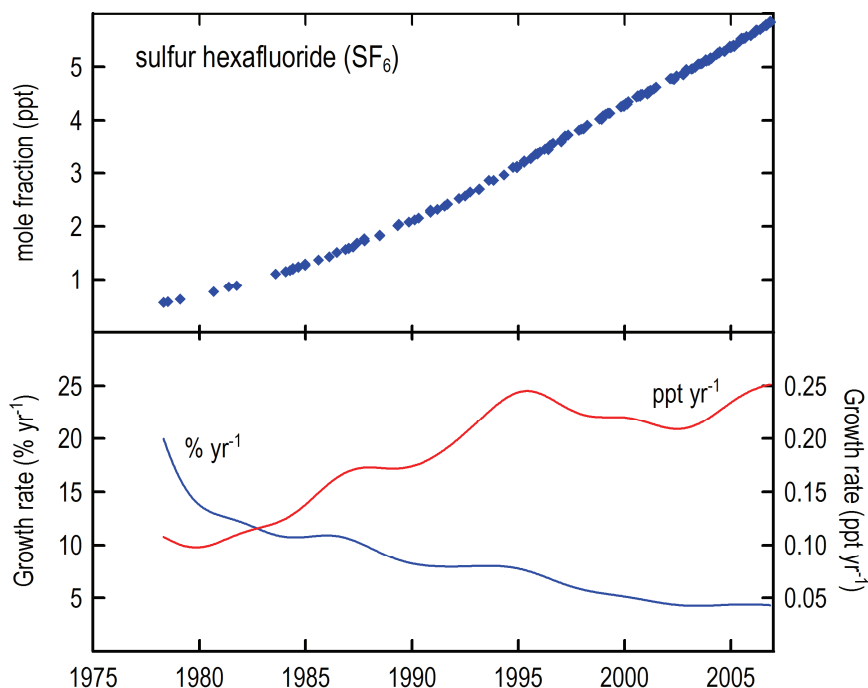


Figure 1. Top panel: SF₆ mole fraction at Cape Grim from measurements of the Cape Grim Air Archive and direct flask sampling since 1995. Lower panel: SF₆ growth rate obtained using the curve-fitting method of Thoning *et al.* [1989].

4.10. MEASUREMENTS OF ATMOSPHERIC O₂/N₂ RATIOS AT CAPE GRIM

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[Cooperative Research report.]

The Atmospheric Oxygen Project at the Scripps Institution of Oceanography has produced records of the changes in atmospheric oxygen and carbon dioxide concentrations that are relevant for documenting sources and sinks of carbon dioxide in relation to global climate change. The records are produced via a flask sampling network involving collections at nine background air stations, distributed globally. The principle scientific goals of this program are to place constraints on the land and oceans sinks of CO₂, both globally and on smaller spatial scales, to improve estimates of the rates and dynamics of the ocean biological carbon pump, and to provide insights into the sensitivity of land and ocean biogeochemistry to climate changes on inter-annual time scales. The flasks for this program are now also routinely analyzed for changes in the Ar/N₂ ratio, with the goal of using these data for placing constraints on air-sea heat exchanges.

Our program has depended since its inception on collaborations with field stations for the collection of air samples. Cape Grim was among the first stations chosen for our network, with sampling commencing in 1991 and continuing at roughly two-week periods without interruption.

The procedures for collecting and analyzing flasks are described in Keeling *et al.* [1998a] and [2007]. The intake system at Cape Grim is currently being reconfigured with an aspirated intake [Blaine *et al.*, 2006], in order to eliminate any thermal fractionation. Changes in O₂ abundance are reported as changes in O₂/N₂ ratio, according to

$$\delta(O_2/N_2) = (O_2/N_2 \text{ ratio of sample}) / (O_2/N_2 \text{ ratio of reference}) - 1$$

The resulting δ value is typically multiplied by 106 and expressed in 'per meg' units. The N₂ abundance is sufficiently constant that the O₂/N₂ ratio largely reflects changes in O₂. For the purpose of comparing molar amounts of O₂ and CO₂, 4.8 per meg is equivalent to 1 $\mu\text{mol mol}^{-1}$ in CO₂ abundance. The O₂/N₂ record from Cape Grim is shown in Figure 1, showing a long-term decrease and a quasi-regular seasonal cycle. Measurements of O₂/N₂ ratio are useful for distinguishing ocean and land sources of CO₂ because land uptake involves photosynthesis, which produces O₂, while oceanic uptake mostly involves inorganic chemical reactions (e.g. reactions of CO₂ with CO₃²⁻ to produce HCO₃⁻) which do not involve O₂. If corrections are applied for the O₂ loss due to fossil-fuel burning, the residual change in O₂

can thus be taken as a measure of net photosynthetic production by land plants, which is directly related to the net CO₂ sink from land plants, i.e. the net imbalance between photosynthesis and losses due to respiratory and biomass burning. The records from Cape Grim as well as other stations in our network show that the decrease in O₂/N₂ ratio has been slower than expected from fuel burning alone, indicating that the land biota have recently operated as a sink for CO₂.

The data from Cape Grim have been used in support of numerous publications. The data have been used in support of estimates of land and ocean carbon sinks by Keeling *et al.* [1996], Manning [2001], Keeling and Garcia [2002], and Manning and Keeling [2006]. The Manning results [2001] and the Manning and Keeling [2006] results formed the basis of estimates of the global land and ocean CO₂ sinks in the last two assessments reports of the Intergovernmental Panel on Climate Change (IPCC) [Prentice *et al.*, 2001; Denman *et al.*, 2007]

The data from Cape Grim have also been used to provide tests of ocean biological models [Stephens *et al.*, 1998; Gruber *et al.*, 2001; McKinley *et al.*, 2003; Battle *et al.*, 2006; Naegler *et al.*, 2007] and constrain rates of air-sea gas exchange [Keeling *et al.*, 1998b]. Recent Ar/N₂ results from Cape Grim are reported in Keeling *et al.* [2004].

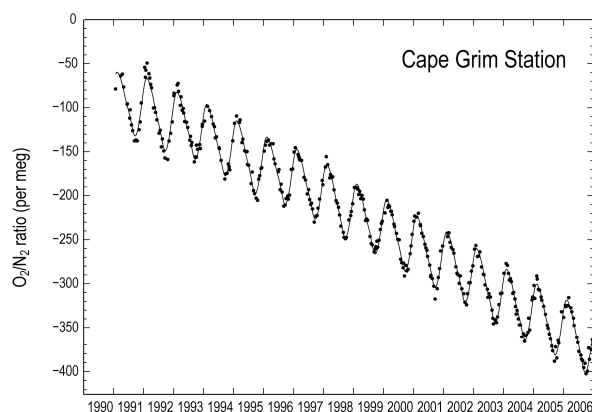


Figure 1. Flask results from Cape Grim through December 2006. Also shown is a curve fit, consisting of a regular seasonal cycle (fundamental plus 3 harmonics) and an interannual trend (stiff spline).

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4.11. ATMOSPHERIC METHANE, CARBON DIOXIDE, HYDROGEN, CARBON MONOXIDE AND NITROUS OXIDE FROM CAPE GRIM FLASK AIR SAMPLES ANALYSED BY GAS CHROMATOGRAPHY

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Air samples are regularly collected at Cape Grim in flasks, and returned to CSIRO Marine and Atmospheric Research's (CMAR) Global Atmospheric Sampling Laboratory (GASLAB) for analysis of trace gas composition [Francey *et al.*, 1996; 2003]. Gas chromatographic (GC) measurements of methane (CH₄), carbon dioxide (CO₂) and carbon monoxide (CO) commenced in 1980 [Fraser and Hyson, 1986; Fraser *et al.*, 1986; 1994]. New and upgraded instrumentation was introduced in 1991/92 as part of the GASLAB development and led to improved precision and calibration of previously measured species, and measurement of two additional species, hydrogen (H₂) and nitrous oxide (N₂O).

Atmospheric mole fractions and growth rates to the end of 2006 are shown for CH₄ and CO (Figure 1) and for CO₂, H₂ and N₂O (Figure 2). Data are displayed for all analysed samples, with different symbols used to distinguish retained and rejected data. Reasons for rejection are described by Steele *et al.* [1996] and Cooper *et al.* [1999]. Mean growth rates calculated over both the full record of measurement, and over 2005/2006 are listed in Table 1.

Table 1. Mean growth rates during 2005/2006 and over the full record of measurement.

Trace gas species	Period of full record	----- Mean Growth Rate -----		Unit
		full record	2005/06	
CH ₄	1984-2006	6.1	0.1	nmol mol ⁻¹ yr ⁻¹
CO ₂	1991-2006	1.7	1.9	µmol mol ⁻¹ yr ⁻¹
H ₂	1992-2006	0.8	-0.1	nmol mol ⁻¹ yr ⁻¹
CO	1985-2006	-0.1	-1.1	nmol mol ⁻¹ yr ⁻¹
N ₂ O	1992-2003	0.7	-	nmol mol ⁻¹ yr ⁻¹

The CH₄ data presented here are expressed in the CSIRO94 CH₄ scale. Recent work presented by Dlugokencky *et al.* [2005] describing a gravimetrically prepared CH₄ standard scale has paved the way for conversion of these Cape Grim CH₄ data to this new gravimetric scale, now endorsed by WMO/GAW.

During 2005-2006 the mean CO₂ growth rate was 1.9 µmol mol⁻¹ yr⁻¹, slightly higher than the mean value of 1.7 µmol mol⁻¹ yr⁻¹ for the period 1991-2006. For H₂, there was virtually no change in the annually averaged mixing ratios during 2005-2006, while for CO there was a slight decline.

The mean growth rate of 0.1 nmol mol⁻¹ yr⁻¹ observed for CH₄ during 2005-2006 means that its annually averaged mole fraction has remained remarkably stable for 7 years (1999-2006). While this

feature is quite apparent in Figure 1, it is shown again in Figure 3 to highlight such a major change in the trend of this important greenhouse gas. In a modelling study Bousquet *et al.* [2006] used a global inversion model of atmospheric transport and chemistry, constrained by measurements of atmospheric CH₄ from a global network of sites (including Cape Grim), to quantify the processes which contributed to methane emissions during the period 1984-2003. Bousquet *et al.* [2006] conclude that since 1999, anthropogenic emissions of CH₄ have increased, but such increases have been masked by a coincident decrease in emissions of methane from wetlands due to widespread drought conditions.

The low growth rates for CH₄ over recent years are in stark contrast to the SRES scenarios for future changes in CH₄ abundances compiled and presented by the IPCC [2001] and the IPCC Special Report on Emission Scenarios [Nakićenović *et al.*, 2000], where the reference scenario A1B has CH₄ rising from 1760 nmol mol⁻¹ in the year 2000 to 2026 nmol mol⁻¹ in 2020 (see Figure 4) an average annual growth rate of 13.3 nmol mol⁻¹. Even the most conservative IPCC SRES scenario for CH₄ abundance (B1p) has CH₄ increasing from 1760 nmol mol⁻¹ in 2000 to 1878 nmol mol⁻¹ in 2020, an average annual increase of 5.9 nmol mol⁻¹. This issue has been raised with the teams responsible for developing the IPCC SRES scenarios, but, to date, a scenario with lower CH₄ growth than B1p has not been included.

The N₂O flask data since mid-2003 shown in Figure 2 have been flagged, pending further investigation of a small but subtle influence on the N₂O data caused by a change in the supplier of the chemical drying agent (anhydrous magnesium perchlorate) used during sample collection.

These data are available from the following international archives:

World Data Centre for Greenhouse Gases WDCGG;
<http://gaw.kishou.go.jp/wdcgg/>
 Carbon Dioxide Information Analysis Center CDIAc;
<http://cdiac.ornl.gov/>
 CSIRO Marine and Atmospheric Research ftp site;
<ftp://gaspublic:gaspublic@ftp.dar.csiro.au/data/gaslab>
 The CO₂ and CH₄ data are contributed regularly to the 'Globalview' data sets generated by integration of measurements from participating international laboratories [Globalview-CH₄, 2005; Globalview-CO₂, 2007].

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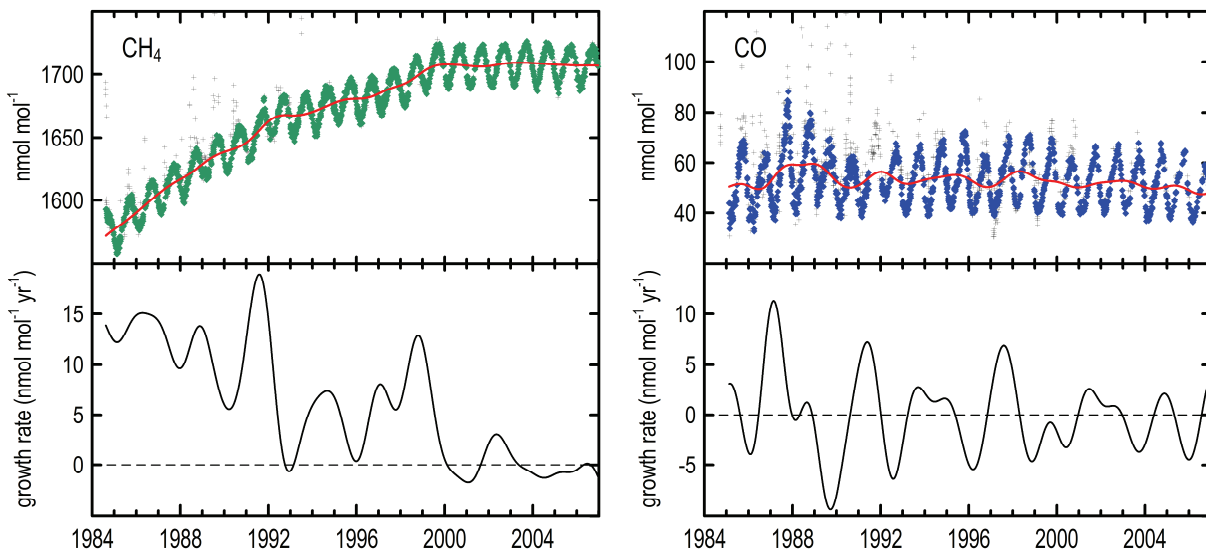


Figure 1. Top panels: Atmospheric CH₄ and CO in nmol mol⁻¹ (mole fraction in parts per 10⁹ in dry air). CSIRO data are from individual Cape Grim flask air samples and are shown as retained (diamonds) or rejected (crosses), based on selection for baseline conditions and analytical quality assessment. The solid curves indicate long-term trends obtained from the curve fitting method described by Thoning *et al.* [1989]. Bottom panels: Growth rate curves as given by the first derivative of the long-term trends.

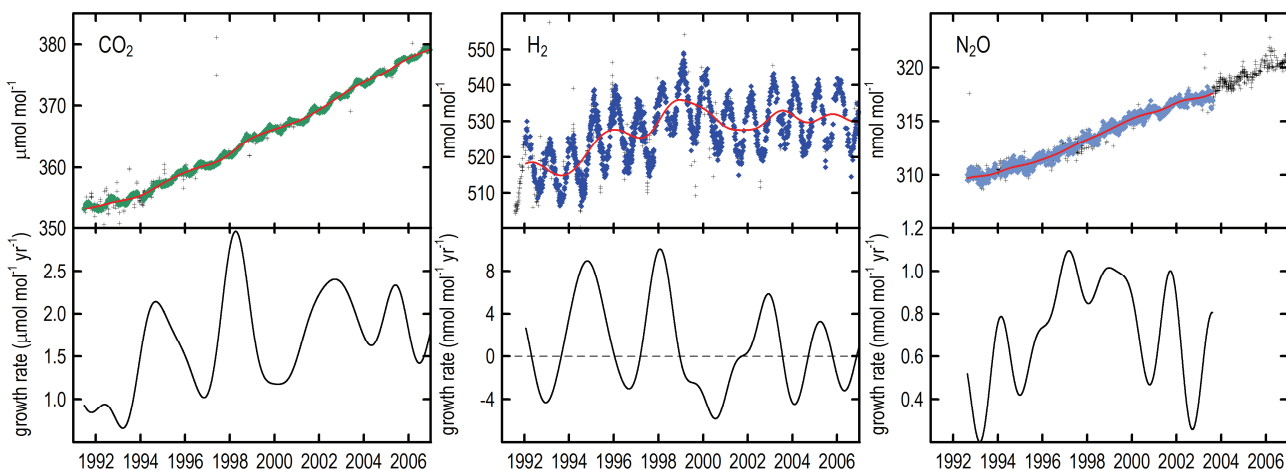


Figure 2. Top panels: Cape Grim records of CO₂, H₂ and N₂O. Results from all individual flask air samples are classified as retained (diamonds) or rejected (crosses). Solid curves indicate long-term trends. Bottom panels: Growth rate curves as given by the first derivative of the long-term trends.

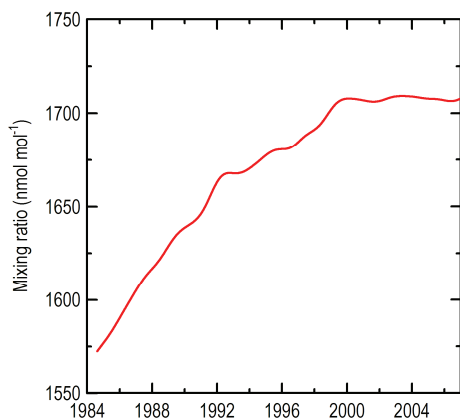


Figure 3. The long-term trend of atmospheric CH₄ at Cape Grim. This is identical to the red curve in the top left panel of Figure 1, displayed here by itself to emphasise the remarkable period of stability during 1999-2006.

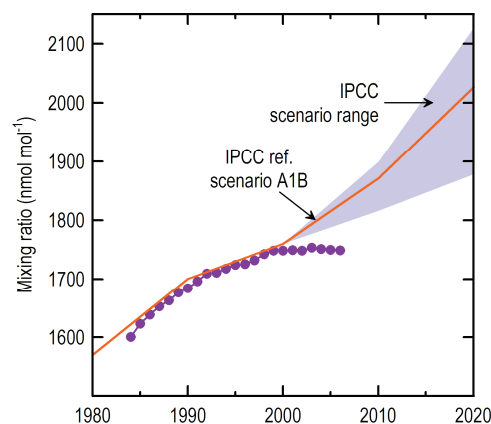


Figure 4. IPCC SRES scenarios for CH₄ (see text), compared with the global average CH₄ atmospheric mixing ratio. The global average CH₄ since 1992 is based upon weekly flask data from the CSIRO global cooperative network. For the period 1984-1991, the CH₄ global average is estimated from the Cape Grim CH₄ data, by a simple scaling factor, based upon the known relationship between Cape Grim CH₄ and global average CH₄ for 1992-2006.

4.12. THE AGAGE *IN SITU* PROGRAM FOR NON-CO₂ GREENHOUSE GASES AT CAPE GRIM, 2005–2006: METHANE, NITROUS OXIDE, CARBON MONOXIDE, HYDROGEN, CFCs, HCFCs, HFCs, PFCs, HALONS, CHLOROCARBONS, HYDROCARBONS AND SULFUR HEXAFLUORIDE

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Introduction

This report summarises *in situ* observations at Cape Grim of atmospheric trace gases that are involved in stratospheric ozone depletion, climate change and tropospheric chemistry. During 2005-2006, three instruments were operated at Cape Grim as part of the Advanced Global Atmospheric Gases Experiment (AGAGE): 1) a composite gas chromatograph multi detector (GC-MD) instrument; 2) an advanced gas chromatography-mass spectrometry (GC-MS-Medusa) instrument; and 3) a GC-ECD instrument for sulfur hexafluoride (SF₆). In 2005-2006 over 50 species were measured on the three instruments, including CH₄, N₂O, CO, H₂, six CFCs (-11, -12, -13, -113, -114, -115), five HCFCs (-22, -123, -124, -141b, -142b), ten HFCs (-23, -32, -125, -134a, -143a, -152a, -227ea, -236fa, -245fa, -365mf),

three PFCs (-14, -116, -218), three halons (-1201, -1301, -2402), seven chlorocarbons (CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄, CH₃CCl₃, CHClCCl₂, CCl₂CCl₂), three bromocarbons (CH₃Br, CHBr₃, CHBrCl₂), one iodo-carbon (CH₃I), three sulfur compounds (SF₆, SO₂F₂, COS) and four hydrocarbons (C₂H₂, C₂H₆, C₆H₆, C₇H₈). Some of these species are measured on more than one instrument.

This report summarises details of each instrumental system, the calibration strategies used, instrument performance, and data collected during 2005-2006.

AGAGE instruments

GC-MD

Measurements of CFC-11 (CCl₃F), CFC-12 (CCl₂F₂), CFC-113 (CCl₂FCClF₂), chloroform (CHCl₃), methyl chloroform (CH₃CCl₃), carbon tetrachloride (CCl₄), nitrous oxide (N₂O), methane (CH₄), carbon monoxide (CO) and hydrogen (H₂) have been made at Cape Grim during 1993-2006, using a composite gas chromatograph multi detector (GC-MD) instrument, as part of the AGAGE program [Krummel *et al.*, 2006a]. Specifically, the instrument comprises a Hewlett-Packard gas chromatograph (HP5890 GC) with two electron capture detectors (ECDs), a Carle Series 100 GC with a flame ionization detector (FID) and a Trace Analytical RGA2/RGD2 GC with a mercuric oxide reduction detector (MRD).

The instrument design and methodologies used to make these observations are described in *Baseline 94-95* [Fraser *et al.*, 1996; Steele *et al.*, 1996] and Prinn *et al.* [2000].

GC-MS-Medusa

Advanced gas chromatography-mass spectrometry (GC-MS) instruments [Miller *et al.*, 2007; Prinn *et al.*, 2000] were installed at Mace Head, Ireland, and at

Cape Grim, Tasmania, in late 2003-early 2004 as part of the AGAGE global *in situ* GC-MS program for the measurement of chlorofluorocarbon (CFC) replacements. These instruments ran in parallel with the GC-MS-ADS instruments at both sites throughout 2004 [Greally *et al.*, 2005; Krummel *et al.*, 2006b]; the ADS instruments were phased-out at both sites in late 2004-early 2005.

The new GC-MS instruments (called GC-MS-Medusa, Miller *et al.*, 2007) were developed jointly by SIO (R. Weiss, B. Miller, J. Muhle, P. Salameh) and UB (P. Simmonds, B. Greally, S. O'Doherty). They have also been installed at Trinidad Head (California, 2004), Ragged Point (Barbados, 2005) and Cape Matatula (Samoa, 2006).

Compared to the ADS instrument [Sturrock *et al.*, 2001a,b], the Medusa uses advanced cryo-cooling/trapping (to -180°C), faster chromatography and greatly improved customised mass spectrometry to allow determination of the same HCFCs, HFCs, halons, minor CFCs, chlorocarbons, halomethanes and hydrocarbons measured on the ADS instrument, but with significantly improved precision, as well as the very volatile PFCs (i.e. PFC-14, CF_4) and HFCs (i.e. HFC-23, CHF_3), SF_6 , all CFCs and a range of bromocarbons at a sampling frequency of 12 fully calibrated analyses per 24 hours, twice that of the ADS instrument.

A total of 44 species were measured on the Medusa instrument at Cape Grim during 2005-2006, including six CFCs, five HCFCs, ten HFCs, three PFCs, three halons, seven chlorocarbons, three bromocarbons, one iodocarbon, three sulfur compounds and four hydrocarbons. Not all species currently measured on the Medusa system have calibration scales; as such only those species with traceable scales will be reported here. Also, for those species that are measured on both the GC-MD and Medusa systems, we report only the results from the GC-MD.

GC-ECD-SF₆

A gas chromatograph system with electron capture detector (GC-ECD) was assembled in early 2001 and commenced measurements of atmospheric SF₆ in late March 2001. The instrument used is a Shimadzu model GC-14A, fitted with dual ⁶³Ni 370 MBq electron capture detectors, one of which is used for this program. A full description of the system design and methodologies, standard gases, data and interpretation of initial results is given in Fraser *et al.* [2004] and Porter *et al.* [2006].

Since 2004, SF₆ has also been measured on the Medusa system at Cape Grim [Greally *et al.*, 2005; Krummel *et al.*, 2006c]. The SF₆-ECD monitoring will continue for the foreseeable future because of the higher frequency of ambient air measurements and the resultant better time resolution of pollution episodes compared to that of the Medusa system.

Standard gases

GC-MD

The concentrations of all species are based on comparisons of ambient air to working standards (G- and J-series, Table 1). The concentrations of CFC-11, -12, -113, CH₃CCl₃ and CCl₄ are reported in the SIO05 scale [Miller *et al.*, 2007], while CHCl₃ and N₂O are reported in the SIO98 scale [Prinn *et al.*, 2000]. The CH₄ data are referenced to a gravimetrically prepared CH₄-in-air calibration scale developed by T. Nakazawa and co-workers at Tohoku University [Cunnold *et al.*, 2002]. The link to this scale was established using measurements in CSIRO GASLAB of standards obtained from TU. The CO data are referenced to a CSIRO scale, linked [see Masarie *et al.*, 2001] to a single standard of a CO gravimetric scale developed by NOAA-Earth System Research Laboratory/Global Monitoring Division (NOAA-ESRL/GMD) [Novelli *et al.*, 1991]. The H₂ data are referenced to a calibration scale developed by CSIRO GASLAB, boot-strapped from a gravimetrically prepared CH₄ scale [Simmonds *et al.*, 2000]. The origin of calibration scales used at CSIRO are described by Francey *et al.*, [2003].

GC-MS-Medusa

To date, Medusa data for 35 of the 44 species measured, are reported in a number of standard scales. The remaining species are currently reported as ratios to either the R1 primary calibration tank at SIO or to secondary standards. The scales for the species discussed in this report are listed in Table 2. SIO05 and SIO98 are the long-term AGAGE standard scales and UB98 and SIO-UB1-prov are interim AGAGE standard scales. The origin and propagation of the SIO and UB scales are described elsewhere [Prinn *et al.*, 2000; Sturrock *et al.*, 2001a,b; O'Doherty *et al.*, 2004; Simmonds *et al.*, 2004; Miller *et al.*, 2007]. At present the AGAGE program has adopted the NOAA-ESRL standard scale for HCFC-123, H-2402 and PCE [S. Montzka, NOAA-ESRL personal communication], the NIES standard scale for CH₃I [Li *et al.*, 1999] and the Empa03 scale for HFC-365mfc [Stemmler *et al.*, 2007]. The concentrations of all species are based on comparisons of ambient air to quaternary standards (G- and GR-series, Table 3), and comparisons of quaternary standards to tertiary and secondary standards (G- and J-series, Table 2). These tertiary standards were used on the Medusa system, and simultaneously as working standards on the GC-MD system. Previously, secondary and tertiary standards were calibrated at UB and SIO for applicable gases, and via flask or tank comparisons locally to transfer scales from NOAA-ESRL.

GC-ECD-SF₆

The AGAGE SF₆ ECD measurements are reported here in the SIO05 scale. The SF₆ concentrations are based on comparisons of ambient air to working standards (Table 4).

Table 1. Natural air standards used in the AGAGE program to the end of 2006. Note: The Tank ID descriptors listed in the footnotes below also apply to Tables 2, 3 and 4.

Tank Scale Units	On	CFC-11 SIO05 ppt	CFC-12 SIO05 ppt	CFC-113 SIO05 ppt	CHCl ₃ SIO98 ppt	CH ₃ CCl ₃ SIO05 ppt	CCl ₄ SIO05 ppt	N ₂ O SIO98 ppb	CH ₄ TUgrav ^a ppb	H ₂ CSIRO94 ppb	CO CSIRO94 ppb
G-016 ^b	Aug 93	259.36	499.09	77.54	11.34	117.18	102.01	309.43	1703.41	492.22	62.16
G-023D ^c	Sep 93	261.41	506.71	79.74	6.63	112.40	95.16	309.40	1690.52	512.88	50.51
G-011D	Feb 94	258.06	493.83	74.75	7.02	119.44	91.96	310.38	1690.48	514.39	71.46
G-025	Mar 94	261.41	508.38	80.62	8.89	116.00	101.44	309.83	1702.46	508.53	61.05
G-029	Jul 94	261.78	512.29	81.65	6.07	108.62	101.06	309.86	1674.61	518.52	44.23
G-031	Nov 94	261.31	512.68	81.65	5.77	107.90	100.75	309.77	1682.46	519.12	45.44
G-035	Apr 95	262.66	517.78	82.28	5.42	105.04	100.39	310.75	1699.54	529.29	56.46
G-039	Sep 95	261.63	519.22	82.43	12.03	99.53	100.14	310.47	1690.00	523.09	49.27
J-005 ^d	Apr 96	266.69	537.53	84.61	12.12	124.28	101.46	312.46	1808.82	531.59	175.53
J-011	Nov 96	266.26	536.23	84.47	12.37	101.69	101.55	312.22	1816.10	530.06	149.08
J-018	Aug 97	266.01	535.60	84.40	12.88	100.02	101.40	312.05	1803.84	502.18	156.53
J-023	May 98	264.40	542.73	83.85	13.58	72.18	99.54	314.13	1838.11	506.45	177.95
J-029	Jan 99	264.27	542.15	83.94	12.92	72.24	99.52	313.72	1840.80	512.70	166.39
J-036	Oct 99	264.27	542.10	83.77	13.07	72.33	99.54	313.92	1836.63	501.34	165.48
J-047	Jun 00	260.77	545.63	82.30	10.93	48.81	97.32	316.04	1847.64	542.37	153.69
G-085	Dec 00	256.53	539.20	82.05	6.53	43.88	94.68	315.20	1741.25	522.10	58.80
J-053	Feb 01	260.80	545.62	82.34	11.09	49.01	97.28	316.07	1848.00	541.57	155.91
J-059	Nov 01	260.95	545.69	82.32	12.50	49.06	97.10	316.13	1850.91	534.48	149.32
J-064	Jul 02	260.57	545.97	82.02	11.04	48.35	97.18	316.36	1849.77	548.74	150.05
GR-095 ^e	May 03	253.52	541.87	79.78	6.40	27.94	91.98	316.50	1731.46	548.51	73.61
J-070	Jul 03	255.61	546.50	80.24	10.72	28.08	94.65	318.27	1847.51	523.14	156.06
J-075	Apr 04	255.75	546.50	80.30	10.28	27.95	94.80	318.16	1844.06	524.63	152.79
J-077	Aug 04	255.24	546.70	80.15	11.86	28.12	95.02	318.62	1852.13	540.73	200.06
G-102	Apr 05	251.30	541.57	79.06	4.60	23.65	91.81	317.40	1718.23	541.02	37.94
J-084	May 05	250.95	544.77	78.91	11.73	20.06	92.94	319.07	1850.37	505.61	166.14
J-092	Feb 06	251.00	544.91	78.89	11.70	19.89	93.02	319.18	1850.00	506.34	165.20
J-098	Nov 06	249.17	544.42	78.30	14.85	16.80	91.72	319.99	1855.07	488.66	164.52

^aTohoku University/Nippon Sanso gravimetric CH₄ scale^bG series standards are whole natural air with no active drying, cryo-trapped (-196°C) at Cape Grim into evacuated, welded, electropolished 34 L stainless steel tanks. The condensed water is ejected from the cylinders after warming to room temperature, using the air pressure in the cylinder; D indicates a cryogenically dried (-78°C) air standard.^cStandards used on GAGE and AGAGE simultaneously.^dJ series standards are natural air from Trinidad Head, California, compressed (Rix pump) into evacuated, welded, electropolished 34 L stainless steel tanks and dried to 10 torr of water vapour.^eGR series standards are natural air, filled using a Rix compressor at Cape Grim, into evacuated, welded, electropolished 34 L stainless steel tanks and dried to 10 torr of water vapour.^fCG series tertiary standards are whole natural air with no active drying, cryo-trapped (-196°C) at Cape Grim into evacuated, welded, electropolished 15 L stainless steel tanks. The condensed water is ejected from the cylinders after warming to room temperature, using the air pressure in the cylinder.**Table 2.** AGAGE GC-MS-Medusa tertiary standards employed at Cape Grim for 2004-2006. Also indicated in the table header are the standard scales used in reporting AGAGE GC-MS-Medusa data.

Specie	Formula	Units	Scale	Tank Date On	G-102 ^b Jan-04	J-075 ^d Apr-04	J-077 Aug-04	J-084 May-05	J-092 Feb-06	J-098 Nov-06
HFC-125	CHF ₂ CF ₃	ppt	UB98B		2.40	2.85	2.85	3.96	3.94	4.54
HFC-134a	CH ₂ FCF ₃	ppt	SIO05		24.14	28.48	28.47	38.71	38.65	527.95
HFC-152a	CH ₃ CHF ₂	ppt	SIO05		1.62	4.19	4.41	5.60	5.61	9.47
HFC-365mfc	CH ₂ CF ₂ CH ₂ CF ₃	ppt	Empa03		0.05	0.08	0.08	0.24	0.25	0.34
HCFC-22	CHClF ₂	ppt	SIO05		151.80	167.26	167.46	180.25	180.26	186.72
HCFC-124	CHClFCF ₃	ppt	NOAA2003B		1.26	1.61	1.65	1.64	1.65	1.71
HCFC-141b	CH ₃ CCl ₂ F	ppt	SIO05		15.56	18.63	18.68	19.17	19.08	19.26
HCFC-142b	CH ₃ CClF ₂	ppt	SIO05		13.90	15.39	15.45	16.50	16.43	17.25
PFC-14	CF ₄	ppt	SIO05		73.38	73.98	74.02	75.36	75.35	75.85
PFC-116	CF ₃ CF ₃	ppt	SIO-UB1-prov.		3.18	3.33	3.36	3.51	3.49	3.52
PFC-218	C ₃ F ₈	ppt	SIO-UB1-prov.		0.38	0.42	0.42	0.45	0.46	0.48
CFC-114	CClF ₂ CClF ₂	ppt	SIO05		16.54	16.64	16.65	16.58	16.59	16.56
CFC-115	CClF ₂ CF ₃	ppt	SIO05		8.28	8.30	8.35	8.38	8.39	8.36
PCE	CCl ₂ CCl ₂	ppt	NOAA2003B		0.37	5.55	5.52	5.33	5.60	4.52
H-1211	CBrClF ₂	ppt	SIO05		4.20	4.51	4.50	4.53	4.52	4.50
H-1301	CBrF ₃	ppt	SIO05		2.99	3.05	3.06	3.18	3.16	3.15
H-2402	CBrF ₂ CBrF ₂	ppt	NOAA-92-SIO-prov.		0.48	0.51	0.51	0.50	0.50	0.49
Methyl chloride	CH ₃ Cl	ppt	SIO05		502.13	570.08	566.09	574.77	572.33	549.55
Methyl bromide	CH ₃ Br	ppt	SIO05		7.00	9.65	9.63	8.86	8.79	7.84
Dichloromethane	CH ₂ Cl ₂	ppt	UB98B		7.18	36.56	36.98	36.84	36.42	35.82
Methyl iodide	CH ₃ I	ppt	NIES-prov		0.71	1.07	1.07	0.76	0.65	1.20

Table 3. AGAGE GC-MS-Medusa quaternary (working) standards employed at Cape Grim for 2004-2006.

Tank	Date On	Tank	Date On	Tank	Date On
G-101 ^b	Jan 04	G-114	Mar 05	G-129	Feb 06
GR-103 ^e	Mar 04	G-115	May 05	G-131	Apr 06
G-104	Apr 04	G-117	Jun 05	G-132	Jul 06
G-105	Jun 04	G-116	Aug 05	G-136	Sep 06
G-107	Aug 04	G-121	Nov 05	G-143	Nov 06
G-108	Oct 04	G-122	Dec 05		
G-110	Nov 04				

Table 4. Natural air secondary and tertiary standards used in the calibration of SF₆ ECD *in situ* measurements at Cape Grim. Mole fractions are listed in the SIO05 scale to the end of 2006.

Tank Scale	On	SF ₆ SIO05 Units	Tank	On	SF ₆
CG010618 ^f	Jul 01	4.584	G-094 ^b	May 03	4.837
CG011108	Nov 01	4.635	GR-097 ^e	Jun 03	4.909
CG020328	Apr 02	4.707	CG300404	May 04	5.192
CG020620	Jun 02	4.771	G-109	Aug 04	5.263
CG021022	Oct 02	4.884	G-135	Sep 06	5.741
CG030117	Jan 03	4.918			

Significant Events

In April 2005, a flask experiment was conducted to measure the instrument response function of SF₆ on both the GC-ECD and Medusa systems. The same flask samples also allowed determination of the CHCl₃ response on the GC-MD and Medusa systems.

Elevated HCFC-22 between 26 April and 30 May 2005 indicated local contamination. The cause was the main laboratory air-conditioner, which had lost the entire gas charge of one stage, due to a leaking connection in the outdoor unit. It was re-gassed 13 July.

In August 2005, six new Dekabon (now type 1300 Synflex tubing from Eaton Corporation, Cleveland, Ohio) intake lines of 1/2" OD were commissioned. They were mounted on the top-most inner handrail on the southwest side of the Telstra tower at the 75 m level (see Figure 1). Each line has a stainless steel rain hood fitted with an insect screen. Just outside the station building entry, each intake passes via a short length of grounded stainless steel tube, to bypass any lightning surges to ground. In the main laboratory, each line connects to a flowmeter, then all to a single diaphragm pump to maintain a permanent flushing flow of 10 litres per minute in each tube.

The air sample lines to the instruments were progressively moved to the new intakes: one of the GC-MD inlets (on port 3) was moved on 4 August 2005, and the GC-MS-Medusa inlet on 19 October 2005, while the second GC-MD inlet (port 5) remained on the 70 m (polypipe) intake to provide an overlap comparison. To avoid disruptions due to work on the tower between November 2005 and January 2006, the Medusa and both GC-MD inlets were temporarily connected to the 10-m stack. The GC-MD port 5 air inlet was moved to one of the 75 m Dekabon intakes on 15 June 2006. Now both the GC-MD intakes and

the Medusa are sampling from 75 m above ground level via individual Dekabon lines. The SF₆ GC-ECD continues to sample from the 10 m stack.

The station was affected on 15-16 and 23-24 February 2006, by smoke plumes from a large bush-fire burning on Robbins Island (~20 km east of Cape Grim).

In August 2006 the main AGAGE control PC (AGAGE#2) suffered a hard disk failure. A new disk drive was installed and the operating system upgraded to Fedora Core 5 (Linux). In October, the AGAGE data processing PC at Aspendale (Dagage1-as) was also upgraded with a fresh installation of Fedora Core 5.

**Figure 1.** Image of the six new Dekabon air intake lines and rain hoods at the 75-m level on the Telstra tower.

Instrument maintenance/modifications

GC-MD

2005

In January 2005 the poor precision of CFC-12/N₂O was addressed, the cause was a worn rotor in the channel 1 backflush valve (V5). The valve was cleaned and the rotor replaced, subsequent data showed very significant improvements in precision.

A faulty Barocel pressure transducer was replaced in January 2005 with a new one supplied by from SIO.

Several changes were made to the Trace Analytical GC in January and February to address poor precision in H₂ and CO data. The lamp starter was changed and the UV lamp changed twice. The lamp cooling fan was found to be running slowly, so it was replaced, reducing detector noise. The GC oven temperature and detector temperature settings were both reduced, resulting in improved separation of CO from H₂. These efforts resulted in improvements of around a factor of six in the measurement precision of both CO and H₂. In a further effort to improve precision the sample loop size was changed from 1 ml to 2 ml in March. A set of flask samples (prepared at CMAR) were analysed before and after the change to determine CO/H₂ response functions. Some adjustments were also made to carrier head pressure and GC oven temperature to improve peak separation further. In November further efforts were

made to improve the CO/H₂ separation, the CO/H₂ sample loop was changed from 2 ml to 0.5 ml to reduce the size of the H₂ peak and a butane-torch bake-out of the molecular sieve column was carried out. Unfortunately, this resulted in a significant loss of CO sensitivity, taking about a month to recover. A replacement column was ordered.

In December, it was discovered that the Trace Analytical sensitivity deteriorated twice per day at about the same times – 0500 and 1500 AEST. This was due to mains voltage fluctuations affecting detector temperature, due to increased electricity demand during morning and afternoon milking periods at the local dairies. The UPS for the Trace Analytical was changed from the 'Best' to the Medusa's 'Falcon', which is continuously 'on-line'. Subsequently, H₂ and CO data improved dramatically.

In March 2005, an 8 port secondary Stream Selector Valve (SSV) was installed to provide seven extra sample inlet ports. The three CO standards were moved to the new valve box, and the Zero air 'Blank' and 'Lab Air' inlets were connected to the new valve box. 'Blank' and 'Lab Air' runs were added to the weekly calibration sequence so that these analyses will be carried out routinely. Subsequent 'Lab Air' data reveal the following concentrations (and enhancements compared to outside air data): CH₄ 1750 ppb (+50 ppb), CFC-12 245 ppt (+4 ppt), CFC-11 265 ppt (+15 ppt), H₂ 800 ppb (+250 ppb). The other species were found to have similar mixing ratios to those in ambient air.

In November 2005, stainless steel tubing serving the GC-MD was re-organised, tidied up and labelled. The Zero air, hydrogen and Ar/CH₄ lines were all altered. A stainless steel ballast tank (~15 litres) was installed in the Ar/CH₄ line down-stream of the cleanup trap to filter out the change in composition and consequent 'glitch' in the data from the two ECD channels, due to the daily cleanup trap switch.

The molecular sieve trap on the FID carrier gas (N₂) line was changed in March, July and December; the molecular sieve trap on the Trace Analytical carrier gas (Zero air) line was replaced in March, June and December.

2006

In March, the Zero air generator output pressure regulator was replaced. The compressed air input pressure was found to be low because the pressure swing dryer had been bypassed (due to a leak) and the air line was full of water. The water was drained and blown out of the air line and the check valve was replaced. To provide a temporary drying facility, the freezer was relocated to pre-dry the air for the compressor.

Carried out a high CO concentration calibration in March using 4 low pressure flasks and one tank prepared at CMAR. This was done to calibrate CO over the range of 300 to almost 3000 ppb, enabling better evaluation of CO concentrations observed during the bushfire plumes.

Five new Essex Cryogenics 34 litre, stainless steel (900 psi rated) cylinders were installed, to serve as CO/H₂ calibration standards, covering the ranges: CO: 30 to 240 ppb; H₂: 400 to 700 ppb; N₂O: 200 to 400 ppb; CH₄: 1100 to 2300 ppb. A sixth (aluminium Luxfer) tank provides a very high CO calibration point ~2740 ppb, it also has CH₄ ~ 4500 ppb. A new routine calibration sequence was set up to run three measurements of each of the six new tanks plus 'lab air' and 'blank' samples each week-end.

Also in March, the FID channel was affected by a faulty actuator on the backflush valve. The actuator was replaced and data quality improved.

In July, one of the Metal Bellows air sampling pumps failed with a broken bearing housing; it was repaired by using parts from another old pump. The Aadco Zero air generator cooling fan was replaced in August due to worn/dry bearings.

GC-MS-Medusa

2005

In several periods during February, May and June the CF₄ data were affected by poor CRYOTIGER performance, the procedure to clear oil from the cooling capillary was carried out. In June, an oil-mist filter was installed in the CRYOTIGER supply hose to avoid condensation of oil in the cold-head. A deflector supplied by SIO was fitted to the GC oven exhaust vent to avoid inadvertent heating of the CRYOTIGER refrigeration hoses. Following these changes, the base-plate temperature has been much more stable.

An MS filament failure caused loss of some data in March.

In April, peak identification and integration parameters were altered to quantify CH₂F₂.

The ions for HFC-365mfc were added in May.

In July, the GC PoraBond Q column was baked out in an attempt to improve separation between CH₂Cl₂ and CFC-11. The bake-out made no difference to CH₂Cl₂/CFC-11 separation or any retention times. In August, due to erratic peak identification with merged peaks, the CH₂Cl₂ quantifying and qualifier ions were swapped, now using m/z 86 as the quantifier instead of 85. M/z 86 also has some CFC-11 corruption.

In August, numerous changes were made to MS acquisition parameters to select optimum ions for various windows. Extra ions were added to the scan to collect data for a range of hydrocarbons. The targeted species are: propene, propane, c-propane, i-butane, n-butane, 1-3 butadiene, i-pentane, isoprene, n-pentane, ethylbenzene, m+p-xylene and o-xylene.

Also in August, a set of tanks was analysed as part of the IHALACE comparison experiment. The MS ion source was cleaned and filaments replaced.

In September the Helium carrier gas was changed from BOC to Linde supply. This virtually removed the large SF₆ blank previously experienced. Subsequent experiments showed that the

remaining blanks in C₂H₆, HCFC-124 and TCE were removed by using the Agilent cleanup trap.

2006

In January, the MS Electron Multiplier and cracked repeller insulators were replaced and the MS tuned. The CF₄ desorption temperature was altered 40°C to 50°C and a series of calibrations run. Occasional periods of noisy data were found to be due to erratic trap heating because of a loose fuse holder.

Since January, the Medusa quaternary standard tanks were filled in non-baseline conditions in an attempt to capture elevated concentrations to improve detection/precision of some sub-ppt level compounds, but this proved to be unreliable. A more reliable method was developed with tanks being deliberately spiked with the contents of flasks prepared at CMAR to elevate the concentrations of several gases: from January for HFC-365mfc; in June HFC-227ea, HFC-236fa, HFC-245fa, TCE, and HCFC-123 were added to the spikes (HFCs courtesy of M. Vollmer, Empa).

In March, April and May the CRYOTIGER regeneration procedure was carried out in attempts to restore its performance. In June, due to continuing data corruption, the oil-mist filter was replaced. In the process some refrigerant leaked rendering the unit in-operable. Another CRYOTIGER borrowed from CMAR was installed; in September its refrigerant charge was topped up.

The molecular sieve/HiSiv pre-column for separating CF₄ was changed in April from 5A to 4A molecular sieve, to improve the retention of CO₂, and hence reduce its interference with CF₄.

An MS filament blew in May.

In June, a four-component HFC mixture was analysed from a flask supplied by M. Vollmer (Empa), to identify HFC-227ea, HFC-236fa and HFC-245fa (also contained HFC-365mfc). Subsequently, data are now routinely collected for these gases.

In August the Aadco Zero air generator was modified to provide a 'dry air' outlet, connected before the methane reactor. The 'dry air' was measured at -78°C dewpoint (<1 ppm H₂O) compared with the regular Aadco Zero air at -68°C dewpoint (~3.5 ppm H₂O) and much drier than the BOC cylinder nitrogen -63°C (7.3 ppm H₂O) previously used. Installed a 'dry air' line from the Aadco to Medusa.

In September, diagnostic pressure sensors were installed to monitor both the T1 downstream pressure, and the EPC4 outlet pressure, as an indication of its flow.

GC-ECD-SF₆

2005

In February the injection valve alignment was adjusted twice. In July, the controlling DOS PC failed, a capacitor and fan in the power supply were replaced. It failed again in September losing three weeks' data before it was replaced with a modern PC with software re-written by CGBAPS staff to run

under Windows. In November and December several periods of data were lost when the PC stalled for no obvious reason.

2006

The instrument was plagued with PC control problems throughout the year with data lost for up to several days at a time averaging about three times per month. CGBAPS IT staff are working on a Linux based computer solution. In August, the sample loop was changed from ~2 ml to 1 ml volume in an attempt to produce a narrower SF₆ peak, and hopefully better precision. Subsequent peaks now have a better shape, but precision is virtually unchanged.

AGAGE data

Identification of pollution

The identification of 'non-baseline' periods in the AGAGE data is achieved using an objective, automated algorithm [Prinn *et al.*, 2000]. The algorithm considers a 4-month period centred on each observation. After removal of a second-order polynomial fit to the data in this period, the algorithm seeks to identify a statistically normal distribution of unpolluted (baseline) mole fractions over this period. This is achieved by iteratively removing (and labelling as pollution) the mole fractions that exceed the median plus 2.5 standard deviations. Simultaneously, the algorithm fits a normal distribution to these baseline values to produce a mean and standard deviation of the distribution. Further checks using standard synoptic analyses and back trajectory calculations ensure that the pollution events so identified are meteorologically reasonable.

The growth rates reported here for each species are calculated using these baseline data and the curve fitting techniques of Thoning *et al.* [1989]. First, a long-term trend curve (with seasonal cycles removed) is found and then the derivative of this curve is taken to give an instantaneous growth rate.

Data availability and publications

The AGAGE data (including pollution flags) are available from Carbon Dioxide Information Analysis Center (CDIAC), Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA). The data can be accessed at: <http://cdiac.ornl.gov/ndps/alegage.html> The Atmospheric Lifetime Experiment (ALE) and Global Atmospheric Gases Experiment (GAGE) data are also available at this site.

The data are also available from the WMO WDCGG (World Data Centre for Greenhouse Gases, Japan Meteorological Organization, Tokyo, Japan): <http://gaw.kishou.go.jp/wdcgg/>

Data on all AGAGE GC-MD species except CO have been published [Prinn *et al.*, 2000 and references therein; Simmonds *et al.*, 2000; O'Doherty *et al.*, 2001; Cunnold *et al.*, 2002; Dunse *et al.*, 2005; Nevison *et al.*, 2005; Prinn *et al.*, 2005; Xiao *et al.*, 2007].

AGAGE data from the GC-MS systems (ADS and Medusa) have been published [Sturrock *et al.*, 2002; Cox *et al.*, 2003a,b; Cox *et al.*, 2004; O'Doherty *et al.*, 2004; Simmonds *et al.*, 2004; Trudinger *et al.*, 2004; Cox *et al.*, 2005; Greally *et al.*, 2005; Simmonds *et al.*, 2006; Greally *et al.*, 2007].

Cape Grim data from all AGAGE instruments are reported in international scientific assessments and reports [Velders *et al.*, 2005; Cunnold *et al.*, 2007; Forster *et al.*, 2007; Montzka and Fraser, 2003].

GC-MD results

Figures 2 - 5 show all AGAGE instrumentally valid GC-MD data (and baseline monthly means in red) for 1993-2006. The growth rates are indicated by the green lines.

Major CFCs

Figure 2 shows the major CFCs: (a) CFC-11 (CCl_3F); (b) CFC-12 (CCl_2F_2); and (c) CFC-113 ($\text{CCl}_2\text{FCClF}_2$). The annual average baseline mixing ratios for CFC-11, -12 and -113 in 2006 were 245.6, 539.7 and 77.8 ppt respectively, with 2006 growth rates of -2.2 (increasing decline), -1.5 (increasing decline) and -0.7 (steady) ppt respectively. Small CFC-11 and -12 pollution episodes were observed at Cape Grim in 2005 and 2006 in air that had previ-

ously passed over or near Melbourne. No detectable CFC-113 pollution episodes were observed in 2005 and 2006.

Chlorocarbons

The chlorocarbons are shown in Figure 3: (a) chloroform (CHCl_3), (b) methyl chloroform (CH_3CCl_3); and (c) carbon tetrachloride (CCl_4). The 2006 annual average mixing ratios for CHCl_3 , CH_3CCl_3 and CCl_4 were 5.3, 15.3 and 89.8 ppt respectively. The downward trend in CHCl_3 appears to have levelled off, with its 2006 growth rate being just -0.02 ppt. The non-baseline CHCl_3 data at Cape Grim show frequent episodes of elevated mixing ratio from local and mainland sources, both natural and anthropogenic. The magnitude of the annual decreases in CH_3CCl_3 over the past ten years have declined from 12 ppt in 1996 to just under 3 ppt in 2006. However, the percentage decline has been relatively stable at about 18% yr^{-1} since 1998, close to the expected maximum decrease of about 20% yr^{-1} , indicating that global emissions are close to zero. There were no detectable CH_3CCl_3 pollution episodes originating from Melbourne in 2005 and 2006. The average annual decrease in CCl_4 for 2005-2006 was -1.1 ppt, which is close to the long-term average decrease for this species of 1.0 ppt.

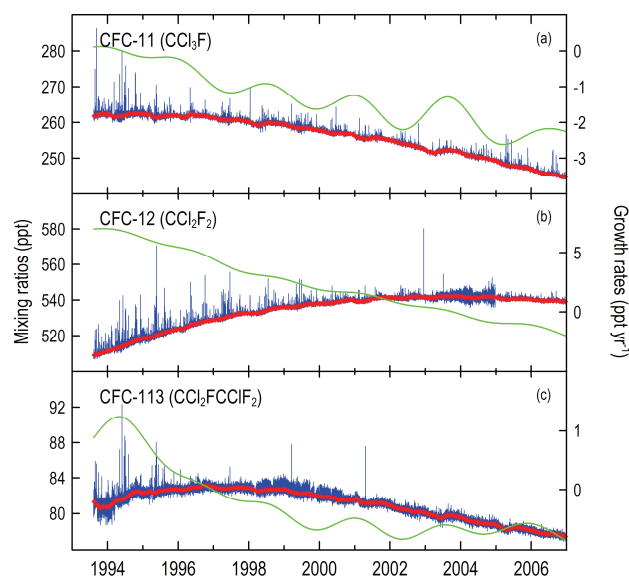


Figure 2. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of CFCs (ppt) at Cape Grim measured on the AGAGE GC-MD system over the period 1993-2006. (a) CFC-11 (silicone column); (b) CFC-12 (Porasil C column); (c) CFC-113 (silicone column). The green line represents the growth rates (ppt yr^{-1}).

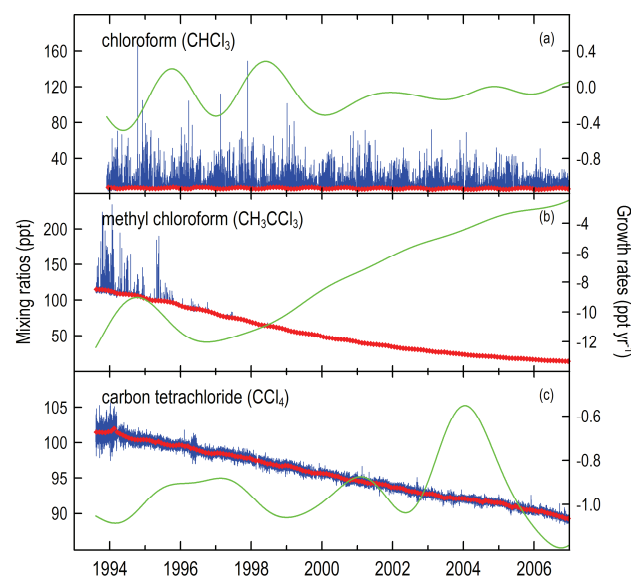


Figure 3. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of chlorocarbons (ppt) at Cape Grim measured on the AGAGE GC-MD system over the period 1993-2006. (a) chloroform; (b) methyl chloroform; (c) carbon tetrachloride. The green line represents the growth rates (ppt yr^{-1}).

Nitrous oxide and methane

Figure 4 shows: (a) nitrous oxide (N_2O); and (b) methane (CH_4). The annual average N_2O mixing ratio in 2006 was 319.1 ppb with a growth rate of 0.7 ppb yr^{-1} , which is the same as the long-term average for the Cape Grim AGAGE N_2O dataset. The CH_4 annual average mixing ratio for 2006 was 1727.7 ppb with a growth rate of -2.0 ppb yr^{-1} . The average growth rate for the seven year period 2000-2006 inclusive is -0.4 ppb yr^{-1} which represents the longest period of sustained low growth rates since systematic measurements began. A modelling study, Bousquet *et al.* [2006], concluded that since 1999, anthropogenic emissions of CH_4 have increased, but such increases have been masked by a coincident decrease in emissions of CH_4 from wetlands due to widespread drought conditions. There are significant CH_4 pollution events observed at Cape Grim (Figure 4b), largely in air influenced by Melbourne CH_4 sources (such as landfills, sewerage treatment and natural gas leakage).

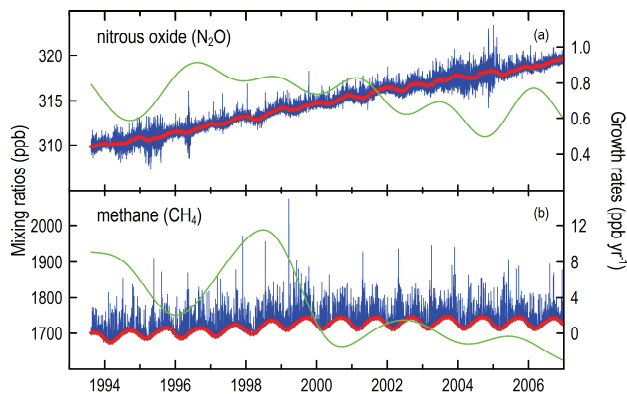


Figure 4. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of (a) nitrous oxide (ppb) and (b) methane (ppb), measured on the AGAGE GC-MD system at Cape Grim over the period 1993-2006. The green line represents the growth rates (ppb yr^{-1}).

Carbon monoxide and hydrogen

Figure 5 shows: (a) carbon monoxide (CO); and (b) hydrogen (H_2). The annual average baseline mixing ratios for CO and H_2 in 2006 were 47.6 and 531.9 ppb respectively, with 2006 growth rates of -2.8 and 0.4 ppb yr^{-1} respectively. There are regular CO pollution episodes at Cape Grim which are usually associated with air that previously passed over Melbourne. The H_2 data show regular elevated episodes, with respect to baseline, that are usually associated with air that previously passed over Melbourne. The H_2 data also show regular events where the mixing ratios drop below baseline, which are usually associated with air that had previously passed over the rural mainland (soil H_2 sink).

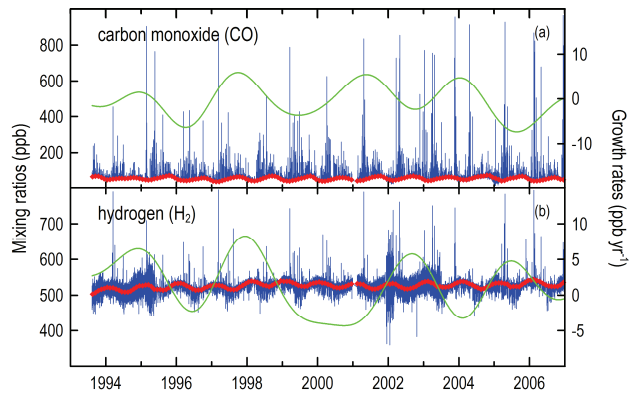


Figure 5. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of (a) carbon monoxide (ppb) and (b) hydrogen (ppb) measured on the AGAGE GC-MD system at Cape Grim over the period 1993-2006. The green line represents the growth rates (ppb yr^{-1}).

GC-MS-ADS and GC-MS-Medusa results

Figures 6 - 12 show all AGAGE instrumentally-valid data for 1998-2006 from the GC-MS-ADS (1998 - January 2004) and GC-MS-Medusa (February 2004 onwards) systems at Cape Grim. The baseline monthly means are shown in red and the growth rates are indicated by the green lines.

Minor CFCs

Figure 6 shows the minor CFCs: (a) CFC-114¹ ($\text{CClF}_2\text{CClF}_2$ and CCl_2FCF_3); and (b) CFC-115 (CClF_2CF_3). In 2006, the annual mean mixing ratios for CFC-114 and -115 were 16.5 and 8.4 ppt respectively, with growth rates of -0.01 and 0.01 ppt yr^{-1} respectively. CFC-115 appears to have now stopped growing in the atmosphere, while CFC-114 is now declining.

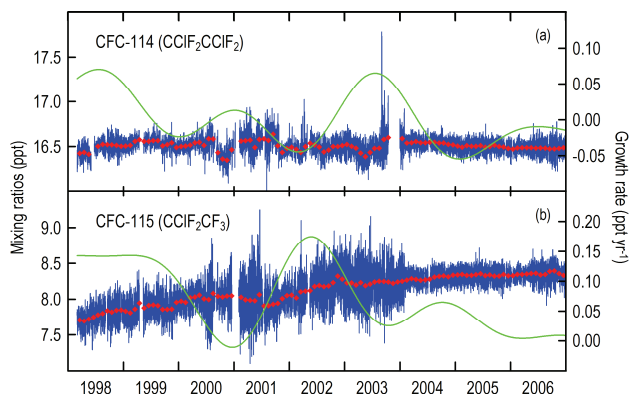


Figure 6. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of minor CFCs (ppt) made at Cape Grim on the AGAGE GC-MS-ADS and GC-MS-Medusa systems for 1998-2006. (a) CFC-114¹; (b) CFC-115. The green line represents the growth rates (ppt yr^{-1}).

¹CFC-114 as listed here is a combination of CFC-114 ($\text{CClF}_2\text{CClF}_2$) and its isomer CFC-114a (CCl_2FCF_3). The contribution of CFC-114a is unknown but it has an atmospheric abundance of 10% of that of CFC-114 [Oram, 1999; Montzka and Fraser, 2003].

HFCs

Figure 7 shows the HFCs: (a) HFC-125 (CHF_2CF_3); (b) HFC-134a (CH_2FCF_3); (c) HFC-152a (CH_3CHF_2); and (d) HFC-365mfc ($\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_3$). In 2006, the annual mean baseline mixing ratios for HFC-125, -134a, -152a and -365mfc were 3.8, 35.0, 2.7 and 0.3 ppt respectively, with 2006 growth rates of 0.7, 4.5, 0.5 and 0.1 ppt respectively. All of these growth rates are increasing, indicating that emissions are increasing. All the HFCs except for HFC-365mfc show significant pollution episodes from Melbourne.

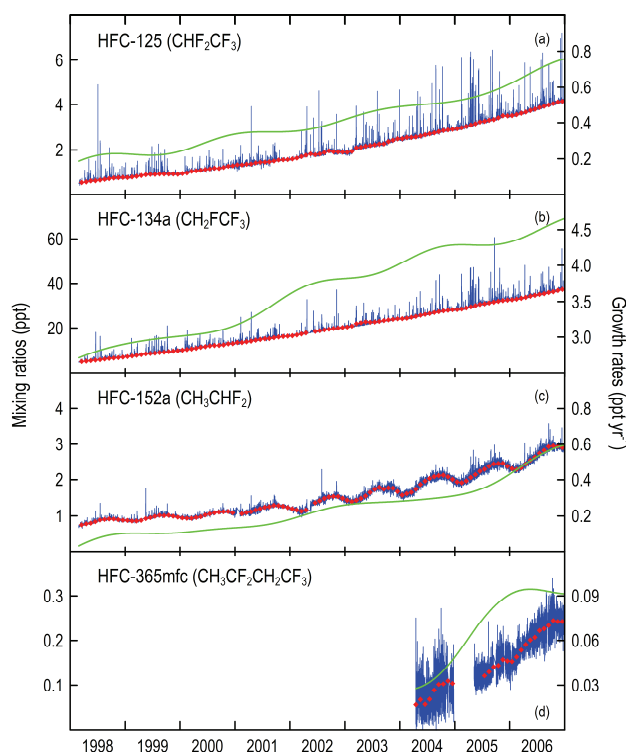


Figure 7. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of HFCs (ppt) made at Cape Grim on the AGAGE GC-MS-ADS and GC-MS-Medusa systems for 1998-2006. (a) HFC-125; (b) HFC-134a; (c) HFC-152a; (d) HFC-365mfc. The green line represents the growth rates (ppt yr^{-1}).

HCFCs

The HCFCs are shown in Figure 8: (a) HCFC-22 (CHClF_2); (b) HCFC-124 (CHClFCF_3); (c) HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$); (d) HCFC-142b (CH_3CClF_2). The 2006 annual mean baseline mixing ratios for HCFC-22, -124, -141b and -142b were 166, 1.34, 17.0 and 15.5 ppt respectively. Their corresponding growth rates for 2006 were 6.8, 0.05, 0.4 and 0.9 ppt respectively. Up to mid-2005 the growth rates for these HCFCs were either steady or declining. However, since mid-2005 they have all started to increase again, presumably in response to increased consumption in the developing world, particularly China. HCFC-22, -124 and -141b show significant pollution episodes from Melbourne emissions.

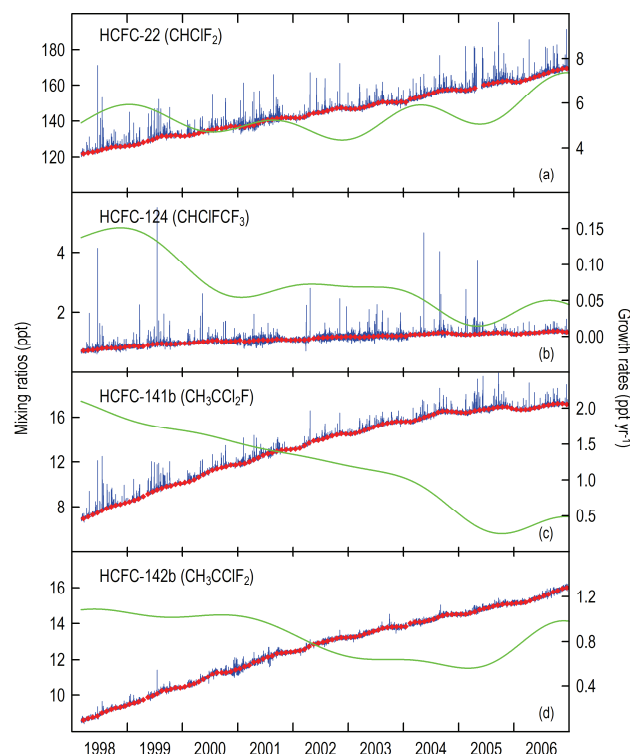


Figure 8. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of HCFCs (ppt) made at Cape Grim on the AGAGE GC-MS-ADS and GC-MS-Medusa systems for 1998-2006. (a) HCFC-22; (b) HCFC-124; (c) HCFC-141b; (d) HCFC-142b. The green line represents the growth rates (ppt yr^{-1}).

PCE

Perchloroethylene, PCE (CCl_2CCl_2) is shown in Figure 9. In 2006, the annual mean PCE mixing ratio was 0.6 ppt with a 2006 growth rate of -0.01 ppt. PCE data show significant pollution episodes from Melbourne emissions.

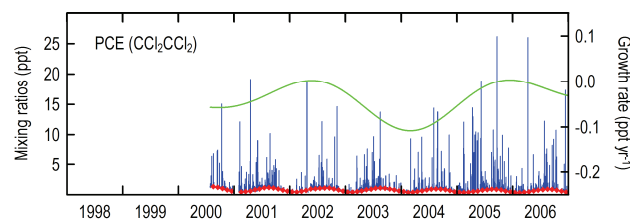


Figure 9. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of perchloroethylene (ppt) made at Cape Grim on the AGAGE GC-MS-ADS and GC-MS-Medusa systems for 2000-2006. The green line represents the growth rate (ppt yr^{-1}).

Halons

The halons are shown in Figure 10: (a) H-1211 (CBrClF_2); (b) H-1301 (CBrF_3); and (c) H-2402 ($\text{CBrF}_2\text{CBrF}_2$). The annual mean mixing ratios for H-1211, -1301 and -2402 in 2006 were 4.3, 3.1 and 0.5 ppt respectively, while their growth rates in 2006 were -0.02 , 0.01 and -0.003 ppt respectively. H-1211 and H-2402 are now declining in the atmosphere, while H-1301 has almost stopped increasing with its growth rate near zero.

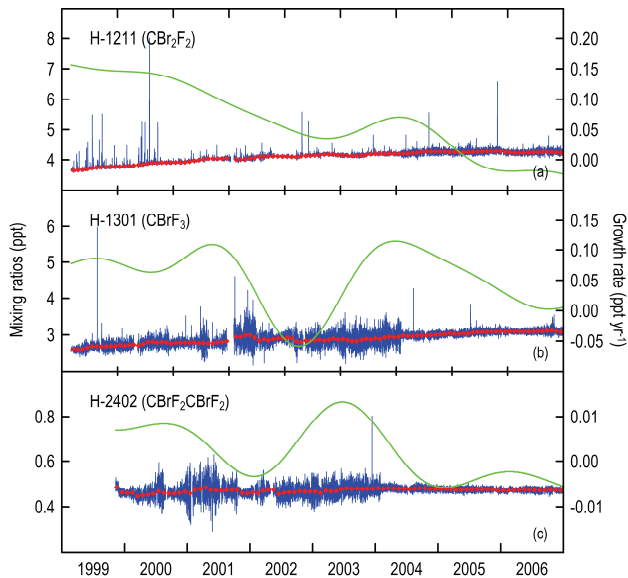


Figure 10. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of halons (ppt) made at Cape Grim on the AGAGE GC-MS-ADS and GC-MS-Medusa systems for 1998-2006. (a) H-1211; (b) H-1301; (c) H-2402. The green line represents the growth rates (ppt yr^{-1}).

Halomethanes

Figure 11 shows the halomethanes: (a) methyl chloride (CH_3Cl); (b) methyl bromide (CH_3Br); (c) methyl iodide (CH_3I); and (d) dichloromethane (CH_2Cl_2). The annual mean baseline concentration of CH_3Cl in 2006 was 517 ppt, with no significant change in concentration since 2002. 1999 to 2001 marked a period of declining CH_3Cl concentrations, possibly in response to reduced CH_3Cl biomass burning emissions following the major fires of 1998 [Simmonds *et al.*, 2004].

The GC-MS-ADS CH_3Br data from June 2002 through to January 2004 have been flagged as unreliable due to a problem in the analyses of CH_3Br (cause still unknown). One of the tertiary tanks (J-084) on the Medusa system during 2005 drifted significantly for CH_3Br and the data are yet to be corrected for this. What can be said from these measurements is that since 1998, baseline CH_3Br has shown an overall downward trend.

In 2006, the annual mean baseline CH_3I mixing ratio was 1.2 ppt. The quality of the GC-MS-ADS data are still being evaluated but the GC-MS-Medusa seems to make reliable measurements of CH_3I .

The 2006 annual mean baseline CH_2Cl_2 mixing ratio was 9.4 ppt with a growth rate of 0.2 ppt yr^{-1} . Since 1998, the concentration of CH_2Cl_2 at Cape Grim has risen by 0.8 ppt, almost entirely since 2003. CH_2Cl_2 data show significant pollution episodes from Melbourne emissions.

PFCs

Figure 12 shows the PFCs: (a) PFC-14 (CF_4); (b) PFC-116 (CF_3CF_3); and PFC-218 (C_3F_8). The annual mean mixing ratios for PFC-14, -116 and -218 in 2006 were 75.2, 3.4 and 0.45 ppt respectively,

while their growth rates in 2006 were 0.7, 0.1 and -0.03 ppt respectively. All three of these PFCs are currently increasing in the atmosphere. The PFC-14 data show pollution episodes from aluminium smelters located on the mainland at Point Henry and Portland, and in Tasmania at Bell Bay.

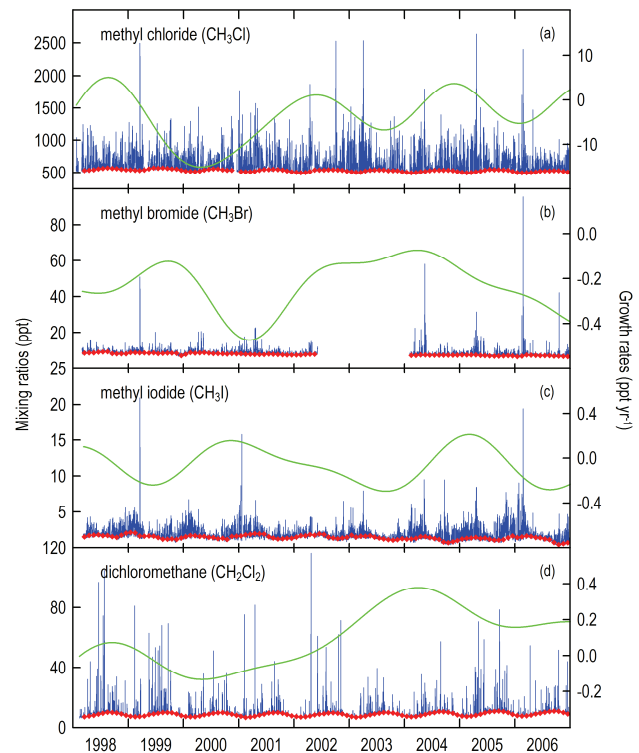


Figure 11. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of the halomethanes (ppt) made at Cape Grim on the AGAGE GC-MS-ADS and GC-MS-Medusa systems for 1998-2006. (a) methyl chloride; (b) methyl bromide; (c) methyl iodide; (d) dichloromethane. The green line represents the growth rates (ppt yr^{-1}).

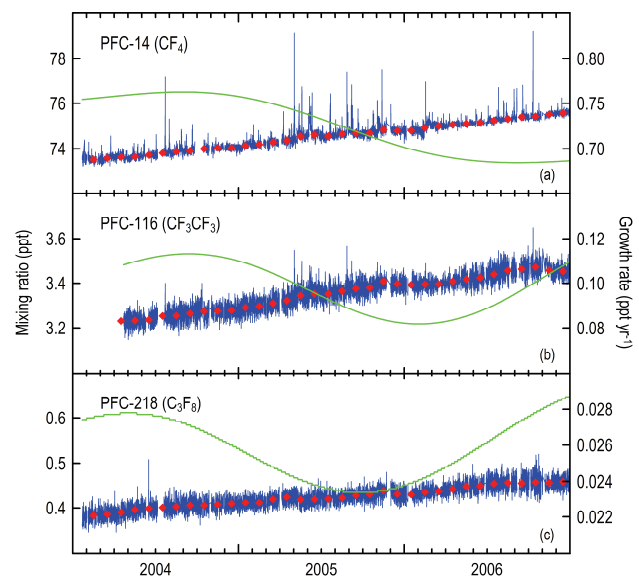


Figure 12. All individual (blue) and baseline monthly mean (\blacklozenge) *in situ* observations of PFCs (ppt) made at Cape Grim on the AGAGE GC-MS-Medusa for 2004-2006. (a) PFC-14; (b) PFC-116; (c) PFC-218. The green line represents the growth rates (ppt yr^{-1}).

ECD Sulfur hexafluoride (SF₆) results

Figure 13 shows the GC-ECD sulfur hexafluoride (SF₆) data for 2001-2006. In 2006, the annual mean SF₆ mixing ratio was 5.7 ppt with a 2006 growth rate of 0.23 ppt. The average growth rate over the period 2001-2006 was 0.22 ppt yr⁻¹ or 4.5 % yr⁻¹. The growth rate at Cape Grim has not increased since 1995, suggesting near constant global emissions [Fraser *et al.*, 2004].

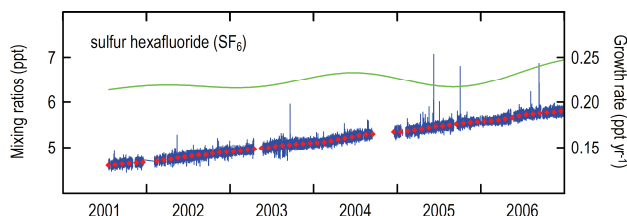


Figure 13. All individual (blue) and baseline monthly mean (♦) *in situ* observations of sulphur hexafluoride (ppt) made at Cape Grim on the AGAGE GC-ECD system for 2001-2006. The green line represents the growth rates (ppt yr⁻¹).

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4.13. REACTIVE GASES IN NEAR SURFACE AIR AT CAPE GRIM, 2005-2006

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Ozone Measurement

The ozone monitoring system at Cape Grim consists of two ozone monitors, TECO 2 and TECO 3, and two ozone calibrators.

Ozone measurements were made on ambient air drawn from 10 m above the laboratory roof through the main station stainless steel inlet, using the absolute ozone monitors designated as TECO 2 and TECO 3 (Models 49 and 49C respectively, Thermo Instruments, USA) for the period January 2005 to December 2006. The components of the system and the gas flows are shown in Figure 1 and the instrument control and data acquisition in Figure 2.

Quality control was carried out during the data analysis using protocols previously described [Galbally and Elsworth, 1984; Elsworth *et al.*, 1985]. Corrections were made for measured ozone losses in the inlet system. The exact nature of the ozone processing has not been published previously. There is an upgrade in the processing algorithms underway, so a summary of the processing procedure that has been used since the commencement of monitoring is presented below.

The absolute accuracy of the ozone monitors were checked regularly against a Thermoelectron Model 49PS ozone calibrator. Automatic calibrations are currently performed approximately every two weeks. Detailed sensitivity tests undertaken in 1988 and 1989 confirmed that TECO 2 was not sensitive to water vapour concentration [Meyer *et al.*, 1991]. An ozone calibrator (Model 49C-PS, Thermo Instruments, USA) was also installed. The new ozone calibrator is not fully operational yet. The last system and performance audit was conducted at the Global Atmosphere Watch station Cape Grim from 26 November to 3 December 2002 by the World Calibration Centre (WCC) for surface ozone, carbon monoxide and methane. It was the first audit by WCC-EMPA at Cape Grim.

Ozone Processing

The procedure used for ozone processing is:

1. Extract the zeros, spans and filter time periods, namely
 - Zero:
 - 0155 - 0204
 - 0555 - 0604
 - 1000 - 1029
 - 1355 - 1404
 - 1755 - 1804
 - 2155 - 2204
 - Calibration: 1040 to 1059
 - Filter_bypass: 1556 to 1604 (Note this is a 1 micron Teflon particulate filter located within OMCS)
2. Convert the zero data to real quantities. For TECO 2 the signal is recorded in mV. The conversion that has been determined at Cape Grim is:
TECO 2 (ppb) = TECO 2 (mV)/9.998
For TECO 3 the data is acquired digitally as ppb.
3. Apply digital filter to the 1 minute zero data: this is a 2 sigma filter in which outliers are repeatedly removed until all data is within 2 sigma of the mean. The mean zero is accepted if more than 75% of the number of values remain in the data set. This filtering works because the zero data set is normally 10 readings per zero period.
4. Apply a digital filter to the time series of mean zeros (each mean being for a successive zero time period, see 2 above). This calculates successive differences and reject spikes that persists for one or two time steps above the baseline. A spike is defined as a successive difference > 2ppb from the baseline (positive or negative)
5. Process the ambient data:
 - i. Correct for zero readings and Inlet loss
Ambient = 1.031*(Measured – Zero)
The inlet loss has previously been determined to be 3.1%. The zero is the average of the two bracketing zeros (before and after).
 - ii. Filter the ambient data. This is a finite difference filter looking for successive differences between 1 minute data of greater than 10ppb. Throughout the series 3 successive differences are calculated on a moving basis. Rejection criteria (i.e. data flagged for manual inspection) are:
 1. Spikes of 1, 2 or 3 minutes duration
 2. Ramps of 1, 2 or 3 minutes duration
 3. Successive differences > 10 ppb that are observed in only one instrument.
6. Calculate hourly means of ambient data. A valid mean must contain >40 minutes data
7. Output filtered minutely data, flagged data and hourly mean data. All data (including flagged data) is subject to a visual check, causes of discrepancies are investigated and data edited as appropriate.

8. These data sets are archived at Cape Grim and the World Data Center for Greenhouse Gases (WDCGG) and can be accessed at this web site <http://gaw.kishou.go.jp/wdccc/>.

Ozone Results

The provisional surface ozone monthly mean concentrations for all conditions for January 2005 to December 2005 are presented in Table 1. The data is from TECO 2 except for July 2005 which is from TECO 3 adjusted according to the regression relationship between the measurements on the two instruments. The standard deviations are calculated over the full month of data.

Table 1. Provisional surface ozone (nmol mol⁻¹) at Cape Grim, all observations.

Month	Mean	sd	Hourly Min	Hourly Max	# of Hours
2005 TECO 2 & TECO 3					
Jan	17.3	4.1	8.1	43.9	672
Feb	18.3	4.5	10.0	52.3	641
Mar	20.1	3.8	11.0	43.2	698
Apr	25.8	4.8	9.8	48.2	669
May	27.4	3.9	14.7	37.7	697
Jun	26.9	4.9	10.0	34.6	647
Jul	31.5	4.1	14.4	36.9	695

The relationship for the TECO 2 and TECO 3 hourly data during 2005 is

$$\text{TECO 3 (ppb)} = 1.006 \text{ TECO 2 (ppb)} - 0.235 \text{ ppb}, R^2 = 0.997, N = 6873$$

The long term trend in surface ozone in baseline conditions at Cape Grim is given in Figure 3. Further discussion of these trends is in Oltmans *et al.*, [2006].

The data set for 2006 is delayed pending new processing software.

VOC Measurement

During February and March 2006, a Proton Transfer Reaction Mass Spectrometer was deployed at Cape Grim to measure VOCs in baseline air during the P2P Campaign. The results are presented in Galbally *et al.*, [2007].

Acknowledgement

We acknowledge the contribution of Michael Douglas who was responsible for the writing of the original processing software.

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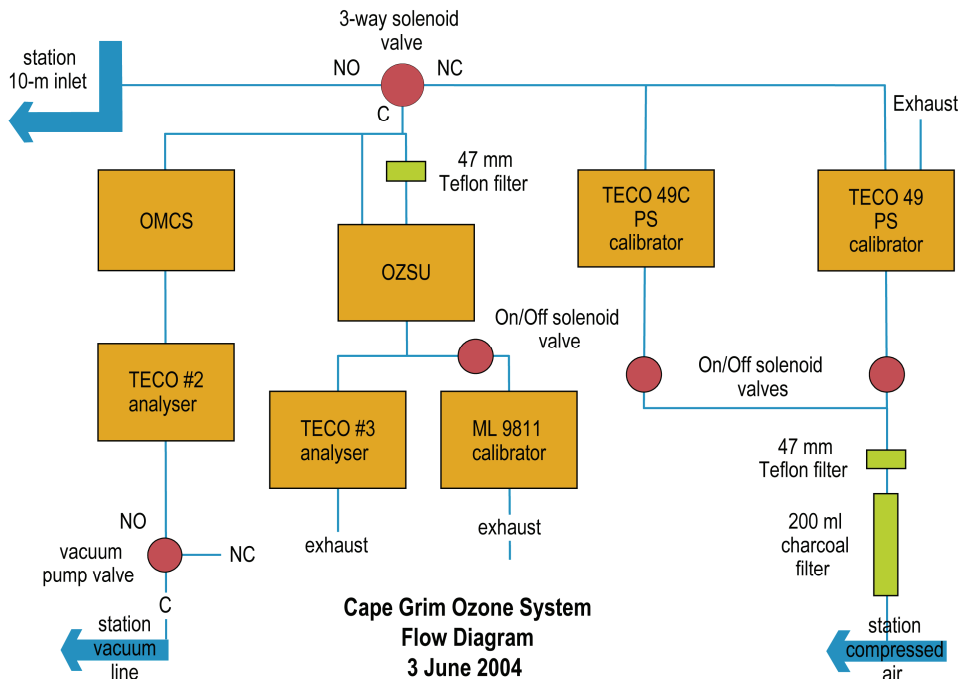


Figure 1. A schematic of the ozone gas flows. OMCS is Ozone Monitoring and Comparison System, OZSU is Ozone Zero and Span Unit (both designed and manufactured by CSIRO).

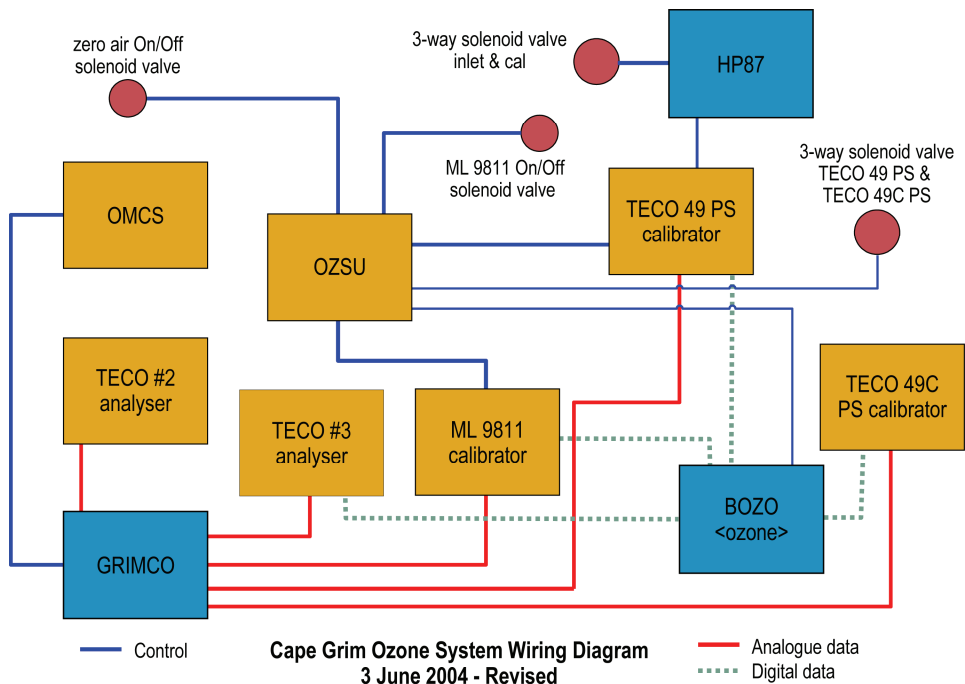


Figure 2. A schematic of the ozone control and data acquisition system. BOZO identifies a Personal Computer. GRIMCO is a main computing system at Cape Grim. HP87 is a Hewlett Packard computer.

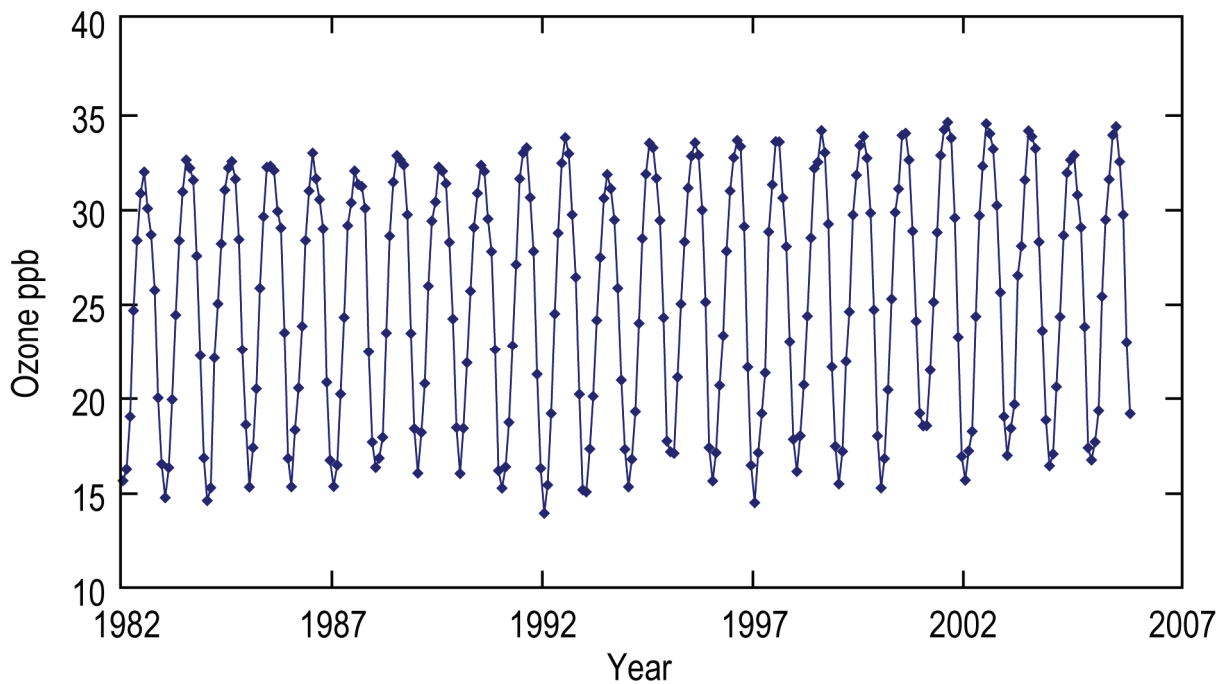


Figure 3. The long term baseline ozone record at Cape Grim.

4.14. PHYTOPLANKTON DYNAMICS AND THE PRODUCTION OF METHYL BROMIDE AND METHYL IODIDE AT CAPE GRIM: 2005-2006

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At present there is an incomplete understanding of the environmental cycling of methyl bromide (CH_3Br) and methyl iodide (CH_3I). This introduces significant uncertainty into the global inventories of these trace gases and, in the case of CH_3Br , into estimates of future concentrations under Montreal Protocol restrictions. This has been the main driver for an investigation of biological production of methyl halide gases by phytoplankton in coastal waters at Couta Rocks south of Cape Grim running since the year 2000 [Corno *et al.*, 2004; Sturrock *et al.*, 2003a,b]. The main aims of this program are to investigate the relationships between phytoplankton dynamics and methyl halide production, including spatial, seasonal and inter-annual variability.

Here, we report on the continued sampling program at a site 9 km offshore (5 nautical miles) from Couta Rocks, as well as along a transect from Cape Grim to 5 km offshore. Michael Grose, a Cape Grim funded PhD student from the University of Tasmania continued to work on this program. In early December 2006, the GC-ECD on long-term loan from the University of East Anglia, UK, failed and so measurements of methyl halides in air and seawater could not continue. However, there are sufficient data for the project to be concluded successfully.

Sampling sites

Sampling of air and surface seawater samples commenced in November 2000 at a site 9 km offshore from Couta Rocks (Site A, Figure 1), with supporting measurements of phytoplankton parameters measured by IASOS, University of Tasmania. Couta Rocks is a small fishing community, approximately 50 km south of Cape Grim. Sampling trips are made when sea-state and weather are suitable and when a boat and master is available. Four trips were made in 2005 and one in January 2006.

In February 2005 and 2006, measurements were made along a transect from the coast at Cape Grim to 5 km offshore (Site B, stations at 100 m, 1 km, 2 km, 5 km). Three transects were made each summer. The results from the February 2006 sampling are shown in Figure 2.

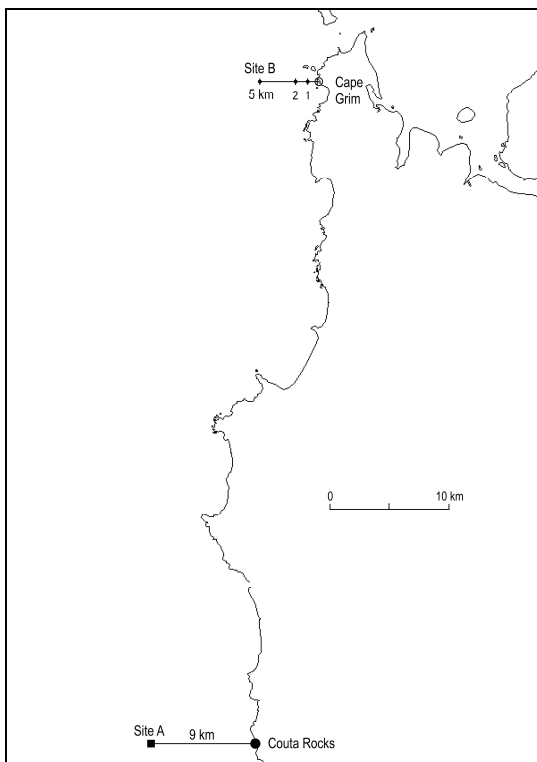


Figure 1. Sampling sites: Site A is 9 km (5 nautical miles) offshore at Couta Rocks, approximately 50km south of Cape Grim; Site B is 5 km off Cape Grim and is part of the four station, 5 km transect along 270°.

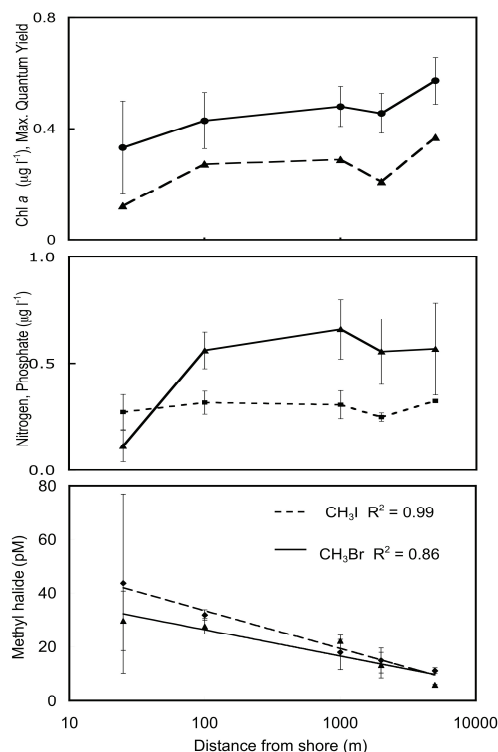


Figure 2. Measurements made along the Cape Grim transects, combined with data from an inshore sampling site, February 2006. Note log scale. Top panel: Chlorophyll a (solid line) and phytoplankton maximum quantum yield (a measure of stress; dashed line). Middle panel: nitrogen (solid line) and phosphorous (dashed line) showing nitrogen depletion at the inshore site. Bottom panel: seawater concentration of methyl bromide (triangles) and methyl iodide (diamonds) and fitted log trendlines for methyl bromide (solid line) and methyl iodide (dashed line) showing a significant relationship.

Air samples of methyl halides

At each sampling location, a 6 litre glass-lined stainless steel flask was first flushed and then filled to a pressure of 1.6 bar with a battery operated pump. The samples were analysed on a gas chromatograph, with electron capture detection (GC-ECD) and the details of the method can be found in Sturrock *et al.* [2003].

Methyl bromide levels ranged from 14.2 to 36 pptv and methyl iodide ranged from 0.8 to 6.7 pptv in the near surface atmosphere. As in previous reports, no definitive seasonal cycle can be discerned in either gas although there is some indication for a lar-

ger and more variable source in late spring and summer (November-February). Unfortunately, it is difficult to obtain measurements in winter due to poor weather and high seas and this limits the ability to assess seasonal variation.

Concentrations of methyl iodide in air at Couta Rocks, shown in Table 1, broadly agreed with those measured at the Cape Grim station at the same time. However, concentrations measured in air directly above kelp beds at the inshore environment were significantly higher than at the station (on top of a 90 m cliff), indicating a strong localised source from kelp [Grose *et al.*, 2007a].

Table 1. Physical conditions and methyl halide concentrations in surface water and air at Couta Rocks in 2005/2006.

Date	Swell (m)	Seas	Wind (knots)	Cloud (oktal)	Turbidity secchi disc (m)	Air Temp (°C)	Water CH ₃ Br (pM)	Water CH ₃ I (pM)	Air CH ₃ Br (pptv)	Air CH ₃ I (pptv)
11-Mar-05	1	slight	5	5	7.5	18.5	10.33		19.7	1.54
05-Sep-05	1.5	slight	5	3	14.0	11.0	69.36	2.87	16.3	0.84
30-Nov-05	1.5	medium	15	2	8.5	19.0	10.95	8.50	35.8	1.46
22-Dec-05	2	slight	10	1	7.5	20.0	42.25	7.97	19.2	1.01
21-Jan-06	1	slight	5	0	12.5	16.8			23.5	6.70

Surface seawater samples of methyl halides

At all sites and locations, surface seawater samples were collected in a bucket and 200 ml glass syringes were flushed with seawater before being filled and sealed. The syringes were kept on ice until analysis on return to the laboratory in Smithton. The methyl halide concentration was measured using GC-ECD with a helium purge system.

Methyl bromide concentration in surface seawater ranged from 5.2 to 69.4 pM (average 17.4 pM), and CH₃I ranged from 2.9 to 12.5 pM (average 9.8 pM), see Figure 3. The peak in CH₃Br occurred in September 2005 (69.4 pM), coinciding with a period of very high nitrate concentration and high numbers of diatoms. The lowest concentrations of CH₃Br were at the 5 km site of the Cape Grim transect in summer, and at Cousta Rocks in March 2005. Conversely, CH₃I was highest in summer at the 5 km site of the Cape Grim transect (average 11 pM) and lower at the Cousta Rocks site in the colder months.

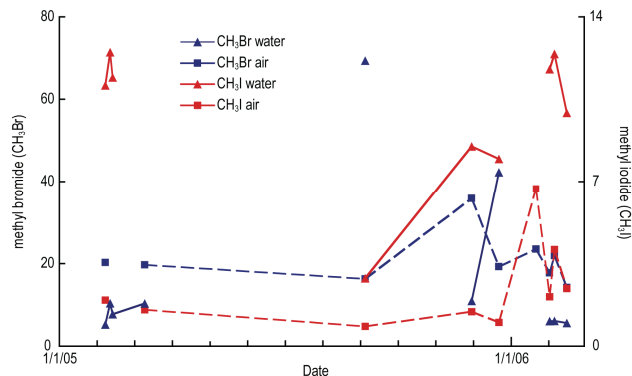


Figure 3. Methyl halide concentrations in surface seawater (in pM) and air (in pptv) measured at Cousta Rocks and Cape Grim (5 km site) in 2005/2006.

At Cape Grim, CH₃I showed a consistent pattern of fall along the transect, from high and variable concentrations at the inshore to lower and more consistent concentration at 5 km in a significant log fit relationship ($R^2 = 0.95$) [see Grose *et al.*, 2007a]. Methyl bromide also showed a similar pattern of fall, but with a poorer log fit ($R^2 = 0.8$). The higher concentration and increased variability at the coast is likely to be due to a source of methyl halides from the Bull Kelp on the rocky reef at the shore, which is influenced by daylight and tidal cycles.

Biological sampling

Salinity and temperature measurements were made with a Platypus Instruments CTD, to a maximum depth of 20 m. Turbidity was determined using a Secchi Disc. Seawater samples were collected in Niskin bottles at 0, 5, 10 and 20 m. Sub-samples of these seawater samples were then assessed for nutrients, chlorophyll *a*, and cell numbers. Nitrite, nitrate (collectively giving total nitrogen), phosphate and silicate, were measured using an ALPKEM Autoanalyser. One litre samples of seawater were filtered onto 42 mm GF/F glass fibre filters, extracted

in methanol for 8 hours and chlorophyll *a* was measured by the acidification method [Holm-Hansen and Riemann, 1978] using a Turner Instruments 10AU digital fluorometer. Cell counts were performed on a Zeiss Televar inverted microscope, using Utermolh settling chambers. Additional samples were collected using a 20 µm phytoplankton net for the identification of less common taxa.

Temperature, salinity, turbidity, stratification

Sea surface temperature showed a seasonal cycle with a maximum in mid to late summer. Depth profile of temperature showed some surface stratification in summer, with the surface waters up to 1.1°C warmer than water at 20 m in December 2005.

Salinity averaged 34.5‰ over the period, and was marginally stratified on December 2005 with a difference of 0.4‰, otherwise there was no stratification measured. Detection of a seasonal cycle is not possible due to the intermittent failure of the instrument during the winter trips.

Turbidity measured as Secchi disc depth was generally 7 to 8.5 m indicating clear oceanic waters, with occasions of exceptionally clear waters in September 2005 (14 m) and January 2006 (13.5 m) indicating a lack of particulate matter and suspended sediment.

Nutrients

The major macronutrients for phytoplankton, nitrogen, phosphorous and silicate were measured on each Cousta Rocks trip and along the Cape Grim transects. Nutrient levels were reasonably consistent through different seasons with the exception of very high levels of nitrogen measured in September 2005. There was no vertical stratification of nutrients observed in the top 20 m.

Nutrients were fairly consistent along each transect, except nitrogen was depleted in the inshore environment [see Grose *et al.*, 2007a].

Chlorophyll *a* and cell abundance

Chlorophyll *a* (Chl *a*) concentration measured at Cousta Rocks does not show an obvious seasonal trend. Sampling was not frequent enough to determine if there was a typical spring bloom or minor autumn bloom of phytoplankton, however this has not shown up in any previous years of sampling. The highest biomass was measured in March 2005, represented by moderately high numbers of a large diatom, however this was not a particularly high biomass bloom. Along the Cape Grim transect Chl *a* was lower and more variable at the inshore site, and higher and less variable offshore [see Grose *et al.*, 2007a].

The cell abundance data also shows no clear seasonal pattern of blooms. Cell numbers were generally between 20,000 and 40,000 cells per litre. The community structure was similar to previous years, with moderate amounts of diatoms, dinoflagellates, small flagellates, coccolithophorids and

chlorophytes present in every sample. Colonies of 20-50 cells of the flagellate *Phaeocystis sp.* were consistently present in high numbers. Low numbers of copepod larvae and ciliates were also consistently found.

Other Activities

Other activities during 2005-2006 included an investigation of the daily variation in the biogenic methyl halide source at the inshore environment. This included sampling of seawater from Valley Bay beach below the Cape Grim Station in February 2006 over a series of four daylight cycles (dawn to dusk), this work has been reported in Grose *et al.* [2007a]. Measurements of inshore seawater were made in February 2005 over 24 hours on three days at Stanley wharf east of Cape Grim.

Methyl halide measurements were also made on a voyage of the CSIRO vessel Southern Surveyor from Hobart (Tasmania) to Esperance (Western Australia). Concentrations of methyl halides showed a relationship with temperature, and a strong relationship between high phytoplankton presence and methyl halide concentrations in the water. Coastal waters exhibited much higher concentrations of methyl halides than the open ocean [Grose *et al.*, 2007b].

A laboratory experiment investigating the biochemical inhibition of methyl halide production by *Phaeocystis sp.* by different chemicals was performed, aiming to identify the biochemical cycles involved in the cell. This experiment had inconclusive results.

Conclusions

The inshore environment at Cape Grim (near Bull Kelp beds) is a consistent strong source of methyl halides, and measurements along a transect show a log fit relationship of decrease moving out to 5 km offshore. Coastal waters off Couta Rocks and Cape Grim are consistently supersaturated with both methyl bromide and methyl iodide suggesting the ocean is a net source to the atmosphere at this location.

From the current data there are no clear and consistent seasonal trends in either phytoplankton blooms or methyl halide emissions in the coastal waters near Cape Grim. Despite the lack of a consistent annual trend, there are numerous correlations between biological variables and source strength of methyl halides. Various groups of phytoplankton are known to produce methyl halides. In particular, *Phaeocystis sp.* is known to be a strong producer of methyl halides, and some correlation between this group and methyl halides was found in early data [Corno *et al.* 2004]. In December 2004, there was an indication that the presence of large numbers of diatoms corresponded with high levels of methyl bromide in surface waters. Open ocean measurements suggest that it is a minor source or sink of methyl halides and there is at least a partial influence from a biological source. The controlling factors over biogenic methyl halide production appear elusive, with no clear correlation between methyl halide production and physical conditions. Early indications that nutrient depletion may initiate methyl halide production [Corno *et al.* 2004] have not been confirmed by subsequent measurements.

This program will cease at the end of June 2007 and the current results will be part of a PhD thesis to be submitted in December 2007.

Table 2. Phytoplankton cell counts, Chlorophyll *a*, nutrients, salinity and temperature in seawater for each depth measured in 2005/2006 (shows only the Couta Rocks site, data from Cape Grim not shown).

	Depth (m)	Diatom (cells L ⁻¹)	Dinoflag. (cells L ⁻¹)	Ciliate (cells L ⁻¹)	Small flag. (cells L ⁻¹)	Cocco. (cells L ⁻¹)	Chloro (cells L ⁻¹)	Phaeocystis (cells L ⁻¹)	Phytoplankton (cells L ⁻¹)	Chl <i>a</i> (µg L ⁻¹)
11-Mar-05	0	1640	2260	80	1140	4980	80	14400	24500	1.247
	5	4120	2120	160	840	1420	40	9000	17540	1.350
	10	2640	3020	300	1040	1840	20	11600	20160	1.458
	20	3820	1400	380	760	2020	80	12000	20080	1.051
05-Sep-05	0	6440	3340	820	1780	3760	240	10600	26160	0.648
	5	4920	3060	520	1520	3680	300	10240	23720	0.517
	10	4820	2200	280	1100	3540	280	9200	21140	0.562
	20	12820	1460	260	760	2720	760	7600	26120	0.338
30-Nov-05	0	6080	3120	720	2560	2480	160	27200	41600	0.697
	5	0	0	0	0	0	0	0	0	0.767
	10	8320	1800	200	680	2720	40	9600	23160	0.765
	20	10280	1480	360	2040	2840	40	8000	24680	0.830
22-Dec-05	0	11760	2320	280	1800	2560	120	7600	26160	0.605
	5									
	10	21920	1800	280	520	2960	280	4800	32280	0.617
	20	18600	2560	480	1520	6320	120	7200	36320	0.790
21-Jan-06	0	3760	5040	280	720	1340	60	10400	21320	0.664
	5	2900	4160	320	480	2300	80	4800	14720	0.761
	10	5260	7460	380	820	4340	100	8800	26780	0.783
	20	3300	8940	320	600	2240	100	7600	22780	1.010

Acknowledgements

We would like to thank Graham Airey for supporting this work at Cousta Rock, through providing his boat and skills and Paul Viney for providing his boat and skills for sampling on the Cape Grim transect, Clare Reeves and the University of East Anglia, UK for providing the GC-ECD on which the analytical work for the methyl halides is performed and AGAGE for the provision of air measurements of CH₃Br and CH₃I at Cape Grim.

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4.15. PARTICLES

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[Supported by CGBAPS research funds.]

Introduction: Program and instrumentation

Continuous particle measurements at Cape Grim commenced in 1976; initially comprising only particle number concentration. Subsequent developments of the Cape Grim particle program and WMO Global Atmosphere Watch (GAW) have led to a progressive expansion of the scope of the measurement program which for 2005-2006 included particle number concentration (CN and UCN), cloud condensation nucleus (CCN) concentration, an indirect determination of the particle size distribution of CN using a diffusion battery, and aerosol optical absorption (interpreted as elemental carbon). Also, during this period, measurements of aerosol light scattering coefficient were started. Instrumentation used during 2005 and 2006 is listed in Table 1.

Data summary

As in all previous *Baseline* 'Particles' reports, any data presented here should be considered provisional as it may undergo further editing and revision. Only 'baseline' data obtained when the wind at 10 m is in the 190°-280° 'baseline' sector are reported. No other criteria have been applied for baseline data selection.

Particle number concentration, $D > 3$ nm and $D > 11$ nm (UCN and CN)

Atmospheric concentrations, for particles with a minimum diameter of approximately 3 nm and 11 nm, determined using TSI3025, and TSI3010 counters, are shown in Figure 1 for 2005-2006. Concentrations of particles were also determined continuously using the automated Nolan-Pollak counter. As is evident in Figure 1, concentrations for particles larger than 3 nm and 11 nm show the pronounced annual cycle that is typical at Cape Grim. This underlying annual cycle has a summer concentration maximum and winter minimum; considerable noise is evident on shorter time scales resulting from the numerous dynamical processes maintaining particle number.

CCN concentration

The concentration of particles active at 0.5% supersaturation (CCN) is shown in Figure 2 for the entire CCN record covering 1981-2006. Prior to February 2003 CCN concentrations were determined with a

manually-operated static thermal gradient cloud chamber. Daily mean spectra were obtained from a minimum of three spectra (at 0.23%, 0.47%, 0.71%, 0.96% and 1.2%) and from these, monthly median values were determined. Values plotted in Figure 2 are 'baseline' only, determined for samples collected when the 10-m wind came from the 190°-280° sector. Care in interpretation is necessary, particularly for the manual counter, since in some months the number of baseline samples can be relatively small. Samples from an automated static thermal gradient CCN chamber (ASCCN) are included from an overlap series with the manual counter in 1999. In February 2003 measurements with the manual counter ceased. As is well established for Southern Ocean air at Cape Grim, CCN concentrations show a marked annual cycle, with the phase of the cycle similar to those for CN and UCN concentration, reaching maximum concentrations in summer. A longer-term quasi-cyclic inter-annual variation modulates the annual pattern. Considered as a logarithmic trend over the period the concentration of particles active at 0.5% has decreased, on average, around $1.45 \pm 0.8\% \text{ yr}^{-1}$ (using annually averaged concentrations). This trend needs to be interpreted with some caution given the relatively strong inter-annual variability, as shown in Figure 2.

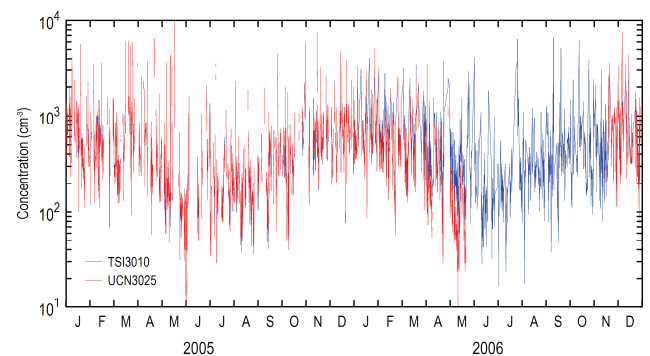


Figure 1. Baseline hourly average UCN and CN concentrations for 2005-2006.

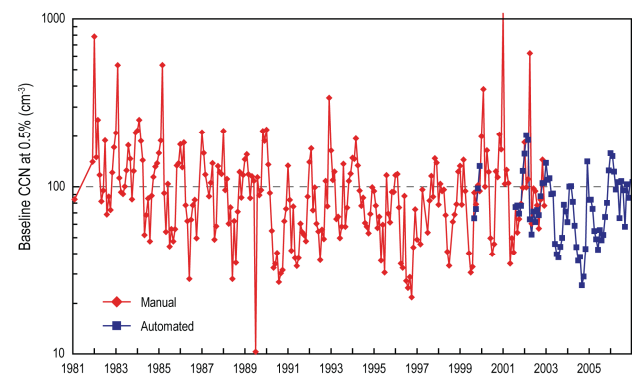


Figure 2. Monthly median concentrations of CCN active at 0.5% for baseline conditions 1981-2006. Includes data from manual and automated CCN counters.

Table 1. Instrumentation for Particles program, 2005-2006.

Instrument	Details of Operation
CN counters	
Manual Nolan-Pollak	CSIRO #2; operated daily; 10-m stack, via particle bench distributor (8 l/min bypass)
Automated Nolan-Pollak	CSIRO #1; quasi-continuous (3 diffusion battery cycles per hour, includes 15 direct CN samples per hour); 10-m stack, via particle bench distributor (8 l/min bypass)
TSI 3025	continuous; break in service 15 May – 16 November 2006 for repair; 10-m stack, via particle bench distributor (8 l/min bypass)
TSI 3010	10-m stack, via particle bench distributor (8 l/min bypass). From 14 December 2006 inlet adjacent to TSI 3025 inlet on distributor
ASCCN	Automated static thermal gradient counter. Operated quasi-continuously 0.5% supersaturation with some spectra. From 10-m stack, via particle bench distributor (8 l/min bypass)
Particle size	Diffusion battery, CSIRO #8. Automatic operation, three cycles per hour in conjunction with Nolan-Pollak CSIRO #1.
Aerosol optical absorption	Bap – aethalometer; Magee scientific; continuous, 30-minute measurement cycle; 10-m stack, via aethalometer; 18 mm diameter outlet, no additional SSI
Aerosol light scattering coefficient	Ecotech M9003, single wavelength 520 nm, 2-18 February 2005, continuous from 23 May 2006; 10-m stack, via nephelometer 18 mm diameter outlet, via RH controlled heater and URG 1 μm cyclone

Aethalometer

At Cape Grim, aerosol light absorption has been determined for several years using a Magee Scientific aethalometer, with the absorption values interpreted as black carbon concentration. Equivalent black carbon loadings are plotted in Figure 3 for baseline sector winds (190° - 280°). No other baseline selection criteria have been applied. Values plotted are determined from hourly absorption measurements, interpreted as aerosol optical absorption per cubic metre (m^{-3}) of air that has passed through the filter, converted to equivalent elemental carbon (EC) concentration using the manufacturer's recommended mass absorption coefficient of $19 \text{ m}^2 \text{ g}^{-1}$. Data are recorded as 30-minute integrals and a three point running average has been applied before the hourly average was taken. Values plotted in Figure 3 are daily means determined from hourly absorption/carbon values. All hourly values of absorption/carbon concentration are included in the averages irrespective of the sign (positive or negative).

Sample air for the aethalometer is taken from the main 10-m inlet stack.

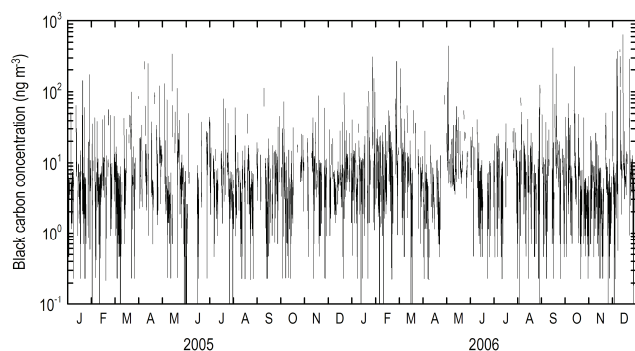


Figure 3. Aethalometer output for baseline sector winds (190° - 280°) for 2005-2006. Inferred black carbon (BC) concentrations assume a mass absorption coefficient of $19 \text{ m}^2 \text{ g}^{-1}$.

Logbook summary (2005-2006)

During 2005-2006 some problems were encountered with the continuous particle counters. The TSI3010 jet required cleaning on 7 October 2005 and 15 August 2006. A more serious failure of the

TSI3025A flow system required an inlet overhaul and the instrument was out of service from 15 May - 16 November 2006.

From 2-18 February 2005 a nephelometer inter-comparison was conducted using 2 Ecotech M9003 nephelometers, and one Radiance nephelometer; on 23 May 2006 Ecotech nephelometer M9003 ID #03-0521 was installed for continuous operation. The installation included a PM1 cyclone following an RH controlled heater, and used a dedicated outlet from the 10-m stack.

A number of system changes included a further aethalometer mass flow controller failure, with reversion to manual flow setting from 3 March 2005. On 23 February 2006 a new PC controlling the TSI CN and UCN was installed. The mast base was opened on 6 September 2006 with the installation of an O_2 analyser. On 6 December 2006 the internal sample pump on the ASCCN was bypassed and a solenoid-valve-controlled bleed system from the main vacuum line put into service in its place.

Additional particle instruments (including APS and SMPS) were operated at the station during Jan-February 2006 as part of the P2P intensive; strong bushfire smoke was observed at the station on 16 February 2006, during this intensive. Additional instrumentation (VH-TDMA) was also operated by QUT during October 2006.

Calibrations

Calibrations during this period included:

ASCCN using monodisperse nebulised 0.1% w/v NaCl with concentration determined using the TSI 3010 CNC, on 16 February 2005 and 24 May 2006.

Nephelometer, using FM200 heptafluoropropane on: 1-2 February 2005, 24 May 2006, 31 August 2006 and 6 December 2006.

4.16. FINE PARTICLE SAMPLING AT CAPE GRIM

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[Cooperative Research report.]

Fine particles (PM_{2.5}) are being sampled at Cape Grim using a cyclone sampler with a 50% cut-off point for a flow rate 22 L min⁻¹. Samples are collected on 250 µg cm⁻² stretched-Teflon filters of 25 mm diameter. Two, 24 hour (midnight-midnight) samples per week are obtained for every Sunday and Wednesday.

These stretched-Teflon filters are ideal for multi-elemental analysis and source apportionment using the accelerator based ion beam analysis (IBA) techniques at the Australian Nuclear Science Technology Organisation (ANSTO). Currently the following elements can be detected at levels around or below 10 ng m⁻³ of air sampled; H, C, N, O, F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, and Pb. Measured average annual concentrations for many of these species for the twelve month period from January to December 2006 are given in Table 1. A box and whisker plot of the average monthly masses, for January 2004 to December 2006 is given in Figure 1. The (+) sign represents the mean and the horizontal bar the median for each month. Outliers are represented by dots.

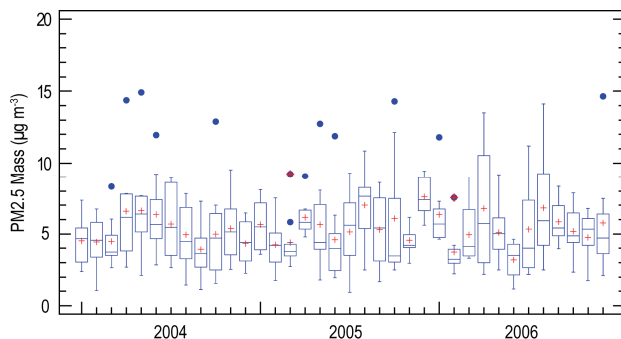


Figure 1. Monthly box and whisker mass plots for PM_{2.5} fine particles at Cape Grim January 2004 to December 2006.

The annual averages are calculated from all the 24 hour samples and contain components from the baseline sector as well as all other sectors (continental and Tasmanian sectors).

If all the elemental sulfur measured on the filter was assumed to occur as fully neutralised ammonium sulfate then this would correspond to an annual average of (0.94±0.6) µg m⁻³ or about 18% of the total fine mass. From the sodium and chlorine values we estimate that sea-salt was about 47% of the total measured fine mass during 2006. Wind-blown soil was estimated from the oxides of Al, Si, Ti, Ca and Fe and represents about 1.9% of the total fine mass at Cape Grim.

Light absorbing Black Carbon (BC) estimates were obtained by standard laser absorption methods, pre- and post- filter exposure assuming a mass absorption coefficient of 7m²g⁻¹ and show that at Cape Grim black carbon is only about 4% of the total average annual fine mass.

Organic matter was estimated from the hydrogen not associated with ammonium ions and assumed the average organic particle was composed of 9% H, 20% O and 71% C. It corresponds to about 2% of the annual average fine particle mass.

As expected at Cape Grim trace metals, not associated with soil, generally occur at very low concentrations below 1 ng m⁻³.

Table 1. 2006 annual average concentrations (ng m⁻³, except where indicated by * (µg m⁻³)) of selected species and some derived parameters in the sub 2.5 µm size fraction at Cape Grim, based on 2 day per week, 24 hour average, non-sectored sampling.

PM _{2.5}	Average	s.d.	Min	Max
Mass*	5.33	2.8	1.2	14.6
Na*	1.02	0.63	0.14	3.0
Al	3.5	3.1	0	19
Si	11	12	2	85
P	0.6	1	0	6
S	227	148	51	918
Cl*	1.49	1.0	0.01	4.6
K	37	21	8	117
Ca	34	21	5	107
Ti	0.6	0.5	0	3
V	1.0	1.2	0	5
Cr	0.1	0.3	0	2
Mn	0.5	0.6	0	3
Fe	3.7	4.9	0	27
Co	0.2	0.2	0	1
Ni	0.5	0.4	0	2
Cu	0.2	0.4	0	3
Zn	0.7	1.3	0	7
Br	1.7	1.7	0	8
Pb	0.4	0.6	0	3
Black carbon*	0.20	0.11	0.02	0.68
Soil*	0.10	0.06	0.03	0.41
Ammon. sulfate*	0.94	0.6	0.2	3.8
Organics*	0.12	0.6	0.0	5.2
Sea salt*	2.6	1.6	0.3	7.6

4.17. MEASUREMENT OF NATURAL LEVELS OF TRITIUM IN PRECIPITATION FOR YEARS 2005-2006 AT CAPE GRIM

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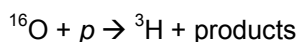
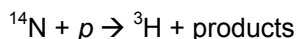
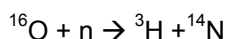
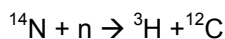
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[Cooperative Research report.]

Introduction

Tritium (^3H or T) is a naturally occurring isotope of Hydrogen. It has a half-life of 4500 ± 8 days (12.33 years) and decays by weak beta emission, with a maximum energy of 18.6 keV [Lucas and Unterweger, 2000]. Tritium activity can be expressed in TU where one TU corresponds to one ^3H atom per 10^{18} atoms of hydrogen (protium) or 0.11919 ± 0.00021 Bq kg^{-1} [Kaufman and Libby, 1983].

Tritium occurs naturally, but can also be created as a result of atmospheric testing of thermonuclear devices. Measurable amounts of tritium are produced in the Earth's crust from the spontaneous fission of uranium and in the upper atmosphere by nuclear reactions of cosmic rays with atmospheric atoms [Kaufman and Libby, 1983];



Once in the atmosphere, tritium is readily incorporated into water and reaches the Earth's surface in rainwater, snow and atmospheric moisture.

Tritium concentrations in rainfall in the southern hemisphere peaked in 1963 due to tritium fallout, averaging approximately 30 TU for both oceanic and continental stations. The tritium activity has been decreasing since the last tritium fallout, to reach almost natural levels. Tritium activity in rainfall, however can peak in the austral spring, which is in August and September [IAEA, 1967].

Monthly precipitation samples have been collected from various weather stations throughout Australia including Cape Grim, for the Australian Nuclear Science and Technology Organisation (ANSTO), as part of the Global Network of Isotopes in Precipitation project. This global project is conducted by the International Atomic Energy Agency (IAEA) in cooperation with the World Meteorological Organisation (WMO).

Sampling and tritium analysis

Monthly precipitation samples collected from Cape Grim are analysed for tritium at ANSTO, which has the only facility in Australia capable of low level tritium analysis.

An accepted methodology for the determination of low level tritium in environmental water samples is a process referred to as electrolytic enrichment fol-

lowed by Liquid Scintillation Counting. This is an established technique being employed by ANSTO and numerous laboratories worldwide.

A sub-sample of the monthly precipitation received from each weather station is also supplied to CSIRO Land and Water, Isotope Analysis Service, Waite Rd, Urrbrae, SA 5064, for deuterium and oxygen-18 analysis.

Results

Tritium activity in precipitation from Cape Grim during the period 2005 – 2006 is presented in Table 1. The yearly mean for tritium, weighted by the total amount of precipitation has been calculated according to the formula:

$$\text{Yearly weighted mean} = \frac{\sum (P \times [T])}{\sum (P)}$$

Where P = Monthly precipitation

[T] = Monthly tritium concentration

Samples for tritium analysis were not collected for January, April and December 2005 due to insufficient sample volume. Hence, the resulting yearly weighted mean is reduced for 2005.

Table 1. Monthly tritium precipitation data for the Cape Grim sampling station during 2005 and 2006.

	2005		2006	
	precipitation (mm)	tritium TU	precipitation (mm)	tritium TU
January	31.0	*	23.8	2.4±0.2
February	32.6	3.1±0.2	20.8	3.3±0.1
March	15.2	2.0±0.3	40.8	2.8±0.2
April	50.8	*	90.2	1.6±0.1
May	26.0	1.9±0.2	36.8	1.5±0.2
June	84.6	2.2±0.1	61.6	1.5±0.2
July	76.2	1.4±0.2	79.2	1.5±0.2
August	81.6	1.7±0.1	29.4	3.6±0.1
September	98.0	3.4±0.2	37.0	4.6±0.2
October	92.4	2.9±0.1	22.2	2.4±0.2
November	49.8	3.1±0.2	19.8	2.5±0.4
December	59.6	*	17.6	2.7±0.3
Weighted mean		2.0 ± 0.1 [#]		2.2 ± 0.2 [#]
		79.7%**		100.0%**

* Tritium levels in TU for these months are not available, monthly precipitation in mm are indicated where data was supplied

[#] Yearly weighted mean for tritium (TU), weighted by the total amount of precipitation

** Percentage of the total precipitation for which tritium data are available to calculate the weighted mean

Acknowledgments

We would like to acknowledge the staff at the Cape Grim Baseline Air Pollution Station who collected the samples and the Bureau of Meteorology for supplying the relevant precipitation values.

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- IAEA. Tritium and other environmental isotopes in the hydrological cycle. Technical Reports Series No. 73, 1967.
Kaufman, S. and W. F. Libby, The Natural distribution of tritium, *Physical Review*, 93(6), 1337-1344, 1983.
Lucas, L. L., and M. P. Unterweger, Comprehensive Review and Critical Evaluation of the Half-Life of Tritium, *J. Res. Natl. Inst. Stand. Technol.*, 105, 541-549, 2000.

4.18. THE STABLE ISOTOPIC COMPOSITION, δD AND $\delta^{18}O$, OF RAINFALL

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[Cooperative Research report.]

Introduction

In 1961, the International Atomic Energy Agency, in co-operation with the World Meteorological Organisation, commenced a world-wide survey of the isotopic composition of monthly precipitation. Tritium, oxygen-18 and deuterium, the main isotopes of interest, offer a range of possibilities for studying processes within the water cycle.

Data collected from this global network of stations, GNIP [2001] provide an important tool for the interpretation of past climate changes, the validation of current global circulation models and contribute towards an understanding of regional and global scale water balances studies.

Method

Samples of rainfall were collected by staff at Cape Grim and sent to the Australian Nuclear Science and Technology Organisation (ANSTO) for tritium analyses. Results of these analyses and the methodology for their collection are described elsewhere in this report.

Deuterium and oxygen-18 analyses of the sub samples were performed using standard gas equilibration techniques and stable isotope ratio mass spectrometry. The results are expressed in standard notation, parts per mil (‰), relative to V-SMOW (Standard Mean Ocean Water) given by the following equation:

$$\delta = ((R \text{ sample}/R \text{ standard}) - 1) \times 1000$$

Where R equals the ratio of the minor and major isotopes :

For meteoric waters, there is a systematic relationship between delta ^{18}O and delta D.

$$\delta D \approx 8 * \delta^{18}O + 10$$

This global relationship first reported by Craig [1961] is a function of the Raleigh distillation equation. The isotopic composition of precipitation at any point on the globe is related to the temperature of the event and the distance from the coast that this event took place. The 'long-term'- (for a period of at least three years) - monthly averages for a station contribute towards the calculation of the 'local meteoric water line'. For Cape Grim this is (after the elimination of outliers showing obvious evaporation) and from the limited data set.

$$\delta D \approx 7.3 * \delta^{18}O + 9.0$$

Results

The table below shows data for Cape Grim from the calendar years 2003 – 2005.

Table 1. Deuterium (δD) and oxygen-18 ($\delta^{18}O$) data for Cape Grim from the calendar years 2003 – 2005 in Cape Grim rainfall.

Month	2003		2004		2005	
	$\delta^{18}O$ ‰	δD ‰	$\delta^{18}O$ ‰	δD ‰	$\delta^{18}O$ ‰	δD ‰
[relative to V-SMOW]						
Jan	N.D.	N.D.	-4.64	-30.9	-0.27	-1.1
Feb	-0.76	-7.8	-2.39	-12.7	-3.77	-20.5
Mar	-1.15	1.8	-3.28	-12.5	-2.49	-6.8
Apr	0.87	-4.4	-1.75	-3.4	N.D.	N.D.
May	-3.97	-21.9	-0.1	2.7	-3.02	-13.8
Jun	-6.78	-41.7	-4.97	-27.7	-4.69	-23.3
Jul	-6.59	-39.3	-2.45	-11.9	-3.23	-13.5
Aug	-5.91	-34.6	3.23	21.3	-3.13	-9.0
Sep	-3.55	-17.2	1.4	16.2	-4.41	-23.5
Oct	-3.48	-16.8	N.D.	N.D.	-3.87	-18.2
Nov	N.D.	N.D.	-3.37	-13.4	-2.2	-3.0
Dec	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

References

- Craig, H., Isotopic variations in natural waters, *Science*, 133, 1702-1703, 1961.
IAEA/WMO, Global Network of Isotopes in Precipitation, The GNIP Database, accessible at:
<http://www.iaea.org/programmes/rial/pci/isotopehydrology>

4.19. AEROSOL SAMPLERS

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[Supported by CGBAPS research funds]

Three instruments continued to collect samples for the long term record of PM10 and PM2.5 aerosol composition during 2005 and 2006. The high volume sampler HVA with a PM10 inlet operated on the baseline event switch 3 (BEVS3)¹ until May 2005, when it was moved to the northeast end of the sampling deck and placed on the Northern Exposure switch². In October 2005 it was moved back to the southwest corner of the deck and placed on BEVS2³ until August 2006. On 29 August 2006 the inlet of HVA was replaced with a PM2.5 inlet and the sampler switched to baseline event switch 3 (BEVS3). The high volume sampler HVB with PM10 inlet operated on BEVS2, until July 2005 when it was

¹ BEVS3 utilises the previous five year's CN data for the current month selected for a 50 m level wind direction between 190° and 280°, and the CN threshold is based on the 90 percentile of CN hourly medians for this period, interpolated using cubic splines to give daily values.

² Northern Exposure Switch criteria is for CN > 1000 particles cm⁻³ and wind direction between 315° and 60°.

³ The sampler was switched on when the wind direction was between 190° and 280° and the condensation nucleus (CN) concentration was < 600 cm. Note that BEVS2 is the same as BEVS1 except that BEVS2 has a manual override

changed to BEVS3. Between 1 May and 21 June 2006 HVB was out of commission due to the instrument failing electrical safety tests. The low volume sampler (LV) with PM_{2.5} inlet operated on BEVS3 for the entire period. Table 1 outlines the changes made to the MAC program aerosol samplers.

HVA is an Ecotech 2000 High Volume sampler, with a PM₁₀ impactor for size selection (until September 2006). The ambient flow rate through the inlet is 67.8 m³ hr⁻¹. Flow rate is controlled with a mass flow controller, thus to ensure the correct volumetric flow rate, the mass flow controlled flow rate is adjusted for seasonally averaged temperature and pressure conditions. The flow rate is audited and calibrated using a calibration orifice plate every 3 months. The size selective inlet is cleaned and re-greased every 2 months. Particles were collected on 250 mm x 200 mm EMFAB⁴ filters (Pallflex Membrane filters EMFAB TX40H120-WW, P/N 7224), with filters being exchanged weekly. Table 2 presents PM₁₀ data for HVA operated on BEVS3. Table 3 presents PM₁₀ data for HVA operated on the Northern Exposure Switch. Table 4 presents PM₁₀ data for HVA operated on BEVS2 between September 2005 and August 2006. After September 2006, HVA was fitted with a PM_{2.5} inlet. The same flow settings, calibration procedures and filter papers were used as for HVA with the PM₁₀ inlet. However, the impaction plate on the PM_{2.5} inlet was cleaned and re-greased monthly.

HVB is an Ecotech 3000 High Volume sampler, with a PM₁₀ impactor for size selection. The ambient flow rate through the inlet is 67.8 m³ hr⁻¹. The flow rate is controlled with a mass flow controller, and the ambient temperature and pressure are monitored during sampling so that both the ambient volumetric and standard flow rates can be determined. The flow rate is audited and calibrated using a calibration orifice plate every 3 months. The size selective inlet is cleaned and re-greased every 2 months. Samples are collected on 250 mm x 200 mm EMFAB filters that are exchanged weekly. The data determined from samples collected with PM₁₀ HVB operated on BEVS2 between January and July 2005 are presented in Table 5 and on BEVS3 after July 2005 are presented in Table 6.

LV is an Ecotech 1500 Dual Flow sampler with a PM_{2.5} cyclone size selective inlet. The ambient volumetric flow rate through the inlet is 16.7 LPM. Flow rate is controlled with a mass flow controller, thus to ensure the correct volumetric flow rate through the size-selective inlet, the mass flow controlled flow rate is adjusted for seasonally averaged temperature and pressure conditions. The flow is split evenly between two filters, the first a 47 mm Teflo⁵ filter (Pall R2PJ047, 2 µm pore size) and the second a 47 mm tissue quartz filter (Pallflex Membrane Filter Tissuequartz 2500QAT-UP, P/N 7202).

The flow rate is audited and inlet cleaned every 3 months. Sampling blank checks were performed monthly. The data determined from samples collected with the LV are presented in Table 7.

After sample collection, filters are sent to CSIRO Marine and Atmospheric Research, Aspendale for analysis. Gravimetric mass measurements are performed on the 47 mm Teflo filters using a Mettler UMTA2 microbalance at < 20% relative humidity. Electrostatic charging is reduced by the presence of radioactive static discharge sources within the balance chamber. The resolution of the balance is 0.0001 mg (0.1 µg). Each 47 mm Teflo filter is weighed repeatedly, both before and after sampling, until three weights within 0.001 mg are obtained. Gravimetric mass measurements were performed on the HVA and HVB filters using a Sartorius Master Pro LA130S-F balance at relative humidity of approximately 50%. The resolution of the balance is 0.0001 g. Each 250 mm x 200 mm filter is weighed before and after sampling until three weights within 0.0010 g.

After mass determination, the Teflo filters are wetted with methanol before being extracted in 5 ml of MQ-grade⁶ water. The sample is then preserved using 1% chloroform. A 6.25 cm² section of the HVA and HVB filters are extracted in the same way (except that 10 ml of MQ-grade water is used). Anion and cation concentrations are determined by suppressed ion chromatography (IC) using a Dionex DX500 gradient ion chromatograph. Anions are determined using an AS11 column and an ASRS ultra-suppressor and a gradient eluent of sodium hydroxide. Cations are determined using a CS12 column and a CSRS ultra-suppressor and a methanesulfonate acid eluent.

The data displayed in Tables 2-7 have been subjected to preliminary data quality checks. Particularly the impact of local soil on the sample has been assessed using the unique chemical source signature determined for the soil on the cliff at Cape Grim, and the procedure outlined in Ayers 2001. Sampling blanks were determined monthly on either HVA or HVB and LV.

Reference

Ayers, G. P. Influence of local soil dust on composition of aerosol samples at Cape Grim, in *Baseline Atmospheric Program (Australia 97-98)* edited by N. W. Tindale, N. Derek and R. J. Francey, Bureau of Meteorology and CSIRO Atmospheric Research, Melbourne, Australia, 50-56, 2001.

⁴ EMFAB is borosilicate glass fibres reinforced with woven glass and bonded with PTFE.

⁵ Teflo is a PTFE disc with a support ring

⁶ MQ-grade water is 18 mΩ de-ionized water

Table 1. Changes to MAC Program aerosol samplers.

Name	Instrument	Date	Event	Size Selection	Flow rate (L min ⁻¹)	Analysis/Data
HVA	Ecotech 2000	24-May-05	Moved to NE end of deck		PM10	1145
HVA	Ecotech 2000	24-May-05	Changed to Northern Exposure		PM10	1145
HVB	Ecotech 3000	26-Jul-05	Changed to BEVS3		PM10	1145
HVA	Ecotech 2000	27-Sep-05	Moved to SW corner of deck		PM10	1145
HVA	Ecotech 2000	27-Sep-05	Changed to BEVS2		PM10	1145
HVA	Ecotech 2000	29-Aug-06	Size-selective inlet changed		PM2.5	1145
HVA	Ecotech 2000	29-Aug-06	Changed to BEVS3		PM2.5	1145

Table 2. Baseline (BEVS3) gravimetric mass, air volume and ion concentrations of PM10 aerosol at Cape Grim collected using HVA. MSA is methanesulfonate. Filter numbers in bold represent samples where the Na_{soil}/Na_{seasalt} is greater than 20%. All samples were collected on EMFAB filters.

Filter #	Date On	Time	Date Off	Time	Mass (µg m ⁻³)	Air volume (m ³)	Na ⁺ [K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	MSA
							nmoles m ⁻³							
HVA178	29 Dec	04 0956	04 Jan	05 1358	15	3777	149	3.63	14.40	2.93	164	0.58	11.9	1.14
HVA180	04 Jan	05 1543	11 Jan	05 1307	16	3329	165	3.95	15.07	3.09	183	1.23	12.3	1.23
HVA181	11 Jan	05 1421	18 Jan	05 1035	24	4352	239	5.33	24.90	5.12	273	0.66	16.5	3.47
HVA182	18 Jan	05 1119	25 Jan	05 1124	13	5896	133	3.16	13.47	2.87	148	0.90	10.7	1.89
HVA183	25 Jan	05 1207	01 Feb	05 1357	13	3080	128	3.35	11.79	2.83	134	3.03	12.8	1.93
HVA184	01 Feb	05 1448	08 Feb	05 1425	12	3675	110	2.38	10.14	2.28	121	0.97	8.2	0.02
HVA185	08 Feb	05 1532	15 Feb	05 1500	11	6587	108	2.36	10.81	2.31	119	0.43	8.0	0.43
HVA186	15 Feb	05 1550	22 Feb	05 1314	22	2704	212	4.86	21.23	4.68	237	1.42	16.2	1.07
HVA187	22 Feb	05 1358	01 Mar	05 1349	10	1956	92	3.20	6.87	1.98	86	3.63	11.3	1.81
HVA189	01 Mar	05 1505	08 Mar	05 1111	18	9074	185	4.06	19.36	4.31	199	0.71	11.9	0.18
HVA190	08 Mar	05 1212	15 Mar	05 1401	9	4674	74	1.99	7.13	1.92	78	1.74	7.9	0.75
HVA191	15 Mar	05 1455	22 Mar	05 1046	11	777	362	9.63	30.96	8.18	374	9.17	31.6	1.85
HVA192	22 Mar	05 1135	24 Mar	05 1405	9	3160	28	0.97	1.41	0.48	25	0.52	1.9	0.34
HVA193	29 Mar	05 1513	05 Apr	05 1344	19	2558	188	4.41	17.43	3.77	209	0.55	11.6	0.02
HVA194	05 Apr	05 1424	12 Apr	05 1219	19	3053	180	3.94	18.07	4.08	200	2.62	13.0	1.15
HVA195	12 Apr	05 1350	19 Apr	05 1151	22	2143	213	4.76	20.39	4.68	237	1.71	13.8	0.83
HVA196	19 Apr	05 1259	26 Apr	05 1334	20	4278	195	4.40	19.67	4.47	220	1.89	13.1	0.27
HVA198	26 Apr	05 1459	03 May	05 1213	25	3841	259	5.89	26.15	5.76	296	0.38	16.0	0.16
HVA199	03 May	05 1256	10 May	05 1221	16	5624	151	3.60	15.71	3.54	172	0.49	9.8	0.15
HVA200	10 May	05 1301	17 May	05 1056	16	4789	128	3.75	14.66	3.65	145	0.68	9.3	0.06
HVA201	17 May	05 1205	23 May	05 1414	22	93	316	18.54	6.93	4.62	178	2.94	10.4	9.45

Table 3. Northern Exposure Switch gravimetric mass, air volume and ion concentrations of PM10 aerosol at Cape Grim collected using HVA. MSA is methanesulfonate. Filter numbers in bold represent samples where the Na_{soil}/Na_{seasalt} is greater than 20%. All samples were collected on EMFAB filters.

Filter #	Date On	Time	Date Off	Time	Mass (µg m ⁻³)	Air volume (m ³)	Na ⁺ [K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	MSA
							nmoles m ⁻³							
HVA202	24 May	05 1549	31 May	05 1221	39	40	604	26.94	5.19	4.76	354	2.19	19.7	1.47
HVA204	07 Jun	05 1347	14 Jun	05 1518	26	191	254	10.75	2.36	4.23	214	7.35	14.8	2.37
HVA205	14 Jun	05 1523	21 Jun	05 1135	12	2261	116	4.24	9.79	3.13	120	0.01	10.0	0.27
HVA207	21 Jun	05 1303	28 Jun	05 1551	8	1515	70	2.90	3.64	1.25	64	8.27	6.5	0.04
HVA208	28 Jun	05 1559	05 Jul	05 1430	15	1241	161	6.20	11.87	2.71	158	13.96	14.8	0.05
HVA209	05 Jul	05 1435	12 Jul	05 1030	24	1451	247	8.58	22.85	5.27	259	15.97	20.4	0.04
HVA210	12 Jul	05 1114	19 Jul	05 1149	10	176	161	7.32	0.60	0.91	108	3.32	8.5	0.39
HVA211	19 Jul	05 1303	26 Jul	05 1155	27	2984	304	8.63	32.27	6.39	326	19.00	24.2	0.02
HVA212	26 Jul	05 1247	09 Aug	05 1129	29	2415	270	8.04	27.28	6.21	289	15.65	21.9	0.02
HVA213	09 Aug	05 1216	16 Aug	05 1127	21	2073	223	5.46	20.58	4.73	244	5.66	15.3	0.02
HVA215	16 Aug	05 1249	23 Aug	05 1520	20	2912	192	5.93	18.97	4.37	201	18.05	14.6	0.02
HVA216	23 Aug	05 1559	30 Aug	05 1108	21	4193	168	6.43	17.54	4.27	146	33.83	24.5	0.06
HVA217	30 Aug	05 1153	06 Sep	05 1005	12	4778	104	4.09	10.57	2.56	96	16.90	15.6	0.04
HVA218	06 Sep	05 1220	13 Sep	05 1113	22	4424	148	6.15	15.04	3.65	138	31.75	24.3	0.02
HVA219	13 Sep	05 1229	20 Sep	05 1151	37	1269	469	10.85	45.60	9.40	532	1.48	29.4	0.05
HVA220	20 Sep	05 1228	27 Sep	05 1440	15	2327	87	5.79	7.08	2.05	62	37.45	18.7	0.11

Table 4. Baseline (BEVS2) gravimetric mass, air volume and ion concentrations of PM10 aerosol at Cape Grim collected using HVA. MSA is methanesulfonate. Filter numbers in bold represent samples where the $Na_{soil}/Na_{seasalt}$ is greater than 20%. All samples were collected on EMFAB filters.

Filter #	Date On	Time	Date Off	Time	Mass ($\mu\text{g m}^{-3}$)	Air volume (m^3)	Na^+ [K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	MSA
							nmoles m^{-3}]							
HVA221	27 Sep	05 1517	04 Oct	05 1308	26	3139	233	6.83	23.56	5.38	255	11.50	20.6	0.29
HVA223	11 Oct	05 1551	18 Oct	05 1047	21	3288	201	4.79	20.38	4.11	235	0.68	13.0	0.17
HVA225	25 Oct	05 1135	01 Nov	05 1135	31	169	363	13.53	6.67	3.66	351	1.47	19.7	4.64
HVA226	01 Nov	05 1230	08 Nov	05 1438	26	1648	239	5.84	21.41	4.27	281	0.01	15.8	0.36
HVA227	08 Nov	05 1601	15 Nov	05 1443	20	2137	189	4.45	17.51	3.62	215	1.49	13.3	0.03
HVA228	15 Nov	05 1555	22 Nov	05 1439	16	3081	148	3.53	14.27	3.19	169	0.77	11.1	0.02
HVA229	22 Nov	05 1459	29 Nov	05 1114	21	499	190	5.41	6.61	1.45	210	0.58	11.9	0.12
HVA232	06 Dec	05 1440	13 Dec	05 1436	25	1257	252	6.14	20.08	3.84	285	1.04	16.8	0.25
HVA237	03 Jan	06 1530	10 Jan	06 1250	19	1209	203	5.77	14.59	3.46	226	1.06	14.4	0.42
HVA238	10 Jan	06 1458	17 Jan	06 1315	19	3628	213	5.04	20.79	4.56	254	0.00	15.7	0.26
HVA240	24 Jan	06 1504	31 Jan	06 1355	10	1579	93	3.45	5.22	0.91	85	3.05	10.0	0.04
HVA241	31 Jan	06 1529	07 Feb	06 1046	11	3797	107	2.66	9.37	1.96	109	0.64	9.0	0.02
HVA242	07 Feb	06 1132	14 Feb	06 1414	15	4428	161	4.26	16.88	3.28	173	0.41	10.9	0.14
HVA243	14 Feb	06 1458	21 Feb	06 0940	9	3604	99	2.57	8.59	1.64	99	1.21	8.9	0.02
HVA244	21 Feb	06 1034	28 Feb	06 1437	9	4300	91	2.30	8.08	1.89	92	0.52	8.0	0.01
HVA246	28 Feb	06 1600	07 Mar	06 1310	13	2262	129	3.11	10.99	2.68	142	0.71	9.3	1.69
HVA247	07 Mar	06 1406	14 Mar	06 1152	16	4856	160	3.71	16.66	3.50	180	0.98	11.6	0.44
HVA248	14 Mar	06 1225	21 Mar	06 1322	10	4572	109	2.75	11.03	2.30	120	0.94	7.9	0.36
HVA249	21 Mar	06 1410	28 Mar	06 1115	20	271	169	7.79	2.49	2.01	140	1.06	9.0	10.38
HVA251	28 Mar	06 1239	04 Apr	06 1429	12	4526	116	2.94	11.63	2.23	132	0.86	8.0	0.25
HVA252	04 Apr	06 1551	11 Apr	06 1113	16	6837	167	3.78	17.08	3.84	188	0.20	10.2	0.30
HVA253	11 Apr	06 1157	18 Apr	06 1421	6	2923	105	2.86	8.98	2.11	114	0.36	6.6	0.40
HVA254	18 Apr	06 1512	26 Apr	06 1200	15	5119	163	3.87	16.55	3.32	184	0.16	9.9	0.02
HVA256	02 May	06 1509	09 May	06 1507	23	5205	242	5.58	25.32	5.23	280	0.21	14.6	0.26
HVA257	09 May	06 1550	16 May	06 0000	15	8215	152	3.60	16.24	3.39	166	1.94	12.1	0.15
HVA258	16 May	06 1456	23 May	06 1410	16	3894	179	4.25	18.08	3.75	203	0.27	11.0	0.15
HVA261	06 Jun	06 1317	13 Jun	06 1529	9	3487	98	2.63	8.70	1.75	106	0.32	5.8	0.14
HVA262	13 Jun	06 1635	20 Jun	06 1423	14	6427	143	3.58	15.02	3.10	162	0.78	9.2	0.14
HVA263	20 Jun	06 1523	27 Jun	06 1505	10	3440	113	2.95	10.40	2.06	126	0.25	6.7	0.09
HVA264	27 Jun	06 1531	04 Jul	06 1407	14	1454	136	3.66	9.69	2.30	144	0.31	7.7	0.00
HVA265	04 Jul	06 1501	11 Jul	06 1458	21	5267	228	5.54	25.30	5.24	255	0.84	14.5	0.00
HVA266	11 Jul	06 1551	18 Jul	06 1349	12	2540	135	3.60	12.04	2.38	146	0.32	7.7	0.07
HVA268	25 Jul	08 1408	01 Aug	06 1517	13	2907	138	3.67	12.68	2.49	152	0.74	8.2	0.06
HVA269	01 Aug	06 1517	08 Aug	06 1430	12	3244	129	3.61	11.65	2.53	141	1.55	9.1	0.02
HVA270	08 Aug	06 1602	15 Aug	06 1223	18	5487	190	4.28	18.48	4.08	210	0.88	11.3	0.03
HVA272	15 Aug	06 1507	22 Aug	06 1521	26	4003	281	6.64	29.48	6.02	315	0.42	16.9	0.00
HVA273	22 Aug	06 1614	29 Aug	06 1233	14	4851	147	3.67	14.96	2.96	162	0.85	8.8	0.02

Table 5. Baseline (BEVS2) gravimetric mass, air volume and ion concentrations of PM10 aerosol at Cape Grim collected using HVB. MSA is methanesulfonate. Filter numbers in bold represent samples where the $Na_{soil}/Na_{seasalt}$ is greater than 20%. All samples were collected on EMFAB filters.

Filter #	Date On	Time	Date Off	Time	Mass ($\mu\text{g m}^{-3}$)	Air volume (m^3)	Na^+ [K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	MSA
							nmoles m^{-3}]							
HVB94	01 Feb	05 1448	08 Feb	05 1425	9	2510	92	2.23	7.47	1.87	99	0.76	6.8	0.42
HVB95	08 Feb	05 1532	15 Feb	05 1500	9	3198	96	2.12	8.54	1.94	105	0.71	7.4	0.50
HVB96	15 Feb	05 1550	22 Feb	05 1314	22	1883	224	5.07	21.63	4.79	256	0.66	15.0	0.86
HVB97	22 Feb	05 1358	01 Mar	05 1349	8	1462	90	3.15	6.07	1.90	87	2.13	8.4	0.54
HVB98	01 Mar	05 1505	08 Mar	05 1111	18	6956	180	4.03	18.43	4.30	206	0.68	12.4	0.38
HVB99	08 Mar	05 1212	15 Mar	05 1401	9	4332	88	2.34	8.42	2.02	94	1.00	8.0	0.42
HVB100	15 Mar	05 1455	22 Mar	05 1046	11	406	136	5.85	5.09	1.95	114	1.90	7.0	0.14
HVB101	22 Mar	05 1135	24 Mar	05 1405	9	1596	93	2.72	6.70	2.05	94	1.38	6.7	0.33
HVB103	29 Mar	05 1513	05 Apr	05 1344	20	2068	195	4.74	19.85	4.40	222	0.84	12.6	0.24
HVB104	05 Apr	05 1424	12 Apr	05 1219	12	859	134	3.94	8.35	2.70	132	1.83	7.8	0.07
HVB105	12 Apr	05 1350	19 Apr	05 1151	18	1585	193	4.34	16.74	3.92	208	0.85	11.4	0.04
HVB106	19 Apr	05 1259	26 Apr	05 1334	19	3693	215	5.08	21.52	4.73	227	0.79	13.0	0.19
HVB107	26 Apr	05 1459	03 May	05 1213	28	3680	291	7.77	32.78	6.57	325	0.46	18.9	0.11
HVB108	03 May	05 1256	10 May	05 1221	18	5610	177	4.20	18.53	3.91	201	0.50	11.3	0.11
HVB109	10 May	05 1301	17 May	05 1056	18	4791	172	4.04	16.73	4.11	189	0.73	10.6	0.13
HVB110	17 May	05 1205	24 May	05 1414	25	73	397	21.72	7.06	4.68	215	2.65	12.8	0.79
HVB112	24 May	05 1549	31 May	05 1221	15	7194	161	3.71	16.24	3.54	173	0.19	9.4	0.04
HVB113	31 May	05 1325	07 Jun	05 1256	20	4619	110	2.57	10.09	1.95	115	0.47	6.5	0.06
HVB115	14 Jun	05 1503	21 Jun	05 1135	8	3189	95	2.51	7.37	1.65	99	0.21	5.4	0.01
HVB116	21 Jun	05 1303	28 Jun	05 1511	10	1371	117	3.34	6.62	1.49	117	1.32	7.4	0.02
HVB117	28 Jun	05 1559	05 Jul	05 1406	12	3737	133	3.47	12.76	2.63	141	1.46	9.1	0.05
HVB118	05 Jul	05 1452	12 Jul	05 1030	9	4090	101	2.40	9.00	1.88	106	0.46	6.1	0.02
HVB119	12 Jul	05 1114	19 Jul	05 1149	18	4470	191	4.40	19.34	4.39	208	0.35	11.4	0.02
HVB121	19 Jul	05 1303	26 Jul	05 1155	27	3765	282	6.41	28.95	6.29	308	1.37	17.6	0.03

Table 6. Baseline (BEVS3) gravimetric mass, air volume and ion concentrations of PM10 aerosol at Cape Grim collected using HVB. MSA is methanesulfonate. Filter numbers in bold represent samples where the $\text{Na}_{\text{soil}}/\text{Na}_{\text{seasalt}}$ is greater than 20%. All samples were collected on EMFAB filters.

Filter #	Date On	Time	Date Off	Time	Mass ($\mu\text{g m}^{-3}$)	Air volume (m^3)	Na^+ [K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	MSA]
nmoles m^{-3}														
HVB122	26 Jul	05 1247	09 Aug	05 1129	19	9554	147	3.42	17.14	4.29	165	0.22	9.7	0.02
HVB124	16 Aug	05 1249	23 Aug	05 1520	15	4572	141	3.62	13.93	3.15	153	0.31	8.5	0.01
HVB125	23 Aug	05 1559	30 Aug	05 1108	10	5186	104	2.76	10.22	2.28	113	0.71	6.8	0.08
HVB126	30 Aug	05 1153	06 Sep	05 1005	22	2634	232	5.87	20.95	4.59	252	0.46	13.3	0.01
HVB127	06 Sep	05 1220	13 Sep	05 1113	2	1817	82	2.89	3.79	1.00	83	0.15	4.4	0.03
HVB129	13 Sep	05 1229	20 Sep	05 1151	6	4464	26	1.14	1.40	0.51	24	2.25	2.1	0.01
HVB130	20 Sep	05 1228	27 Sep	05 1440	14	4955	132	3.16	13.13	2.93	145	1.11	8.8	0.10
HVB131	27 Sep	05 1517	04 Oct	05 1308	33	2919	303	6.61	30.97	6.75	342	0.34	17.8	0.04
HVB132	04 Oct	05 1517	11 Oct	05 1439	19	6260	166	3.60	17.27	3.78	189	0.20	9.6	0.03
HVB133	11 Oct	05 1551	18 Oct	05 1047	20	3512	149	3.85	17.51	3.78	170	0.33	10.1	0.04
HVB134	18 Oct	05 1155	25 Oct	05 1253	26	198	95	5.72	1.46	0.07	48	0.07	10.0	0.29
HVB135	25 Oct	05 1338	01 Nov	05 1135	30	1447	258	5.66	22.68	5.45	285	0.29	15.0	0.12
HVB136	01 Nov	05 1230	08 Nov	05 1438	23	1818	196	4.90	17.84	4.24	216	1.30	12.1	0.13
HVB138	08 Nov	05 1601	15 Nov	05 1443	24	5145	216	4.68	22.61	4.95	245	0.89	13.9	0.24
HVB139	15 Nov	05 1555	22 Nov	05 1435	15	5556	132	3.09	13.99	2.90	144	0.55	9.3	0.44
HVB140	22 Nov	05 1459	29 Nov	05 1114	22	3277	192	4.66	20.64	4.55	218	0.27	12.0	0.45
HVB142	06 Dec	05 1440	13 Dec	05 1436	27	2694	246	5.36	25.64	5.47	274	0.75	15.7	0.46
HVB143	13 Dec	05 1543	20 Dec	05 1315	27	5495	231	5.12	25.54	5.38	265	0.52	15.3	0.54
HVB144	20 Dec	05 1435	28 Dec	05 1111	37	4411	317	6.90	34.85	7.54	363	0.74	21.4	0.93
HVB145	28 Dec	05 1154	03 Jan	06 1414	19	4215	173	4.03	18.24	3.81	191	0.70	12.2	0.68
HVB146	03 Jan	06 1530	10 Jan	06 1250	18	1871	175	4.70	16.67	3.79	186	2.04	14.0	0.51
HVB147	10 Jan	06 1458	17 Jan	06 1315	21	5252	225	5.09	23.50	5.02	249	0.90	15.1	1.14
HVB148	17 Jan	06 1428	24 Jan	06 1407	12	3814	112	2.64	10.85	2.38	118	1.21	9.2	0.78
HVB149	24 Jan	06 1509	31 Jan	06 1355	11	3270	105	2.96	9.72	2.18	102	2.51	10.6	0.75
HVB151	31 Jan	06 1529	07 Feb	06 1046	12	7520	120	2.69	12.71	2.65	130	0.57	9.3	0.89
HVB152	07 Feb	06 1132	14 Feb	06 1414	15	7451	170	3.54	16.63	3.55	191	0.35	10.4	0.54
HVB153	14 Feb	06 1458	21 Feb	06 1059	11	6222	110	2.71	11.64	2.55	115	1.44	10.4	0.60
HVB154	21 Feb	06 1143	28 Feb	06 1437	11	5503	99	2.20	10.17	2.47	103	1.03	9.7	0.85
HVB155	28 Feb	06 1600	07 Mar	06 1310	15	2262	148	3.49	12.65	3.06	164	0.65	10.4	0.58
HVB156	07 Mar	06 1406	14 Mar	06 1152	23	4856	235	5.48	25.30	5.00	267	1.49	17.2	0.72
HVB157	14 Mar	06 1225	21 Mar	06 1322	13	4572	128	3.18	13.18	2.51	144	1.59	9.9	0.35
HVB158	21 Mar	06 1410	28 Mar	06 1115	29	271	323	12.67	15.05	3.71	311	5.79	19.2	0.81
HVB159	28 Mar	06 1239	04 Apr	06 1429	14	4940	140	3.45	14.97	3.01	162	0.72	10.0	0.37
HVB160	04 Apr	06 1551	11 Apr	06 1113	19	6958	199	4.77	22.01	3.99	232	0.27	12.9	0.24
HVB161	11 Apr	06 1157	18 Apr	06 1421	16	4016	162	4.01	16.21	3.08	187	0.39	10.6	0.22
HVB162	18 Apr	06 1512	26 Apr	06 1200	18	5334	124	2.93	13.19	3.40	143	0.17	9.0	0.10
HVB165	13 Jun	06 1635	20 Jun	06 1423	16	6339	134	3.56	16.29	3.14	157	0.81	10.1	0.09
HVB167	20 Jun	06 1523	27 Jun	06 1505	12	3411	120	3.04	12.06	2.22	139	0.36	7.4	0.08
HVB168	27 Jun	06 1540	04 Jul	06 1407	16	1437	175	4.51	15.13	2.61	194	0.51	10.0	0.04
HVB169	04 Jul	06 1501	11 Jul	06 1458	24	5082	256	5.78	27.66	5.47	299	0.99	17.3	0.04
HVB170	11 Jul	06 1551	18 Jul	06 1349	1	25240	15	0.36	1.43	0.29	17	0.04	0.9	0.00
HVB173	25 Jul	06 1408	01 Aug	06 1406	15	2836	162	4.09	16.10	3.22	185	0.85	10.0	0.02
HVB174	01 Aug	06 1517	08 Aug	06 1430	14	2956	143	3.97	13.26	2.81	157	1.76	9.9	0.07
HVB175	08 Aug	06 1602	15 Aug	06 1223	21	5401	213	4.92	22.59	4.58	242	1.03	13.5	0.08
HVB176	15 Aug	06 1507	22 Aug	06 1521	30	3873	291	7.02	31.99	6.15	341	0.47	18.5	0.04
HVB177	22 Aug	06 1614	29 Aug	06 1233	13	3619	144	3.59	14.63	2.76	164	1.15	9.0	0.07
HVB178	31 Aug	06 1558	05 Sep	06 1411	25	1622	256	6.54	24.23	4.70	290	0.84	14.9	0.06
HVB179	05 Sep	06 1508	12 Sep	06 1337	9	1462	95	2.94	5.74	1.42	99	0.72	5.1	0.05

Table 7. Baseline (BEVS3) gravimetric mass, air volume and ion concentrations of PM2.5 aerosol at Cape Grim collected using LV. MSA is methanesulfonate. Filter numbers in bold represent samples where the $\text{Na}_{\text{soil}}/\text{Na}_{\text{seasalt}}$ is greater than 20%. All samples were collected on Teflo filters.

Filter #	Date On	Time	Date Off	Time	Mass ($\mu\text{g m}^{-3}$)	Air volume (m^3)	Na^+ [K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	MSA]
nmoles m^{-3}														
LV153	04 Jan	05 1543	11 Jan	05 1307	6.9	26.2	70	1.45	7.08	1.52	78	0.49	5.89	0.75
LV154	11 Jan	05 1421	18 Jan	05 1035	8.4	32.1	71	1.97	7.38	1.88	78	0.41	5.77	0.64
LV155	18 Jan	05 1119	25 Jan	05 1124	3.3	43.3	35	0.72	3.57	0.69	37	0.42	4.47	0.54
LV156	25 Jan	05 1207	01 Feb	05 1357	3.5	22.8	33	0.77	3.32	0.91	33	0.92	7.16	0.68
LV158	01 Feb	05 1448	08 Feb	05 1425	3.3	26.5	29	0.58	2.90	0.58	31	0.46	3.21	0.35
LV159	08 Feb	05 1532	15 Feb	05 1500	2.7	27.1	25	0.50	2.58	0.52	27	0.34	2.61	0.27
LV160	15 Feb	05 1550	22 Feb	05 1314	6.2	19.7	60	2.32	5.96	1.18	62	0.93	6.42	0.44
LV161	22 Feb	05 1358	01 Mar	05 1349	3.2	14.6	22	0.63	2.08	0.56	20	0.88	6.96	0.49
LV163	01 Mar	05 1505	15 Mar	05 1401	4.6	69.5	48	1.01	5.37	1.04	54	0.53	4.00	0.32
LV164	15 Mar	05 1455	22 Mar	05 1046	7.6	5.7	29	0.94	3.39	1.63	35	1.40	3.94	0.25
LV165	22 Mar	05 1135	24 Mar	05 1400	3.0	23.6	23	0.52	2.24	0.52	23	0.66	4.05	0.33
LV167	29 Mar	05 1513	05 Apr	05 1344	9.8	18.9	60	1.13	5.94	1.44	72	0.55	3.21	0.18
LV168	05 Apr	05 1424	12 Apr	05 1219	7.4	12.4	92	1.87	9.77	2.48	98	2.47	8.79	0.39
LV169	12 Apr	05 1350	19 Apr	05 1151	4.9	15.7	56	1.31	5.63	1.37	60	1.10	4.06	0.12

Table 7. continued....

LV170	19 Apr 05	1259	26 Apr 05	1334	5.8	31.1	57	1.30	6.22	1.32	63	0.94	4.38	0.22
LV172	26 Apr 05	1459	03 May 05	1213	4.3	3.8	35	0.82	3.15	1.07	37	0.85	2.39	0.28
LV173	03 May 05	1256	10 May 05	1221	4.2	41.2	45	0.95	5.10	1.08	51	0.38	2.80	0.08
LV174	10 May 05	1301	17 May 05	1056	4.4	35.5	46	0.93	5.09	1.02	51	0.54	3.26	0.12
LV175	17 May 05	1205	23 May 05	1414	17.3	1.0	50	2.67	4.65	6.74	60	4.07	4.76	1.05
LV177	24 May 05	1549	31 May 05	1221	4.4	52.5	46	0.98	5.11	1.10	52	0.21	2.67	0.03
LV178	31 May 05	1325	07 Jun 05	1256	3.0	33.7	32	0.66	3.53	0.79	36	0.48	2.13	0.06
LV180	14 Jun 05	1503	21 Jun 05	1135	2.1	22.0	21	0.51	2.34	0.60	23	0.29	1.08	0.05
LV182	21 Jun 05	1303	28 Jun 05	1511	3.9	7.1	26	0.59	2.68	1.06	27	0.93	1.69	0.15
LV183	28 Jun 05	1559	05 Jul 05	1406	4.1	22.9	37	0.80	6.20	2.24	40	0.79	4.18	0.05
LV184	05 Jul 05	1452	12 Jul 05	1030	2.4	29.5	24	0.46	2.66	0.65	27	0.42	1.72	0.04
LV185	12 Jul 05	1114	19 Jul 05	1149	6.0	32.5	59	3.22	6.41	1.25	67	0.41	3.86	0.03
LV187	19 Jul 05	1303	26 Jul 05	1155	9.3	19.4	97	1.98	10.84	2.10	112	0.75	5.60	0.06
LV188	26 Jul 05	1247	02 Aug 05	1202	6.5	36.5	68	1.43	7.65	1.64	79	0.33	3.90	0.03
LV189	02 Aug 05	1250	09 Aug 05	1129	5.6	33.6	57	1.18	6.45	1.50	66	0.42	3.24	0.03
LV190	09 Aug 05	1216	16 Aug 05	1127	3.9	51.0	42	0.85	4.67	0.90	47	0.51	2.96	0.03
LV192	16 Aug 05	1249	23 Aug 05	1520	5.1	34.0	52	1.07	5.82	1.19	60	0.40	2.95	0.03
LV193	23 Aug 05	1559	30 Aug 05	0000	3.6	37.3	35	0.75	3.94	0.86	38	0.70	2.54	0.09
LV194	30 Aug 05	1153	06 Sep 05	1005	8.2	19.3	65	1.32	7.20	1.83	73	0.64	3.55	0.06
LV195	06 Sep 05	1220	13 Sep 05	1113	2.7	13.6	25	0.68	2.34	1.22	26	0.30	1.05	0.08
LV197	13 Sep 05	1229	20 Sep 05	1151	3.6	32.3	42	1.31	4.66	0.78	48	0.37	2.72	0.03
LV198	20 Sep 05	1228	27 Sep 05	1440	3.6	36.2	40	1.13	4.39	0.84	43	0.78	3.85	0.10
LV199	27 Sep 05	1517	04 Oct 05	1308	9.8	21.6	95	2.32	10.80	3.32	108	0.71	6.06	0.05
LV200	04 Oct 05	1517	11 Oct 05	1439	8.7	27.0	84	1.97	9.59	3.93	97	0.58	5.46	0.04
LV202	11 Oct 05	1551	18 Oct 05	1047	9.5	15.0	87	2.10	10.33	2.51	100	0.88	5.94	0.07
LV203	18 Oct 05	1155	25 Oct 05	1253	0.3	1.5	36	3.25	2.68	4.14	25	2.22	8.86	0.72
LV204	25 Oct 05	1338	01 Nov 05	1135	7.3	10.7	85	2.00	10.01	1.92	95	0.45	5.46	0.14
LV205	01 Nov 05	1230	08 Nov 05	1438	4.8	13.3	56	1.39	6.35	1.47	61	1.14	4.37	0.12
LV207	08 Nov 05	1601	15 Nov 05	1443	5.1	37.7	56	1.30	6.86	1.24	62	0.69	4.56	0.20
LV208	15 Nov 05	1555	22 Nov 05	1459	3.0	41.1	33	0.84	4.03	0.74	35	0.43	3.60	0.40
LV209	22 Nov 05	1459	29 Nov 05	1114	3.7	24.2	46	1.11	5.62	0.95	51	0.22	3.49	0.29
LV212	06 Dec 05	1703	13 Dec 05	1436	6.1	19.8	68	1.57	5.62	0.91	76	0.60	5.75	0.37
LV213	13 Dec 05	1543	20 Dec 05	1314	6.2	40.8	66	1.46	6.51	1.10	74	0.46	5.55	0.41
LV214	20 Dec 05	1435	28 Dec 05	1111	9.2	32.3	95	2.14	9.50	2.24	107	0.68	8.69	0.80
LV215	28 Dec 05	1154	03 Jan 06	1414	0.0	18.7	79	1.92	6.95	1.28	88	0.84	8.20	0.89
LV217	03 Jan 06	1530	10 Jan 06	1250	8.0	13.6	43	1.09	3.07	0.68	46	1.06	6.52	0.38
LV218	10 Jan 06	1458	17 Jan 06	1315	8.5	23.4	92	2.07	9.01	0.78	99	0.96	10.25	1.45
LV219	17 Jan 06	1428	24 Jan 06	1407	3.5	28.1	30	0.64	2.40	0.60	32	0.55	5.46	0.63
LV220	24 Jan 06	1509	31 Jan 06	1355	2.9	24.2	26	0.66	2.02	0.40	24	1.01	6.50	0.63
LV222	31 Jan 06	1529	07 Feb 06	1046	3.2	55.0	34	0.76	3.28	0.60	35	0.44	4.77	0.71
LV223	07 Feb 06	1132	14 Feb 06	1414	3.5	54.4	39	0.87	3.85	0.87	43	0.34	3.84	0.45
LV224	14 Feb 06	1458	21 Feb 06	1301	3.1	46.4	29	0.62	2.69	0.45	28	0.57	6.42	0.51
LV225	21 Feb 06	1344	28 Feb 06	1437	3.0	39.4	24	0.56	2.13	0.49	23	0.81	5.44	0.64
LV227	28 Feb 06	0000	07 Mar 06	0000	3.7	16.5	41	0.82	3.67	0.67	45	0.54	3.99	0.40
LV228	07 Mar 06	1406	14 Mar 06	1152	5.4	35.4	60	1.20	6.32	1.01	64	0.80	5.99	0.50
LV229	14 Mar 06	0000	21 Mar 06	0000	3.0	33.4	30	0.60	2.93	0.44	32	0.72	3.62	0.24
LV232	28 Mar 06	1239	04 Apr 06	1429	3.2	36.1	34	0.67	3.46	0.53	37	0.35	3.03	0.23
LV233	04 Apr 06	1551	11 Apr 06	1113	4.3	51.0	48	0.96	5.13	0.90	54	0.16	3.16	0.13
LV234	11 Apr 06	1157	18 Apr 06	1421	3.7	29.5	39	0.80	3.93	0.57	44	0.22	2.61	0.11
LV235	18 Apr 06	1512	26 Apr 06	1200	3.8	39.0	45	0.92	4.73	0.71	50	0.17	2.80	0.08
LV238	02 May 06	1509	09 May 06	1507	9.9	22.3	119	2.35	12.71	0.00	134	0.28	7.07	0.11
LV239	09 May 06	1550	16 May 06	1456	7.1	34.1	72	1.60	7.87	1.38	74	1.42	9.08	0.14
LV240	16 May 06	1540	23 May 06	1410	2.9	18.1	31	0.65	2.84	0.46	36	0.35	1.85	0.05
LV242	25 May 06	1027	30 May 06	1436	0.9	6.5	21	0.40	1.03	0.42	20	0.94	2.78	0.07
LV244	06 Jun 06	1317	13 Jun 06	1529	2.1	25.1	24	0.46	2.12	0.38	27	0.17	1.48	0.03
LV245	13 Jun 06	1635	20 Jun 06	1423	3.9	46.5	44	0.88	4.65	0.78	48	0.41	3.17	0.06
LV247	20 Jun 06	1523	27 Jun 06	1505	2.4	25.1	28	0.57	2.54	0.42	32	0.23	1.70	0.03
LV248	27 Jun 06	1540	04 Jul 06	1407	4.1	10.4	36	0.77	2.65	0.40	41	0.29	1.74	0.10
LV249	04 Jul 06	1501	11 Jul 06	1458	5.7	37.3	65	1.35	6.92	1.24	73	0.54	4.66	0.03
LV250	11 Jul 06	1551	18 Jul 06	1349	4.0	18.5	46	1.04	4.31	0.73	52	0.31	2.63	0.02
LV253	25 Jul 06	1408	01 Aug 06	1406	3.3	20.9	39	0.81	3.68	0.52	43	0.47	2.45	0.03
LV254	01 Aug 06	1517	08 Aug 06	1430	3.5	21.3	36	0.89	3.49	0.59	39	0.80	3.68	0.04
LV255	08 Aug 06	1602	15 Aug 06	1223	5.7	39.3	62	1.23	6.62	1.08	69	0.63	4.13	0.05
LV257	15 Aug 06	1507	22 Aug 06	1521	7.9	28.6	88	1.76	9.35	1.61	98	0.35	5.06	0.02
LV258	22 Aug 06	1614	29 Aug 06	1233	3.2	26.5	34	0.69	3.51	0.49	38	0.51	2.15	0.03
LV259	31 Aug 06	1330	05 Sep 06	1411	5.1	12.0	59	1.31	5.64	0.83	67	0.52	3.29	0.04
LV260	05 Sep 06	1508	12 Sep 06	1337	2.1	10.6	21	0.57	1.47	0.17	24	0.35	1.32	0.10

4.20. PRECIPITATION CHEMISTRY

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Tables 1 and 2 show the results of the chemical analysis of rainwater collected at Cape Grim under baseline conditions. Samples are collected in an ERNI wet only sampler as described by Ayers and Ivey [1990]. The sampler opens after activation from the baseline event switch (BEVS1) when the wind direction is between 190° and 280° and the condensation nucleus (CN) concentration is < 600 cm⁻³.

Samples were collected on a weekly basis. As suggested by Gillett and Ayers [1991], and further quantified by Ayers *et al.*, [1998], thymol was added to the collection bottle before sampling, to inhibit biological degradation of ions such as organic acids and ammonia.

After collection samples were sent to CSIRO Atmospheric Research where the chemical analysis was carried out. Anion and cation concentrations were measured by suppressed ion chromatography (IC) using a Dionex DX500 gradient ion chromatograph. Anions were determined using a Dionex AS11 column, a Dionex ASRS ultra suppressor and a

gradient eluent of sodium hydroxide. Cations were determined using a Dionex CS12 column and a Dionex CSRS ultra suppressor with a 20 millimolar methanesulfonic acid eluent. Conductivity was measured in a flow system using a Waters auto-sampler to inject samples into a Milli-Q water stream; detection was done using a Dionex conductivity detector. pH measurements were carried out using an Orion Ross pH electrode calibrated with Orion low ionic strength buffers.

The data set presented in Tables 1 and 2 is raw data and has not been subjected to more than preliminary quality checks. The cation anion balance is a useful quality control check since the total number of cation equivalents should equal the total number of anion equivalents because electroneutrality is assumed.

References

- Ayers G. P., and J. P. Ivey, Methanesulfonate in rainwater at Cape Grim, Tasmania, *Tellus*, 428, 217-222, 1990.
Gillett, R. W., and G. P. Ayers, The use of thymol as a bactericide in rain water samples, *Atmos. Environ.*, 25a, 2677-2681, 1991.
Ayers G. P., N. Fukuzaki, R. W. Gillett, P. W. Selleck, J.C. Powell and H. Hara, Thymol as a biocide in Japanese rainwater, *J. Atmos. Chem.*, 30, 301-310, 1998.

Table 1. Baseline rainfall (mm) and anion concentrations ($\mu\text{mol l}^{-1}$) in precipitation collected at Cape Grim.

Sample	Date	Time	Date	Time	rain	Cl ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	C ₂ O ₄ ²⁻	CH ₃ COO ⁻	HCOO ⁻	CH ₃ SO ₃ ⁻	Total Anions	
	On		Off		mm	$\mu\text{mol l}^{-1}$									$\mu\text{eq l}^{-1}$
755	11/01/05	09:50	08/02/05	13:45	4.1	4427	6.3	18.9	252	0.4	0.1	2.8	0.8	4960	
756	08/02/05	13:45	08/03/05	13:15	9.0	2662	3.8	4.8	149	0.1	0.1	1.9	0.7	2972	
757	08/03/05	13:15	05/04/05	11:32	2.0	1955	2.8	5.2	119	0.2	0.6	5.4	0.6	2209	
758	05/04/05	11:32	12/04/05	10:02	1.0	10804	16.1	1.8	531	0.7	0.0	0.0	<0.1	11885	
759	12/04/05	10:02	26/04/05	12:25	1.0	1837	3.3	6.9	102	4.5	1.9	8.2	0.5	2072	
760	26/04/05	12:25	03/05/05	11:45	2.0	4699	6.5	4.3	252	4.2	0.9	9.3	<0.1	5233	
761	03/05/05	11:45	10/05/05	10:11	2.2	1740	2.8	2.4	92	2.4	1.3	5.5	0.1	1942	
762	10/05/05	10:11	17/05/05	10:05	0.8	3484	4.6	1.9	177	2.2	8.3	21.2	0.2	3880	
763	17/05/05	10:05	24/05/05	10:15	1.4	7576	12.3	14.5	410	1.6	0.0	7.9	<0.1	8433	
764	24/05/05	10:15	31/05/05	10:50	4.8	8030	10.5	0.9	417	2.6	0.0	4.9	<0.1	8885	
765	31/05/05	10:25	21/06/05	11:25	4.3	1265	1.4	1.4	68	2.2	0.9	6.4	0.1	1415	
766	21/06/05	11:25	12/07/05	12:00	2.4	1401	2.2	3.1	77	5.0	9.0	33.7	0.1	1614	
767	12/07/05	12:00	18/07/05	12:00	5.5	2769	3.2	5.7	151	2.5	0.2	0.7	<0.1	3087	
768	18/07/05	12:00	26/07/05	12:00	5.3	7287	9.3	0.8	375	4.2	0.0	2.0	<0.1	8058	
769	26/07/05	12:00	02/08/05	12:00	6.0	2015	2.6	0.3	103	1.4	0.2	0.7	0.0	2227	
770	02/08/05	12:00	09/08/05	12:00	10.4	2657	3.8	0.7	142	1.3	0.1	2.3	0.0	2951	
771	09/08/05	12:00	16/08/05	12:00	11.2	1488	1.7	0.6	77	0.6	0.3	1.5	<0.1	1648	
772	16/08/05	12:00	23/08/05	12:00	6.8	2752	3.6	0.3	137	0.9	0.0	2.2	<0.1	3033	
773	23/08/05	12:00	06/09/05	12:00	3.4	6254	9.1	2.2	325	2.3	0.0	4.8	<0.1	6926	
774	06/09/05	12:00	20/09/05	12:00	9.5	1414	1.7	0.7	78	1.4	0.1	1.4	<0.1	1576	
775	20/09/05	12:00	11/10/05	12:00	12.9	1615	2.0	0.6	88	1.0	0.0	0.6	<0.1	1797	
776	11/10/05	12:00	18/10/05	12:00	1.2	2021	4.7	1.7	102	1.7	4.6	10.9	0.1	2251	
777	18/10/05	12:00	15/11/05	12:00	4.7	2593	3.3	6.1	139	3.1	2.7	7.1	0.2	2896	
778	15/11/05	12:00	20/12/05	12:00	5.1	4263	5.5	1.1	227	3.6	1.0	1.1	0.2	4732	
779	20/12/05	12:00	04/01/06	12:00	4.9	1691	1.8	1.0	93	0.1	0.0	0.4	0.3	1880	
780	21/02/06	12:00	28/02/06	12:00	40	10764	17.8	17.4	634	2.5	0.0	0.0	1.0	12073	
781	28/02/06	12:00	04/04/06	12:00	800	1161	2.0	0.3	64	0.2	0.0	0.4	0.2	1292	
782	04/04/06	12:00	11/04/06	12:00	765	2318	3.7	0.5	137	0.7	0.9	1.3	0.2	2600	
783	11/04/06	12:00	18/04/06	12:00	470	532	0.9	0.8	28	0.6	0.9	2.1	0.2	595	
784	18/04/06	12:00	26/04/06	12:00	572	2094	0.5	3.4	110	0.5	0.9	1.6	0.4	2321	
785	26/04/06	12:00	09/05/06	12:00	725	3507	5.0	3.0	178	0.9	1.8	4.9	0.4	3881	
786	09/05/06	12:00	16/05/06	12:00	370	2131	3.3	0.9	112	1.0	1.6	3.2	0.6	2367	
787	16/05/06	12:00	30/05/06	12:00	88	2325	4.9	2.6	129	2.9	5.0	10.8	1.7	2614	
788	30/05/06	12:00	22/06/06	12:00	400	1590	1.7	1.1	88	1.9	2.5	4.9	0.1	1781	
789	22/06/06	12:00	27/06/06	12:00	258	635	1.5	0.8	34	1.1	0.9	3.1	0.3	711	
790	27/06/06	12:00	11/07/06	12:00	800	1324	2.3	1.2	70	1.0	1.3	2.0	0.4	1473	

Table 1. continued....

Sample	Date	Time	Date	Time	rain	Cl ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	C ₂ O ₄ ²⁻	CH ₃ COO ⁻	HCOO ⁻	CH ₃ SO ₃ ⁻	Total Anions
	On		Off		mm	[μmol l ⁻¹]								μeq l ⁻¹
791	11/07/06	12:00	18/07/06	12:00	80	12441	0.1	18.8	610	0.1	0.1	0.1	0.1	13680
792	18/07/06	12:00	01/08/06	12:00	438	1376	2.3	0.8	75	1.1	0.9	2.5	0.1	1535
793	01/08/06	12:00	08/08/06	12:00	90	1358	2.6	2.8	70	1.4	3.6	10.5	0.2	1521
794	08/08/06	12:00	15/08/06	12:00	122	1987	2.3	3.2	107	1.6	3.1	8.0	0.7	2222
795	15/08/06	12:00	22/08/06	12:00	374	1506	1.2	2.4	80	1.4	2.1	5.2	0.2	1679
796	22/08/06	12:00	29/08/06	12:00	70	3822	2.0	6.5	202	1.8	1.9	6.7	0.0	4247
797	29/08/06	12:00	05/09/06	12:00	90	4596	7.1	7.6	244	1.4	1.4	11.2	0.3	5115
798	05/09/06	12:00	19/09/06	12:00	60	3831	6.9	3.4	254	5.6	3.7	15.4	0.0	4379
799	19/09/06	12:00	26/09/06	12:00	255	4026	6.8	0.6	218	1.7	1.0	4.4	0.0	4477
800	26/09/06	12:00	03/10/06	12:00	200	2277	4.8	0.2	136	2.4	1.7	3.3	0.5	2565
801	03/10/06	12:00	31/10/06	12:00	215	5752	8.1	11.1	329	4.2	0.4	3.0	0.0	6441
802	31/10/06	12:00	27/12/06	12:00	145	10177	14.5	11.7	616	1.7	0.0	0.0	0.0	11437
803	27/12/06	12:00	09/01/07	12:00	305	1031	0.8	11.0	65	2.7	4.6	9.9	0.8	1192

Table 2. Baseline cation concentrations, pH and conductivity in precipitation collected at Cape Grim.

Sample	Date	Time	Date	Time	pH	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Total Cations	Conductivity Meas.	Conductivity Calc.
	On		Off			[μmol l ⁻¹]						μeq l ⁻¹	[μs cm ⁻¹]	
755	11/01/05	09:50	08/02/05	13:45	6.52	0.3	4033	7.0	82	406	125	5184	646	646
756	08/02/05	13:45	08/03/05	13:15	6.54	0.3	2498	2.9	46	213	66	3105	386	387
757	08/03/05	13:15	05/04/05	11:32	6.72	0.2	1842	0.4	41	134	52	2257	281	285
758	05/04/05	11:32	12/04/05	10:02	5.49	3.2	8324	0.0	140	937	254	10850	1419	1467
759	12/04/05	10:02	26/04/05	12:25	6.27	0.5	1726	2.5	41	131	48	2129	256	268
760	26/04/05	12:25	03/05/05	11:45	6.45	0.4	4126	0.9	76	341	112	5110	658	662
761	03/05/05	11:45	10/05/05	10:11	6.22	0.6	1560	3.4	39	145	44	1982	241	251
762	10/05/05	10:11	17/05/05	10:05	6.03	0.9	2956	2.8	62	319	87	3834	485	494
763	17/05/05	10:05	24/05/05	10:15	5.48	3.3	6144	5.0	122	676	174	7976	1053	1056
764	24/05/05	10:15	31/05/05	10:50	6.86	0.1	6753	0.0	103	577	186	8384	1090	1109
765	31/05/05	10:25	02/06/05	11:25	6.42	0.4	1202	0.1	27	89	29	1465	187	183
766	21/06/05	11:25	12/07/05	12:00	6.07	0.9	1320	0.4	30	107	41	1649	210	207
767	12/07/05	12:00	18/07/05	12:00	6.52	0.3	2548	0.4	50	187	63	3098	393	395
768	18/07/05	12:00	26/07/05	12:00	6.40	0.4	6022	0.0	110	622	172	7721	990	1013
769	26/07/05	12:00	02/08/05	12:00	6.46	0.3	1800	0.0	40	164	42	2253	287	286
770	02/08/05	12:00	09/08/05	12:00	6.48	0.3	2285	0.0	46	246	76	2975	375	379
771	09/08/05	12:00	16/08/05	12:00	6.39	0.4	1353	0.5	32	117	34	1687	214	213
772	16/08/05	12:00	23/08/05	12:00	6.22	0.6	2354	0.2	50	248	71	3043	385	389
773	23/08/05	12:00	06/09/05	12:00	6.51	0.3	5147	0.0	91	563	165	6695	858	874
774	06/09/05	12:00	20/09/05	12:00	6.48	0.3	1299	0.6	32	110	31	1614	206	204
775	20/09/05	12:00	11/10/05	12:00	6.61	0.2	1440	0.1	33	138	42	1834	234	232
776	11/10/05	12:00	18/10/05	12:00	6.03	0.9	1703	1.4	41	204	63	2280	290	290
777	18/10/05	12:00	15/11/05	12:00	6.59	0.3	2301	2.3	52	213	68	2918	369	372
778	15/11/05	12:00	20/12/05	12:00	6.74	0.2	3721	0.0	62	326	122	4680	593	602
779	20/12/05	12:00	04/01/06	12:00	6.83	0.1	1619	0.0	30	96	37	1917	247	242
780	21/02/06	12:00	28/02/06	12:00	7.21	0.1	8544	2.1	149	901	321	11139	1479	1497
781	28/02/06	12:00	04/04/06	12:00	6.76	0.2	1074	0.3	25	69	25	1287	161	165
782	04/04/06	12:00	11/04/06	12:00	6.37	0.4	2022	0.6	40	183	56	2541	313	330
783	11/04/06	12:00	18/04/06	12:00	6.26	0.6	461	1.0	11	46	17	598	75	76
784	18/04/06	12:00	26/04/06	12:00	6.05	0.9	1844	1.6	40	187	49	2359	291	299
785	26/04/06	12:00	09/05/06	12:00	6.36	0.4	2994	0.6	56	303	82	3820	471	493
786	09/05/06	12:00	16/05/06	12:00	6.37	0.4	1814	0.2	41	186	51	2330	295	301
787	16/05/06	12:00	30/05/06	12:00	6.42	0.4	2022	1.0	44	202	64	2598	326	333
788	30/05/06	12:00	22/06/06	12:00	6.31	0.5	1315	2.5	29	156	45	1749	224	226
789	22/06/06	12:00	27/06/06	12:00	6.24	0.6	598.6	0.7	13	38	10	710	94	91
790	27/06/06	12:00	11/07/06	12:00	6.16	0.7	1110	1.2	22	120	35	1444	185	187
791	11/07/06	12:00	18/07/06	12:00	6.58	0.3	10179	1.5	158	1101	289	13118	1632	1721
792	18/07/06	12:00	01/08/06	12:00	6.11	0.8	1204	0.8	27	113	27	1512	192	195
793	01/08/06	12:00	08/08/06	12:00	6.08	0.8	1195	3.7	30	130	37	1563	195	197
794	08/08/06	12:00	15/08/06	12:00	6.34	0.5	1719	2.8	35	188	59	2252	285	286
795	15/08/06	12:00	22/08/06	12:00	6.18	0.7	1346	2.6	30	128	32	1699	215	216
796	22/08/06	12:00	29/08/06	12:00	6.32	0.5	3284	3.3	64	399	112	4375	522	550
797	29/08/06	12:00	05/09/06	12:00	6.52	0.3	4099	3.2	78	431	116	5275	631	662
798	05/09/06	12:00	19/09/06	12:00	5.97	1.1	3157	3.4	58	452	122	4369	518	561
799	19/09/06	12:00	26/09/06	12:00	6.27	0.5	3592	2.3	65	355	98	4566	534	577
800	26/09/06	12:00	03/10/06	12:00	6.34	0.5	1996	2.2	34	233	65	2627	310	331
801	03/10/06	12:00	31/10/06	12:00	6.57	0.3	5277	2.0	94	455	153	6590	751	831
802	31/10/06	12:00	27/12/06	12:00	6.65	0.2	9074	27.8	185	899	286	11657	1304	1476
803	27/12/06	12:00	09/01/07	12:00	6.93	0.1	985	6.0	28	78	24	1222	150	154

4.21. SPECTRAL SOLAR RADIATION

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Reported here are the data from the Spectral Radiation program, which includes measurements of spectral irradiance and turbidity.

Optical depth

Optical depth is measured with two sunphotometers, have been plagued by a number of problems related to instrument and solar tracker degradation. On 17 March 2005 the SPO2 (#1029: with measurements at 368, 412, 500 and 812nm) was removed for service and replaced with (#1021: 412, 500, 610 and 778nm). Problems related to work on the tracker resulted in the instrument returning to service on 29 April 2005. On 3 June 2005 it was noticed that the filter wheel on the SPO1A was not functioning properly and was adjusted. On 2 November 2005 the SPO1A failed to start, and needed replacing, which occurred on 21 August 2006. Unfortunately, signal problems continued that were not resolved until 22 December 2006 which affected both sunphotometers. This is reflected in the low data retrieval success shown in Table 1.

To minimise the risk of future data loss a second SPO2 is being configured to the same wavelengths as #1029, and a redesign of the filter-wheel configuration for SPO1A is hoped to be completed in 2007.

Table 1. The number of days per year when data was collected from SRAD and the two sun photometers. The SPO sun photometers were purchased from Carter Scott Design (also Known as Middleton Solar). The data shown covers the years since the radiation equipment was shifted to the radiation enclosure.

Year	SRAD	Aureole SPO1A sunphotometer	SPO2 sunphotometer
1997	246	29	
1998	197	272	
1999	350	334	
2000	355	351	
2001	128	294	143
2002	310	285	323
2003	350	357	365
2004	265	365	365
2005	365	258	311
2006	355	10	239

Spectral irradiance

This section reports on measurements from two instruments; a spectral radiometer (SRAD) (Optronics Laboratories OL-752), and a broad band UV-B detector (Solar Light model 501 UV-Biometer). Included in this section are changes of note that occurred during the two years.

For most of 2005 and 2006 SRAD worked reliably, with data loss primarily due to rodent attack on the optical fibre, which led to intermittent communication problems in May – July 2006.

The tracker on which SRAD is mounted had major problems due to wear in both the elevation and azimuth drive. Despite 6 attempts to service the drive mechanism, the performance of the tracker deteriorated significantly. Following a service in February 2005 20% of the tracker zeros were unacceptable. This increased rapidly to over 60% by June 2005. Two services (September and December 2005) returned the error rate to around 30%, but subsequent attempts (May and July 2006) failed to significantly improve the situation, with error rates remaining above 60%.

A sunphotometer is used as the calibration source for SRAD (normally an SPO1A using the channel at 342 nm). With the failure of the SPO1A mentioned above, the SPO2 needed to be used as the calibration reference, with a concomitant change in wavelength. This took some time to be implemented in the operation of SRAD. This, when combined with the progressive failure of the tracker, result in no calibrated data being available beyond 2005.

The Biometer operated through until 26 May 2006, when a signal cable broke disconnecting the instrument from the central computer system. With the problems associated with SRAD, and the fact that the sensor temperature measurement continued to function, this problem was not detected by the normal data checks.

As an example of the data produced, Figure 1 shows the maximum global UV-B irradiance observed for each day of measurement for the time period 2000 – 2005.

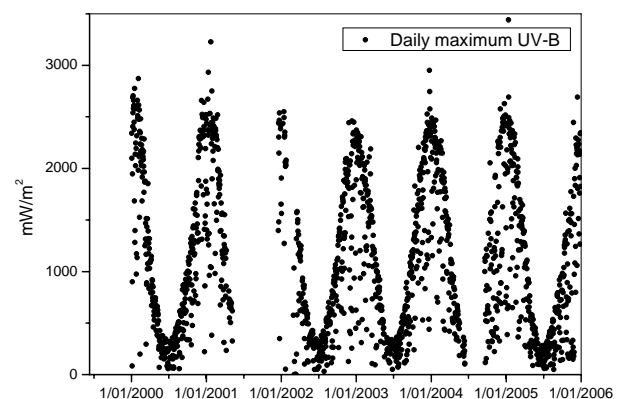


Figure 1. Maximum daily UV-B irradiance observed at Cape Grim for the period 2000 – 2005.

4.22. PASSIVE SOLAR RADIATION

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The Passive Solar Radiation monitoring program continued throughout 2005-2006. The Australian Regional Instrument Centre the Bureau of Meteorology is responsible for the maintenance and calibration of the instruments and data processing of all irradiance quantities apart from UV.

Continuous measurements of global, direct, diffuse, and terrestrial measurements continued in 2005-2006.

As reported in *Baseline 2003-2004*, a different algorithm was implemented in October 2003 to collect sunshine data. Dyson [2003] showed that the 95% uncertainty in daily sunshine was less than 1 minute/day using 1 Hz monitoring for sunshine, which was introduced at Cape Grim on 29 October 2003. All sunshine data for the period reported here has been derived via this method.

Two site visits occurred in 2005-2006. The initial visit 15-18 April 2005 identified a number of issues mainly with instrument corrosion, and resulted in the pyrhelimeter Kipp and Zonen CH1-940041 being replaced with a Middleton DN5-5022. CM11-996846 being used for diffuse measurements was removed on 27 January 2006 and replaced with CM11-924013. The next site visit occurred on 15-18 August 2006 and resulted in the replacement of almost all the sensors and tracking systems. The pyranometers CM11-924648 and CM11-924013 were replaced with CM11-058746 and CM11-058750 and the pyrhelimeter DN5-5022 was replaced with CH1-050307.

It is also apparent that corrosion and earthing of equipment remains a significant issue for solar and terrestrial instruments at Cape Grim, particularly with the DataTaker 500 data logger. The gap in the diffuse irradiance data from May 2005 to February 2006 is due to earthing issues that only impacted on the diffuse channel of the data logger. To reduce the likelihood of these issues influencing future measurements it may require a replacement cycle of 2 years at the site which

will increase the cost of solar maintaining measurements. The data logger type will be changed in 2007-2008.

Salt deposition on the optical surfaces is a significant issue. Given the staffing hours at the station it is possible that a significant amount of data is flagged as bad because of dirty optical surfaces, with sun pointing instruments the most affected. Systems are being investigated to reduce the problem but given the corrosive environment any system with electrically driven moving parts may prove difficult.

Routine data processing is automated, but assured daily exposure and irradiance data include edits to exclude those days when instrument failures, data acquisition errors or maintenance events were evident from system logs examination or additional quality control information. Daily exposure data are excluded from the monthly averages when quality control and assurance tests reject more than 2 minutes in a day. Tables 1 and 2 provide monthly statistics of the processed quantities.

Table 1. Monthly mean daily terrestrial (long wave) irradiance for 2005-2006. The sample estimate of the standard deviation and number of days included in the average is given in brackets for each month.

Month	Terrestrial Irradiance (W m ⁻²) 2005			Terrestrial Irradiance (W m ⁻²) 2006		
	s.d	days		s.d	days	
Jan	343.30	22.41	30	348.80	23.23	30
Feb	350.99	18.02	25	351.18	19.52	27
Mar	340.08	20.45	26	342.79	20.95	31
Apr	346.24	18.09	26	335.04	15.32	29
May	334.36	18.16	29	323.21	25.69	29
Jun	327.47	24.74	29	318.80	17.98	30
Jul	324.36	20.66	31	321.40	21.71	30
Aug	329.74	17.49	30	324.02	20.44	21
Sept	319.82	23.19	30	319.46	21.57	29
Oct	328.94	22.67	29	317.23	16.77	31
Nov	331.59	26.20	27	327.46	25.47	29
Dec	345.75	17.31	29	325.71	22.58	30

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Dyson, P., Investigation of the Uncertainty of Sunshine Duration in the Solar and Terrestrial Radiation Network, *Instrument Test Report 674*, Bureau of Meteorology, Melbourne, Australia, 2003.

Table 2. Monthly mean daily solar exposure and sunshine hours for 2005-2006.

	Exposure									Sunshine		
	Direct (MJ m ⁻²)	s.d.	# days/ month	Global (MJ m ⁻²)	s.d.	# days/ month	Diffuse (MJ m ⁻²)	s.d.	# days/ month	# hr per day	s.d.	# days/ month
Jan 05	19.86	11.10	30	25.15	6.53	30	10.43	3.21	30	8.14	3.72	30
Feb 05	13.69	10.47	25	19.32	6.39	26	9.43	2.72	26	5.71	3.94	25
Mar 05	13.14	9.40	25	15.71	4.11	26	8.06	2.50	26	5.76	3.53	25
Apr 05	9.80	7.39	23	10.90	4.03	27	6.23	1.34	25	4.78	3.12	23
May 05	7.46	6.40	26	7.15	2.20	30			0	3.69	2.57	26
Jun 05	7.33	7.21	30	5.54	1.92	28			0	3.61	3.04	30
Jul 05	7.20	5.59	26	6.27	1.81	31			0	3.53	2.31	26
Aug 05	6.33	5.91	21	8.05	2.69	31			0	3.23	2.74	21
Sep 05	12.73	9.31	26	13.56	4.33	29			0	5.72	3.59	26
Oct 05	12.96	9.68	27	17.73	5.71	30			0	5.85	3.73	27
Nov 05	21.61	14.14	22	24.24	8.09	27			0	8.36	4.71	22
Dec 05	12.12	10.13	22	22.89	6.74	29			0	5.66	3.96	22
Jan 06	17.13	13.20	28	23.87	8.00	28			0	6.83	4.54	28
Feb 06	16.55	10.93	23	20.61	6.05	27			0	6.72	3.64	23
Mar 06	16.90	10.55	29	17.36	4.35	31	7.29	2.69	31	7.06	3.59	29
Apr 06	7.78	5.75	21	10.27	2.95	30	6.21	1.23	30	3.89	2.57	21
May 06	9.12	7.38	26	6.96	2.11	27	3.90	0.99	30	4.33	2.97	26
Jun 06	8.38	5.44	28	6.29	1.45	30	3.45	0.69	30	4.16	2.32	28
Jul 06	7.51	7.05	29	6.03	2.10	26	3.60	0.84	31	3.70	2.97	29
Aug 06	10.60	7.32	18	9.78	2.79	24	5.18	1.65	24	4.89	2.94	18
Sep 06	12.27	10.26	22	13.95	4.13	29	7.12	2.45	29	5.27	3.52	22
Oct 06	16.75	8.47	26	20.74	4.06	31	9.17	2.52	31	7.23	3.08	26
Nov 06	17.72	13.44	26	22.58	7.52	29	10.16	3.78	29	6.87	4.54	26
Dec 06	24.02	11.53	25	27.48	6.91	30	10.58	3.61	30	9.74	3.75	25

APPENDICES

Appendix A - PUBLICATIONS

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The following compendium of papers, reviews and data summaries, published or in press to the end of 2006, from the various CGBAPS research programs has been compiled from *Baselines 1976, 1977, 1978, 1979-1980, 1981-1982, 83-84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94-95, 96, 97-98, 1999-2000, 2001-2002, 2003-2004* and from communications with CGBAPS Lead Scientists. Scientists were asked to list all papers that they considered represented their activities in the Cape Grim Program. The papers include those describing techniques that are relevant to the various CGBAPS programs.

Some of the papers are listed as 'in press' and full details will be inserted when the list is next updated.

Prior to *Baseline 1981-1982* the clear distinction between research reports and data summaries was not made. The various contributions to *Baseline* for this period (1976-1980) were classified as either research reports or data summaries based on their content. The list has not been verified by an independent literature search.

In sections 1 to 8 peer-reviewed research and technical papers in national and international journals are listed first. Conference presentations and proceedings are listed next, followed by *Baseline* research reports and *Baseline* data summaries. Note: The numbers in [xx] parentheses represent the number of publications and those in (xx) parentheses represent the number of conferences or *Baseline* publications.

1. CARBON DIOXIDE AND CARBON ISOTOPES

1.1 Research and technical papers [103]

Note: the first nine (9) papers listed below do not involve Cape Grim directly, but provide a context within which the Cape Grim program developed.

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Appendix B - PERSONNEL

P Fraser and N Derek

CSIRO Marine and Atmospheric Research
Aspendale, Victoria 3195, Australia

Cape Grim Baseline Atmospheric Pollution Station (CGBAPS) Management Group, Working Group, Lead Scientists, on-site staff, off-site funded staff and students 1975-2006

The Management Group was formed in 1980. Former and current members are listed below:

1980-1983	P. Free (DST), J. Philip (CSIRO)
1983	P. Free (DST), N. Fletcher (CSIRO)
1984-1992	D. Gauntlett (Bureau ¹), G. B. Tucker (CSIRO)
1993-2000	D. Gauntlett/G. Love (Bureau), G. Pearman (CSIRO)
2001-2002	W. Downey (Bureau), G. Pearman (CSIRO)
2003-2004	R. Brook (Bureau), G. Ayers (CSIRO)
2005	R. Brook/G. Foley (Bureau), G. Ayers (CSIRO)
2006	G. Foley (Bureau), G. Ayers (CSIRO)

Former and current Working Group members are listed in Table 1. It is assumed that 1980 Working Group members remained members if they were listed in *Baseline* as attendees and that all Lead Scientists and the CGBAPS OIC were members of the Working Group, except if they became members of the CGBAPS Management Group.

The total number of Working Group members were/are:

1975-1977	9	1978	10	1979-1980	11	1981-1986	13
1987	14	1988-1989	16	1990	15	1991	16
1992	17	1993-1994	16	1995-1996	14	1997-2000	13
2001	13	2002	11	2003	10	2004-2006	12

The CGBAPS Management Group members were/are represented on the Working Group by:

1983	P. Ford (CSIRO)
1984	R. Dubs (CSIRO)
1985-1988	D. Jasper (Bureau)
1985-2006	W. Bouma ² (CSIRO)
1988-2001	P. Price ³ (Bureau)
2002-2006	B. Forgan

The Working Group was/is chaired by:

1975-1978	L. Wainwright (DS/DST)
1979-1982	C. Norris (AGAL)
1983-1984	R. Francey (CSIRO)
1984-1988	B. Forgan (Bureau)
1988-1992	S. Wilson (Bureau)
1992	J. Warne (Bureau)
1992-1998	A. Dick (Bureau)
1998-2002	N. Tindale (Bureau)
2003-2006	J. Caine (Bureau)

Lead Scientists were first specified in *Baseline 1979-1980*, but not all Lead Scientists were members of the CGBAPS Working Group until 1981. Past/current Lead Scientists are listed in Table 2. Table 3 shows CGBAPS on-site staff, Table 4 shows CGBAPS funded off-site staff and students and Table 5 shows Australian and international post-graduate and summer students.

¹ Bureau = Bureau of Meteorology

² During 2001, W. Bouma was represented by G. Ayers (CSIRO)

³ For extended periods during 1998-2000 P. Price was represented by either B. Dixon (Bureau) or B. Forgan (Bureau).

Table 1. Members of the CGBAPS Working Group, 1975-2006, total membership in parentheses.

1975-1976 (9)	1977 (9)	1978 (10)	1979-1980 (11)	1981-1982 (13)
Wainwright (DS, chair) Bigg (CSIRO) Dyer (CSIRO) Hounam (Bureau) McKay (DEHCD) Pearman (CSIRO) Peters (AGAL) Pottinger (DOE, Tas.) Rhodes (DOS)	Wainwright (DS, chair) Bigg (CSIRO) Dyer (CSIRO) McKay (DEHCD) Norris (AGAL) Pearman (CSIRO) Pottinger (DOE, Tas.) Rhodes (DOS) Trefry (Bureau)	Wainwright (DST, chair) Bigg (CSIRO) Dyer (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Makeham (DST) Norris (AGAL, chair) Pearman (CSIRO) Rhodes (DST) Wise (DST)	Norris (AGAL, chair) Bigg (CSIRO) Briggs (DST) Dyer (CSIRO) Fraser (CSIRO) Free (DST) Galbally (CSIRO) Parker (DST) Pearman (CSIRO) Wilson (AGAL) Wise (DST)	Norris (AGAL, chair) Ayers (CSIRO) Bigg (CSIRO) Briggs (DST) Francey (CSIRO, chair) Fraser (CSIRO) Free (DST) Galbally (CSIRO) Ivey (AGAL) Parker (DST) Pearman (CSIRO) Platt (CSIRO) Wilson (AGAL)
1983-1984 (13)	1985 (13)	1986 (13)	1987 (14)	1988 (16)
Francey/Forgan (CSIRO/Bureau, chair) Ayers (CSIRO) Bigg (CSIRO) Ford, Dubs, Bouma (CSIRO) Forgan (Bureau, chair) Fraser (CSIRO) Galbally (CSIRO) Ivey (AGAL) Norris (AGAL) Pearman (CSIRO) Platt (CSIRO) Whittlestone (ANSTO) Wilson (AGAL)	Forgan (Bureau, chair) Ayers (CSIRO) Bigg (CSIRO) Bouma (CSIRO) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Whittlestone (ANSTO)	Forgan (Bureau, chair) Ayers (CSIRO) Bouma (CSIRO) Burton (Ant. Div.) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Whittlestone (ANSTO)	Forgan (Bureau, chair) Ayers (CSIRO) Bouma (CSIRO) Burton (Ant. Div.) Downey (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Whittlestone (ANSTO)	Forgan/Wilson (Bureau, chairs) Ayers (CSIRO) Bouma (CSIRO) Burton (Ant. Div.) Downey (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Price (Bureau) Whittlestone (ANSTO)
1989 (16)	1990 (15)	1991 (16)	1992 (17)	1993-1994 (16)
Wilson (Bureau, chair) Ayers (CSIRO) Bouma (CSIRO) Burton (Ant. Div.) Downey (Bureau) Forgan (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Price (Bureau) Whittlestone (ANSTO)	Wilson (Bureau, chair) Ayers (CSIRO) Bouma (CSIRO) Downey (Bureau) Forgan (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Price (Bureau) Whittlestone (ANSTO)	Wilson (Bureau, chair) Ayers (CSIRO) Bouma (CSIRO) Downey (Bureau) Forgan (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Price (Bureau) Steele (CSIRO) Whittlestone (ANSTO)	Wilson/Warne/Dick (Bureau, chairs) Ayers (CSIRO) Bouma (CSIRO) Downey (Bureau) Francey (CSIRO) Forgan (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Price (Bureau) Steele (CSIRO) Whittlestone (ANSTO) Wilson (U. Woll)	Dick (Bureau, chair) Ayers (CSIRO) Bouma (CSIRO) Downey (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Jasper (Bureau) Pearman (CSIRO) Platt (CSIRO) Price (Bureau) Steele (CSIRO) Whittlestone (ANSTO) Wilson (U. Woll)
1995-1996 (14)	1997 (13)	1998 (13)	1999 (13)	2000 (13)
Dick (Bureau, chair) Ayers (CSIRO) Bouma (CSIRO) Downey (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Ivey (AGAL) Platt (CSIRO) Price (Bureau) Steele (CSIRO) Whittlestone (ANSTO) Wilson (U. Woll)	Dick (Bureau, chair) Ayers (CSIRO) Boers (CSIRO) Bouma (CSIRO) Downey (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Price (Bureau) Steele (CSIRO) Whittlestone (ANSTO) Wilson (U. Woll)	Dick/Tindale (Bureau, chair) Ayers (CSIRO) Boers/Young (CSIRO) Bouma (CSIRO) Downey (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Price/Dixon (Bureau) Steele (CSIRO) Whittlestone (ANSTO) Wilson (U. Woll)	Tindale (Bureau, chair) Ayers (CSIRO) Boers (CSIRO) Bouma (CSIRO) Downey (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Price/Forgan (Bureau) Steele (CSIRO) Whittlestone (ANSTO) Wilson (U. Woll)	Tindale (Bureau, chair) Ayers (CSIRO) Boers (CSIRO) Bouma (CSIRO) Downey (Bureau) Francey (CSIRO) Fraser (CSIRO) Galbally (CSIRO) Gras (CSIRO) Price (Bureau) Steele (CSIRO) Whittlestone (ANSTO) Wilson (U. Woll)

Table 1. continued....

2001 (13)	2002 (11)	2003 (10)	2004-2006 (12)
Tindale (Bureau, chair)	Tindale (Bureau, chair)	Caine (Bureau, chair)	Caine (Bureau, chair)
Ayers (CSIRO)	Bouma (CSIRO)	Bouma (CSIRO)	Bouma (CSIRO)
Boers (CSIRO)	Downey (Bureau)	Downey (Bureau)	Downey/Gorman (Bureau)
Bouma (CSIRO)	Forgan (Bureau)	Forgan (Bureau)	Forgan (Bureau)
Downey (Bureau)	Francey (CSIRO)	Fraser (CSIRO)	Fraser (CSIRO)
Francey (CSIRO)	Fraser (CSIRO)	Galbally (CSIRO)	Galbally (CSIRO)
Fraser (CSIRO)	Galbally (CSIRO)	Gras (CSIRO)	Gras (CSIRO)
Galbally (CSIRO)	Gras (CSIRO)	Steele (CSIRO)	Keywood (CSIRO)
Gras (CSIRO)	Steele (CSIRO)	Wilson (U. Woll)	Krummel (CSIRO)
Price (Bureau)	Wilson (U. Woll)	Zahorowski (ANSTO)	Steele (CSIRO)
Steele (CSIRO)	Zahorowski (ANSTO)		Wilson (U. Woll)
Wilson (U. Woll)			Zahorowski (ANSTO)
Zahorowski (ANSTO)			

Table 2. CGBAPS Lead Scientists, 1979-2006, total numbers in parentheses.

1979-1980 (7)	1981-1982 (8)	1983-1984 (10)
Ayers (CSIRO) precipitation chemistry	Ayers (CSIRO) precipitation chemistry	Ayers (CSIRO) precipitation chemistry
Bigg (CSIRO) particles	Bigg (CSIRO) particles	Bigg (CSIRO) particles
Fraser (CSIRO) halocarbons, N ₂ O	Francey (CSIRO) C isotopes	Forgan (Bureau) passive radiation
Galbally (CSIRO) ozone, N oxides	Fraser (CSIRO) halocarbons, N ₂ O, CO, CH ₄	Francey (CSIRO) C isotopes
Ivey (AGAL) precipitation chemistry	Galbally (CSIRO) ozone, N oxides	Fraser (CSIRO) halocarbons, N ₂ O, CO, CH ₄
Pearman (CSIRO) carbon dioxide	Ivey (AGAL) precipitation chemistry	Galbally (CSIRO) ozone, N oxides
Platt (CSIRO) radiation	Pearman (CSIRO) carbon dioxide	Ivey (AGAL) precipitation chemistry
	Platt (CSIRO) radiation	Pearman (CSIRO) carbon dioxide
		Platt (CSIRO) active radiation
		Whittlestone (ANSTO) radon
1985 (11)	1986 (11)	1987-1989 (13)
Ayers (CSIRO) precipitation chemistry	Ayers (CSIRO) sulphur	Ayers (CSIRO) sulfur
Bigg (CSIRO) particles	Burton (AAD) sulphur	Burton (AAD) sulfur
Forgan (Bureau) passive radiation	Forgan (Bureau) passive radiation	Downey (Bureau) meteorology/climatology
Francey (CSIRO) C isotopes	Francey (CSIRO) C isotopes	Forgan (Bureau) passive radiation
Fraser (CSIRO) halocarbons, N ₂ O, CO, CH ₄	Fraser (CSIRO) halocarbons, N ₂ O, CO, CH ₄	Francey (CSIRO) C-isotopes, air archive
Galbally (CSIRO) ozone, N oxides	Galbally (CSIRO) ozone, N oxides	Fraser (CSIRO) halocarbons N ₂ O, CO, CH ₄ , air archive
Gras (CSIRO) particles	Gras (CSIRO) particles	Galbally (CSIRO) O ₃ , N oxides
Ivey (AGAL) precipitation chemistry	Ivey (AGAL) precipitation chemistry	Gras (CSIRO) particles
Pearman (CSIRO) carbon dioxide	Pearman (CSIRO) carbon dioxide	Ivey (AGAL) precipitation chemistry
Platt (CSIRO) active radiation	Platt (CSIRO) active radiation	Jasper (Bureau) meteorology/climatology
Whittlestone (ANSTO) radon	Whittlestone (ANSTO) radon	Pearman (CSIRO) carbon dioxide
		Platt (CSIRO) active radiation
		Whittlestone (ANSTO) radon
1990 (12)	1991 (13)	1992 (13)
Ayers (CSIRO) sulphur	Ayers (CSIRO) sulphur	Ayers (CSIRO) sulfur
Downey (Bureau) meteorology/climatology	Downey (Bureau) meteorology/climatology	Downey (Bureau) meteorology/climatology
Forgan (Bureau) passive radiation	Forgan (Bureau) passive radiation	Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights
Francey (CSIRO) C isotopes, air archive	Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights	Fraser (CSIRO) halocarbons, N ₂ O, air archive
Fraser (CSIRO) halocarbons, N ₂ O, CO, CH ₄ , air archive, overflights	Fraser (CSIRO) halocarbons, N ₂ O, air archive	Galbally (CSIRO) O ₃ , N oxides
Galbally (CSIRO) O ₃ , N oxides	Galbally (CSIRO) O ₃ , N oxides	Gras (CSIRO) particles
Gras (CSIRO) particles	Gras (CSIRO) particles	Ivey (AGAL) precipitation chemistry
Ivey (AGAL) precipitation chemistry	Ivey (AGAL) precipitation chemistry	Jasper (Bureau) meteorology/climatology
Jasper (Bureau) meteorology/climatology	Jasper (Bureau) meteorology/climatology	Pearman (CSIRO) carbon dioxide
Pearman (CSIRO) carbon dioxide	Pearman (CSIRO) carbon dioxide	Platt (CSIRO) active radiation
Platt (CSIRO) active radiation	Platt (CSIRO) active radiation	Steele (CSIRO) CH ₄ , CO, H ₂ , overflights
Whittlestone (ANSTO) radon	Steele (CSIRO) CH ₄ , CO, H ₂ , overflights	Whittlestone (ANSTO) radon
	Whittlestone (ANSTO) radon	Wilson (U. Woll) spectral radiation
1993 (13)	1994 (12)	1995 (11)
Ayers (CSIRO) sulfur	Ayers (CSIRO) sulfur	Ayers (CSIRO) sulfur
Downey (Bureau) meteorology/climatology	Downey (Bureau) meteorology/climatology	Downey (Bureau) meteorology/climatology
Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights	Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights	Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights
Fraser (CSIRO) halocarbons, N ₂ O, air archive	Fraser (CSIRO) halocarbons, N ₂ O, air archive	Fraser (CSIRO) halocarbons, N ₂ O, air archive
Galbally (CSIRO) O ₃ , N oxides	Galbally (CSIRO) O ₃ , N oxides	Galbally (CSIRO) O ₃ , N oxides
Gras (CSIRO) particles	Gras (CSIRO) particles	Gras (CSIRO) particles
Ivey (AGAL) precipitation chemistry	Ivey (AGAL) precipitation chemistry	Ivey (AGAL) precipitation chemistry
Jasper (Bureau) meteorology/climatology	Pearman (CSIRO) carbon dioxide	Platt (CSIRO) active radiation
Pearman (CSIRO) carbon dioxide	Platt (CSIRO) active radiation	Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , overflights
Platt (CSIRO) radiation-active	Steele (CSIRO) CH ₄ , CO, H ₂ , overflights	Whittlestone (ANSTO) radon
Steele (CSIRO) CH ₄ , CO, H ₂ , overflights	Whittlestone (ANSTO) radon	Whittlestone (ANSTO) radon
Whittlestone (ANSTO) radon	Wilson (U. Woll) spectral radiation	Wilson (U. Woll) spectral radiation
Wilson (U. Woll) spectral radiation		

Table 2. continued....

1996 (11)	1997 (10)	1998 (10)
Ayers (CSIRO) sulfur	Ayers (CSIRO) sulfur	Ayers (CSIRO) multiphase atmospheric chemistry
Downey (Bureau) meteorology/climatology	Boers (CSIRO) remote sensing of clouds	Boers/Young (CSIRO) remote sensing of clouds
Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights	Downey (Bureau) meteorology/climatology	Downey (Bureau) meteorology/climatology
Fraser (CSIRO) halocarbons, N ₂ O, air archive	Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights	Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights
Galbally (CSIRO) O ₃ , N oxides	Fraser (CSIRO) halocarbons, N ₂ O, air archive	Galbally (CSIRO) O ₃ , N oxides
Gras (CSIRO) particles	Galbally (CSIRO) O ₃ , N oxides	Gras (CSIRO) particles
Ivey (AGAL) precipitation chemistry	Gras (CSIRO) particles	Fraser (CSIRO) halocarbons, N ₂ O, air archive
Platt (CSIRO) active radiation	Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , overflights	Galbally (CSIRO) O ₃ , N oxides
Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , overflights	Whittlestone (ANSTO) radon	Gras (CSIRO) particles
Whittlestone (ANSTO) radon	Wilson (U. Woll) spectral radiation	Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , overflights
Wilson (U. Woll) spectral radiation		Whittlestone (ANSTO) radon
		Wilson (U. Woll) spectral radiation
1999 (10)	2000 (10)	2001 (10)
Ayers (CSIRO) multiphase atmospheric chemistry	Ayers (CSIRO) multiphase atmospheric chemistry	Ayers (CSIRO) multiphase atmospheric chemistry
Boers (CSIRO) remote sensing of clouds	Boers (CSIRO) remote sensing of clouds	Boers (CSIRO) remote sensing of clouds
Downey (Bureau) meteorology/climatology	Downey (Bureau) meteorology/climatology	Downey (Bureau) meteorology/climatology
Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights	Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights	Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights
Fraser (CSIRO) halocarbons, N ₂ O, air archive	Fraser (CSIRO) halocarbons, N ₂ O, air archive	Fraser (CSIRO) halocarbons, N ₂ O, air archive
Galbally (CSIRO) O ₃ , N oxides	Galbally (CSIRO) O ₃ , N oxides	Galbally (CSIRO) O ₃ , N oxides
Gras (CSIRO) particles	Gras (CSIRO) particles	Gras (CSIRO) particles
Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , overflights	Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , overflights	Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , overflights
Whittlestone (ANSTO) radon	Whittlestone (ANSTO) radon	Wilson (U. Woll) spectral radiation
Wilson (U. Woll) spectral radiation	Wilson (U. Woll) spectral radiation	Zahorowski (ANSTO) radon
2002 (8)	2003 (7)	2004-2006 (10)
Downey (Bureau) meteorology/climatology	Downey (Bureau) meteorology/climatology	Downey/Gorman (Bureau) meteorology/climatology
Francey (CSIRO) C isotopes, air archive, O ₂ /N ₂ , overflights	Fraser (CSIRO) halocarbons, N ₂ O, air archive	Fraser/Steele/Krummel (CSIRO) non-CO ₂ greenhouse gases, air archive
Fraser (CSIRO) halocarbons, N ₂ O, air archive	Galbally (CSIRO) O ₃ , N oxides	Galbally (CSIRO) O ₃ , N oxides
Galbally (CSIRO) O ₃ , N oxides	Gras (CSIRO) particles, multiphase atmospheric chemistry	Gras (CSIRO) particles
Gras (CSIRO) particles, multiphase atmospheric chemistry	Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , C isotopes, O ₂ /N ₂	Keywood (CSIRO) multiphase atmospheric chemistry
Steele (CSIRO) CO ₂ , CH ₄ , CO, H ₂ , overflights	Wilson (U. Woll) spectral radiation	Steele/Krummel (CSIRO) CO ₂ , C isotopes, O ₂ /N ₂
Wilson (U. Woll) spectral radiation	Zahorowski (ANSTO) radon	Wilson (U. Woll) spectral radiation
Zahorowski (ANSTO) radon		Zahorowski (ANSTO) radon

Table 3. CGBAPS on-site staff, 1976-2006, total permanent staff above dashed line and in parentheses.

Senior Technical Officer (STO); Technical Officer (TO); Technical Assistant (TA); Research Assistant (RA); Clerical Assistant (CA); Temporary Staff (TS); Computing Systems Officer (CSO); Administrative Services Officer (ASO); Technical Trainee (TT); Exchange Officer (EO); Post-Doctoral Fellow (PDF); Information Technology Officer (ITO); Senior Information Technology Officer (SITO).

1976-1980 (2)	1981 (5)	1982(5)	1983 (4)
G. Wise, STO (DS/DST)	R. Francey, Director (CSIRO)	R. Francey, Director (CSIRO)	R. Francey, Director (CSIRO)
K. Briggs, TO (DS/DST)	K. Briggs, STO (DST)	H. Harrison, CA (DST)	H. Harrison/L. Emmerton, CA (DST)
	H. Harrison, CA (DST)	I. Helmond, STO (CSIRO)	I. Helmond, STO (CSIRO)
	R. Muir-Wilson, TA (DST)	R. Muir-Wilson, TA (DST)	R. Muir-Wilson, TA (DST)
	R. Watson, TO (DST)	R. Watson, TO (DST)	
	G. O'Halloran, TS (DST)	S. Francey, TS (DST)	M. Orchard, TS (DST)
		G. O'Halloran, TS (DST)	
1984 (5)	1985 (5)	1986 (5)	1987 (5)
B. Forgan, OiC (Bureau)	B. Forgan, OiC (Bureau)	B. Forgan, OiC (Bureau)	B. Forgan, OiC (Bureau)
L. Emmerton, CA (Bureau)	L. Emmerton, CA (Bureau)	L. Emmerton, CA (Bureau)	A. Eisman, CA (Bureau)
R. Muir-Wilson/B. Sibson, TA (Bureau)	L. Porter, TO (Bureau)	L. Porter, TO (Bureau)	L. Porter, TO/STO (Bureau)
L. Porter, TO (Bureau)	B. Sibson, STO (Bureau)	B. Sibson, STO (Bureau)	B. Sibson, STO (Bureau)
P. Walford, CSO (Bureau)	P. Walford, CSO (Bureau)	P. Walford, CSO (Bureau)	P. Walford, CSO (Bureau)
M. Lane, TS (Bureau)	M. Lane, TS (Bureau)	A. Eisman, TS (Bureau)	A. Forgan, TS (Bureau)
M. Orchard, TS (Bureau)	R. Paterson, TS (Bureau)	A. Forgan, TS (Bureau)	R. Paterson, TS (Bureau)
		R. Paterson, TS (Bureau)	T. Weaver, TS (Bureau)
		T. Weaver, TS (Bureau)	
1988(5)	1989 (6)	1990-1991 (6)	1992 (6)
B. Forgan/S. Wilson, OiC (Bureau)	S. Wilson, OiC (Bureau)	S. Wilson, OiC (Bureau)	S. Wilson/J. Warne/C. Dick, OiC (Bureau)
A. Eisman, ASO (Bureau)	A. Eisman/C. Schrank, ASO (Bureau)	A. French, TO (Bureau)	A. French/G. Torr, TO (Bureau)
M. Leonard, TO (Bureau)	M. Leonard, TO (Bureau)	R. Paterson, TA (Bureau)	R. Paterson, TA (Bureau)
L. Porter, STO (Bureau)	R. Paterson, TA (Bureau)	L. Porter, STO (Bureau)	L. Porter, STO (Bureau)
P. Walford, CSO (Bureau)	L. Porter, STO (Bureau)	C. Schrank, ASO (Bureau)	C. Schrank/J. Britton, ASO (Bureau)
	P. Walford, CSO (Bureau)	P. Walford, CSO (Bureau)	P. Walford, CSO (Bureau)
K. McKay, TS (Bureau)	T. Weaver, TS (Bureau)	S. Eason, TS (Bureau)	S. Eason, TS (Bureau)
R. Paterson, TS (Bureau)		T. Weaver, TS (Bureau)	T. Weaver, TS (Bureau)
T. Weaver, TS (Bureau)			

Table 3. continued....

1993 (6)	1994 (6)	1995 (6)	1996 (6)
C. Dick, OiC (Bureau)	C. Dick, OiC (Bureau)	C. Dick, OiC (Bureau)	C. Dick, OiC (Bureau)
J. Britton, ASO (Bureau)	J. Britton, ASO (Bureau)	J. Britton, ASO (Bureau)	J. Britton, ASO (Bureau)
R. Paterson, TO3 (Bureau)	J. Mundy/R. Paterson, TO3 (Bureau)	J. Mundy, TO3 (Bureau)	J. Mundy/S. Baly, TO3 (Bureau)
L. Porter, TO4 (Bureau)	B. Weymouth, ITO2 (Bureau)	L. Porter, TO4 (Bureau)	L. Porter, TO4 (Bureau)
G. Torr, TO3 (Bureau)	L. Porter, TO4 (Bureau)	P. Walford, SITO-C (Bureau)	P. Walford, SITO-C (Bureau)
P. Walford, SITO-C (Bureau)	P. Walford, SITO-C (Bureau)	B. Weymouth, ITO2 (Bureau)	B. Weymouth, ITO2 (Bureau)
A. Torr, TS (Bureau)	K. Robinson, TS (Bureau)	C. McCulloch, TT (Bureau)	J. Elphinstone TS (Bureau)
T. Weaver, TS (Bureau)	T. Weaver, TS (Bureau)	K. Robinson, TS (Bureau)	N. Hong, EO (CMA)
	S. Ryan, EO (NOAA)	T. Weaver, TS (Bureau)	C. McCulloch, TT (Bureau)
			K. Robinson, TS (Bureau)
			G. Sturrock, PDF (CSIRO)
			T. Weaver, TS (Bureau)
			A. Zappia, TS (Bureau)
1997 (6)	1998 (6)	1999 (6)	2000 (6)
C. Dick, OiC (Bureau)	C. Dick/N. Tindale, OiC (Bureau)	N. Tindale, OiC (Bureau)	N. Tindale, OiC (Bureau)
S. Baly, TO3 (Bureau)	S. Baly, TO3 (Bureau)	S. Baly, TO3 (Bureau)	S. Baly, TO3 (Bureau)
J. Britton, ASO (Bureau)	J. Britton, ASO (Bureau)	J. Britton, ASO (Bureau)	J. Britton, ASO (Bureau)
A. Gough, ITO2 (Bureau)	A. Gough, ITO2 (Bureau)	A. Gough, ITO2 (Bureau)	A. Gough/R. Wheaton, ITO2 (Bureau)
L. Porter, TO4 (Bureau)	L. Porter, TO4 (Bureau)	L. Porter, TO4 (Bureau)	L. Porter, TO4 (Bureau)
B. Weymouth, SITO-C (Bureau)	B. Weymouth, SITO-C (Bureau)	B. Weymouth, SITO-C (Bureau)	B. Weymouth, SITO-C (Bureau)
J. Elphinstone TS (Bureau)	D. Evenhuis, TS (Bureau)	D. Evenhuis, TS (Bureau)	C. McCulloch, TA (CSIRO)
D. Evenhuis, TS (Bureau)	C. McCulloch, TA (Bureau)	C. McCulloch, TA (CSIRO)	R. Parr, TA (CSIRO)
C. McCulloch, TA (Bureau)	E. Porter, TS (Bureau)	E. Porter, TS (Bureau)	E. Porter, TS (Bureau)
E. Porter, TS (Bureau)	K. Robinson, TS (Bureau)		
K. Robinson, TS (Bureau)	G. Sturrock, PDF (CSIRO)		
G. Sturrock, PDF (CSIRO)			
T. Weaver, TS (Bureau)			
2001 (6)	2002 (5)	2003 (6)	2004 (6)
N. Tindale, OiC (Bureau)	N. Tindale, OiC (Bureau)	J. Cainey, OiC (Bureau)	J. Cainey, OiC (Bureau)
S. Baly, TO3 (Bureau)	S. Baly, TO3/ITO2 (Bureau)	S. Baly, ITO2 (Bureau)	S. Baly, ITO2 (Bureau)
J. Britton, ASO (Bureau)	J. Britton, ASO (Bureau)	J. Britton, ASO (Bureau)	J. Britton/C. Hood, ASO (Bureau)
L. Porter, TO4 (Bureau)	L. Porter, TO4 (Bureau)	F. Quartararo, TO3 (Bureau)	L. Porter, TO4/SOT-C (Bureau)
B. Weymouth, SITO-C (Bureau)	R. Wheaton, SITO-C (Bureau)	L. Porter, TO4 (Bureau)	C. Rickard TO3 (Bureau)
R. Wheaton, ITO2 (Bureau)		R. Wheaton, SITO-C (Bureau)	R. Wheaton/S. McEwan, SITO-C (Bureau)
C. McCulloch, TA (CSIRO)	C. McCulloch, TA (CSIRO)	C. Hood, TS (Bureau)	S. McEwan TS (Bureau)
S. Maguire, ASO (Bureau)	S. Maguire, TS (Bureau)		R. Parr, RA (U. Tas)
R. Parr, TA (CSIRO)	R. Parr, RA (CSIRO/U. Tas)		
E. Porter, TS (Bureau)			
2005 (6)	2006 (6)		
J. Cainey, OiC (Bureau)	J. Cainey, OiC (Bureau)		
S. Baly, ITO2 (Bureau)	S. Baly, ITO2 (Bureau)		
C. Hood, ASO (Bureau)	C. Hood, ASO (Bureau)		
L. Porter, TO4 (Bureau)	L. Porter, TO4 (Bureau; CSIRO secondment)		
C. Rickard TO3 (Bureau)	C. Rickard TO3 (Bureau)		
S. McEwan, SITO-C (Bureau)	S. McEwan, SITO-C (Bureau)		
R. Parr, RA (U. Tas)	P. Armstrong, TS (CSIRO)		

Table 4. CGBAPS funded off-site staff, 1981-2000. After 2000 CSIRO moved to project-based budgeting and CGBAPS funding contributed to overall Cape Grim project staffing costs rather than individual staff.

1981-1982 (6)	1983-1984 (6)	1985 (5)	1986 (11)	1987 (7)
M. Douglas (CSIRO)	D. Davies (AGAL)	D. Davies (AGAL)	A. Becker (CSIRO)	R. Armstrong (CSIRO)
D. Etheridge (CSIRO)	M. Douglas (CSIRO)	N. Derek (CSIRO)	P. Browne (CSIRO)	P. Browne (CSIRO)
C. Evans (CSIRO)	C. Evans (CSIRO)	M. Douglas (CSIRO)	D. Davies (AGAL)	N. Derek (CSIRO)
R. O'Brien (CSIRO)	R. O'Brien (CSIRO)	C. Evans (CSIRO)	N. Derek (CSIRO)	G. Harris (CSIRO)
J. Osborne (CSIRO)	R. Shepherd (CSIRO)	R. Shepherd (CSIRO)	M. Duree (CSIRO)	J. Ivey (AGAL)
R. Shepherd (CSIRO)	S. Vonarx (AGAL)		G. Harris (CSIRO)	R. Paterson (Bureau)
			J. Ivey (AGAL)	F. Robbins (CSIRO)
			S. Lai (CSIRO)	
			D. Oliver (CSIRO)	
			R. Paterson (Bureau)	
			T. Weaver (Bureau)	
1988 (5)	1989-1990 (4)	1991 (5)	1992 (4)	1993-1994 (4)
R. Armstrong (CSIRO)	R. Armstrong (CSIRO)	N. Derek (CSIRO)	N. Derek (CSIRO)	N. Derek (CSIRO)
N. Derek (CSIRO)	N. Derek (CSIRO)	M. Lucarelli (CSIRO)	M. Lucarelli (CSIRO)	M. Lucarelli (CSIRO)
J. Ivey (AGAL)	T. McLean (AGAL)	T. McLean (AGAL)	F. Robbins (CSIRO)	P. Selleck (CSIRO)
R. Paterson (Bureau)	F. Robbins (CSIRO)	F. Robbins (CSIRO)	E. Welch (CSIRO)	E. Welch (CSIRO)
F. Robbins (CSIRO)		E. Welch (CSIRO)		

Table 4. continued....

1995 (4)	1996 (6)	1997 (5)	1998 (6)	1999-2000 (5)
L. Cooper (CSIRO)	L. Cooper (CSIRO)	L. Cooper (CSIRO)	L. Cooper (CSIRO)	L. Cooper (CSIRO)
G. Da Costa (CSIRO)	G. Da Costa (CSIRO)	G. Da Costa (CSIRO)	G. Da Costa (CSIRO)	G. Da Costa (CSIRO)
N. Derek (CSIRO)	N. Derek (CSIRO)	N. Derek (CSIRO)	N. Derek (CSIRO)	N. Derek (CSIRO)
P. Selleck (CSIRO)	M. Lucar elli (CSIRO)	P. Krummel (CSIRO)	P. Krummel (CSIRO)	P. Krummel (CSIRO)
	K. Masarie (NOAA/CSIRO)	P. Selleck (CSIRO)	C. McCulloch (CSIRO)	P. Selleck (CSIRO)
	P. Selleck (CSIRO)		P. Selleck (CSIRO)	

Table 5. Australian and international post-graduate and summer students (ss), 1991-2006 (CGBAPS funded* and non-funded students).

1991 (1)	1992 (3)	1993-1994 (9)
D. Etheridge (PhD, U. Melb/CSIRO)	D. Etheridge (PhD, U. Melb/CSIRO) P. Krummel (Masters prelim., Monash U./CSIRO) R. O'Brien (Masters, Monash U./CSIRO)	H. Beggs (PhD, U. Tas/CSIRO) J. Caine (PhD, Monash U./CSIRO) M. Esler (PhD, U. Woll/CSIRO) D. Etheridge (PhD, U. Melb/CSIRO) P. Krummel (Masters prelim., Monash U./CSIRO) B. Miller (PhD, SIO) R. O'Brien (Masters, Monash U./CSIRO) D. Oram (PhD, U. East Anglia/CSIRO) M. Pickett (Honours, VUT/CSIRO)
1995 (12)	1996 (12)	1997 (13)
H. Beggs (PhD, U. Tas/CSIRO) T. Branson (Honours, U. Woll/CSIRO) J. Caine (PhD, Monash U./CSIRO) M. Esler (PhD, U. Woll/CSIRO) D. Etheridge (PhD, U. Melb/CSIRO) P. Krummel (Masters, Monash U./CSIRO) R. Langenfelds (PhD, U. Tas/CSIRO) B. Miller (PhD, SIO) D. Oram (PhD, U. East Anglia/CSIRO) F. Phillips (PhD, U. Woll) M. Pickett (PhD, VUT/CSIRO) P. Took (ss, U. Woll)	H. Beggs (PhD, U. Tas/CSIRO) J. Caine (PhD, Monash U./CSIRO) B. Dunse (Masters, VUT/CSIRO) M. Esler (PhD, U. Woll/CSIRO) D. Etheridge (PhD, U. Melb/CSIRO) P. Krummel (Masters, Monash U./CSIRO) R. Langenfelds (PhD, U. Tas/CSIRO) B. Miller (PhD, SIO) D. Oram (PhD, U. East Anglia/CSIRO) F. Phillips (PhD, U. Woll) M. Pickett (PhD, VUT/CSIRO) M. Pope (ss, U. Woll)	J. Caine (PhD, Monash U./CSIRO) M. Cox (ss, Monash U.) B. Dunse (Masters, VUT/CSIRO)* M. Esler (PhD, U. Woll/CSIRO) D. Etheridge (PhD, U. Melb/CSIRO) R. Johns (nee Webb, PhD, U. Tas/CSIRO) P. Krummel (Masters, Monash U./CSIRO) R. Langenfelds (PhD, U. Tas/CSIRO) B. Miller (PhD, SIO) D. Oram (PhD, U. East Anglia/CSIRO) B. Pak (PhD, U. Melb/CSIRO)* F. Phillips (PhD, U. Woll) M. Pickett (PhD, VUT/CSIRO)
1998 (14)	1999 (9)	2000 (8)
B. Bradshaw (Masters, U. Woll) M. Cox (PhD, Monash U./CSIRO)* B. Dunse (PhD, U. Woll/CSIRO)* D. Etheridge (PhD, U. Melb/CSIRO) R. Johns (nee Webb, PhD, U. Tas/CSIRO) L. Kivlighon (Masters, Latrobe U./CSIRO) P. Krummel (Masters, Monash U./CSIRO) R. Langenfelds (PhD, U. Tas/CSIRO) B. Miller (PhD, SIO) D. Oram (PhD, U. East Anglia/CSIRO) B. Pak (PhD, U. Melb/CSIRO)* F. Phillips (PhD, U. Woll) M. Pickett (PhD, VUT/CSIRO) T. Potts (ss, U. Tas)	M. Cox (PhD, Monash U./CSIRO)* B. Dunse (PhD, U. Woll/CSIRO)* S. Jimi (PhD, Monash U./CSIRO)* R. Johns (nee Webb, PhD, U. Tas/CSIRO) L. Kivlighon (Masters, Latrobe U./CSIRO) C. MacFarling (PhD, U. Melb/CSIRO) D. Oram (PhD, U. East Anglia/CSIRO) B. Pak (PhD, U. Melb/CSIRO)* M. Pickett (PhD, VUT/CSIRO)	G. Cornu (Honours, U. Tas)* M. Cox (PhD, Monash U./CSIRO)* B. Dunse (PhD, U. Woll/CSIRO)* S. Jimi (PhD, Monash U./CSIRO)* R. Johns (nee Webb, PhD, U. Tas/CSIRO) L. Kivlighon (Masters, Latrobe U./CSIRO) C. MacFarling (PhD, U. Melb/CSIRO) B. Pak (PhD, U. Melb/CSIRO)*
2001 (7)	2002 (5)	2003 (5)
G. Cornu (Honours, U. Tas)* M. Cox (PhD, Monash U./CSIRO)* B. Dunse (PhD, U. Woll/CSIRO)* S. Jimi (PhD, Monash U./CSIRO)* R. Johns (nee Webb, PhD, U. Tas/CSIRO) L. Kivlighon (Masters, Latrobe U./CSIRO) C. MacFarling (PhD, U. Melb/CSIRO)	B. Dunse (PhD, U. Woll/CSIRO)* S. Jimi (PhD, Monash U./CSIRO)* R. Johns (nee Webb, PhD, U. Tas/CSIRO) L. Kivlighon (Masters, Latrobe U./CSIRO) C. MacFarling (PhD, U. Melb/CSIRO)	J. Elkins III (ss, U. Colorado) S. Jimi (PhD, Monash U./CSIRO)* C. MacFarling (PhD, U. Melb/CSIRO) C. Pickett-Heaps (PhD, U. Melb/CSIRO)* G. Sami (PhD, U. Woll)*
2004 (6)	2005 (5)	2006 (3)
M. Grose (PhD, U. Tas/CGBAPS)* J. Gutknecht (ss, James Cook U.) P. Krummel (PhD, U. Woll/CSIRO) C. MacFarling (PhD, U. Melb/CSIRO) C. Pickett-Heaps (PhD, U. Melb/CSIRO)*	M. Grose (PhD, U. Tas/CGBAPS)* P. Krummel (PhD, U. Woll/CSIRO) C. MacFarling Meure (PhD, U. Melb/CSIRO) C. Pickett-Heaps (PhD, U. Melb/CSIRO)	M. Grose (PhD, U. Tas/CGBAPS)* P. Krummel (PhD, U. Woll/CSIRO) C. Pickett-Heaps (PhD, U. Melb/CSIRO)

Appendix C - DEFINITIONS

(Most frequently used acronyms and symbols in this issue)

AGAGE	Advanced Global Atmospheric Gases Experiment
AGAL	Australian Government Analytical Laboratories, Hobart, Tasmania
ANSTO	Australian Nuclear Science and Technology Organisation, Menai, NSW
BoM	Bureau of Meteorology, Melbourne, Victoria
CGBAPS	Cape Grim Baseline Air Pollution Station, Smithton, Tasmania
CMDL	Climate Monitoring and Diagnostics Laboratory, NOAA, Boulder, USA
CSIRO	Commonwealth Scientific and Industrial Research Organisation, Australia
CAR	CSIRO Atmospheric Research, Aspendale, Victoria
CMAR	CSIRO Marine and Atmospheric Research, Aspendale, Victoria
Empa	Swiss Federal Materials Science and Technology Institution, Duebendorf, Switzerland
ESRL	Earth System Research Laboratory, NOAA, Boulder, USA
GASLAB	Global Atmospheric Sampling Laboratory, CMAR
GMD	Global Monitoring Division, ESRL
IASOS	Institute of Antarctic and Southern Ocean Studies, Hobart, Tasmania
LSCE	Laboratoire des Sciences du Climat et de l'Environnement, France
MPI	Max Planck Institute for Chemistry, Mainz, Germany
NIES	National Institute for Environmental Studies, Tsukuba, Japan
NIST	National Institute of Standards and Technology, USA
NIWA	National Institute of Water & Atmospheric research, New Zealand
NOAA	National Oceanic and Atmospheric Administration, USA
PU	Princeton University, Princeton, New Jersey, USA
SIO	Scripps Institution of Oceanography, La Jolla, California, USA
SOLAS	Surface Ocean – Lower Atmosphere Study
UB	University of Bristol, Bristol, England, UK
UCSD	University of California at San Diego, La Jolla, California, USA
UEA	University of East Anglia, Norwich, England, UK
UH	University of Heidelberg, Heidelberg, Germany
TU	Tohoku University, Sendai, Japan
UW	University of Wollongong, Wollongong, NSW
UTAS	University of Tasmania, Hobart, Tasmania
WMO	World Meteorological Organization
AEST	Australian Eastern Standard Time
BEVS	Baseline Events Switch
CCN	Cloud CN
CN	Condensation Nuclei
$\delta^{13}\text{C}$	relative isotopic ratio $^{13}\text{C}/^{12}\text{C}$
GC	Gas Chromatograph
GRIMCO	CGBAPS computing system
HP	Hewlett Packard
NDIR	Non-Dispersive InfraRed
UV	Ultraviolet
ppm	parts per 10^6
ppb	parts per 10^9
ppt	parts per 10^{12}
‰	per mil, parts per 10^3
V-PDB	international scale for expressing C and O isotopic composition relative to PDB carbonate