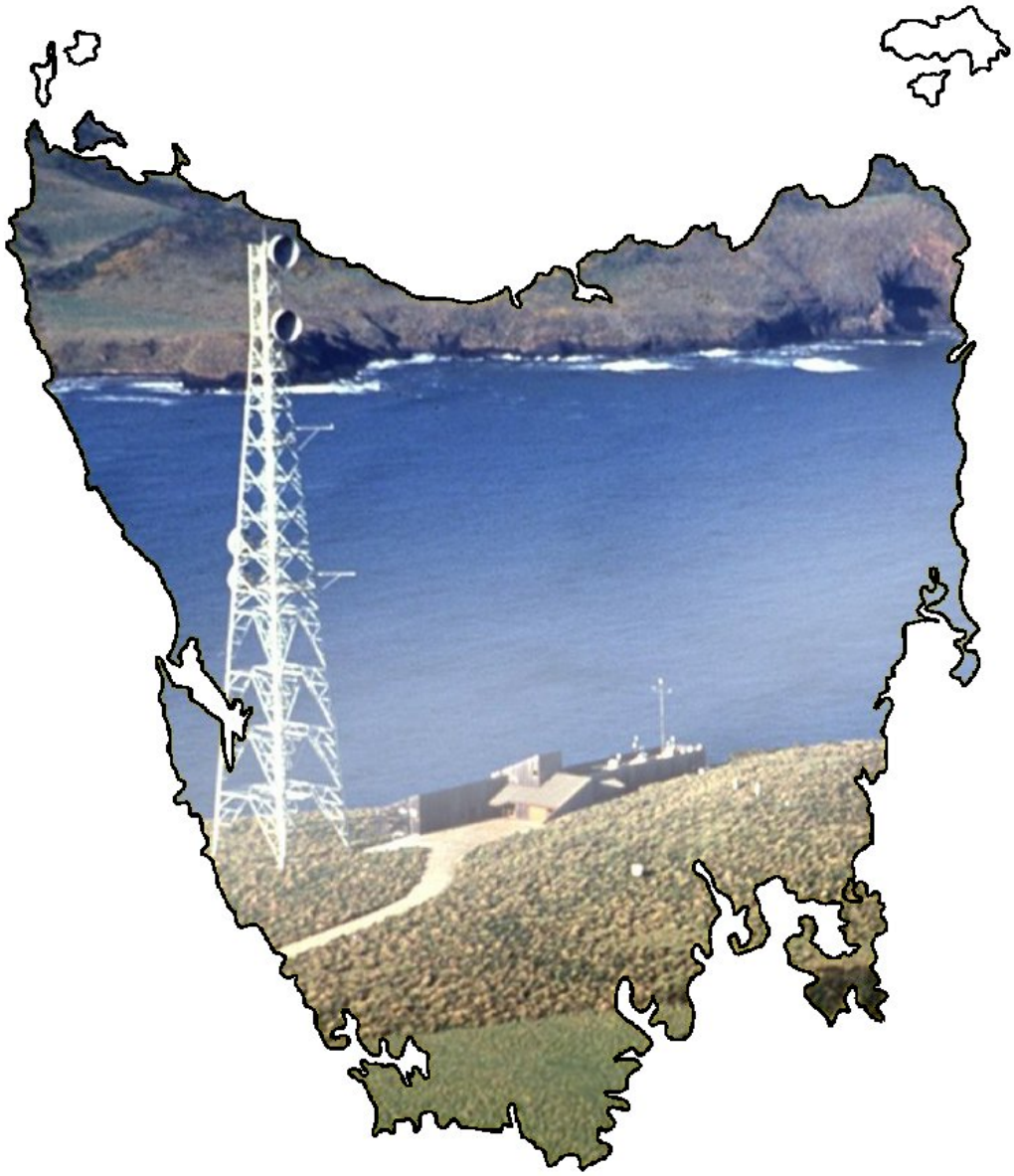
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CSIRO

Cape Grim Baseline Air Pollution Station
Annual Science Meeting 2006

ABSTRACTS



Edited by
Paul Krummel, Nada Derek & Jill Cainey

CSIRO Marine and Atmospheric Research
Hobart, Tasmania
23 – 24 November 2006

Cape Grim Baseline Air Pollution Station
Annual Science Meeting 2006

CSIRO Marine and Atmospheric Research
Hobart, Tasmania

23 – 24 November 2006

Thursday, 23rd November		
Chair	***Paul Fraser***	
09:00	Convenors	General information on arrangements etc.
09:10	John Gunn Steve Pendlebury	Welcome and opening of meeting
09:20	Roger Francey	What is causing the recent high CO_2 growth?
09:45	Michael Raupach	The global carbon cycle: drivers, dynamics and vulnerabilities
10:10	Marcel van der Schoot	Performance of the LoFlo continuous CO_2 analysers: Recent results from Cape Grim and Macquarie Island
10:35	**Morning Tea**	**Provided**
11:00	Andrew Smith	The atmospheric and soil gas $^{14}CO_2$ program at ANSTO
11:25	Wlodek Zahorowski	Radon-222 observations in the Cape Grim baseline sector in 2001-2005
11:50	Mick Meyer	Data filtering approaches for surface ozone time series from Cape Grim and Aspendale
12:15	Paul Krummel	Current status of the 2006 Antarctic ozone hole
12:40	**Lunch**	**Own Arrangements**
Chair	***Jill Cainey***	
13:40	David Hofmann	New indices for climate forcing and ozone depletion
14:05	Paul Fraser	Changes in radiative forcing and ozone depletion driven by changes in trace gas composition of the background atmosphere, from pre-industrial times to the present
14:30	Ian Galbally	Known and unexplored organic constituents in the Earth's atmosphere
14:55	Stephen Wilson	The UoW FTIR trace gas analyzer: progress report. Performance and measurements at Lauder New Zealand
15:20	**Afternoon Tea**	**Provided**
15:45	Ben Miller	The AGAGE GC-MS-Medusa system – recent improvements
16:10	Laurie Porter	Measurement of selected atmospheric trace gases using gas chromatography with the Valco pulsed discharge ionisation detector
16:35	Paul Fraser	Emissions of greenhouse gases and ozone depleting chemicals from the Rye landfill site
17:00	Paul Fraser	Global emissions of halons from AGAGE, NOAA and SIO data
17:25	**Close of Papers**	
19:00	**Meeting Dinner**	**Mezethes Greek Restaurant** **Shop 23, 77 Salamanca Arts Cntr, Salamanca Place (6224 4601)**

Cape Grim Baseline Air Pollution Station
Annual Science Meeting 2006

CSIRO Marine and Atmospheric Research
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Friday, 24th November		
Chair	***Stephen Wilson***	
09:00	Convenors / Hosts	
09:05	Jill Cainey	Particle formation at Cape Grim: Is kelp important?
09:30	Michael Grose	The marine methyl iodide source at Cape Grim
09:55	Ed Butler	The importance of ground stations, such as CGBAPS, in assessing aerosols as source of micronutrients to the Southern Ocean - a prospective project
10:20	Ian Galbally	VOCs, ozone and nitrogen oxides during the Precursors to Particles Campaign
10:45	Ken Ridgway	Oceanic Influences on the waters near Cape Grim
11:10	**Morning Tea**	**Provided**
11:30	Marcel van der Schoot	Development of a continuous oxygen analyser system at Cape Grim
11:55	Cathy Trudinger Paul Fraser	PFC emission factors from global and Australian aluminium production
12:20	Paul Krummel	Identifying seasonal cycles of some atmospheric trace species by time series analysis of measurements made on the Cape Grim air archive
12:45	Paul Steele	An update on the recent trend of atmospheric CH_4
13:10	Colin Allison	*In situ* measurement of halocarbon species at Aspendale
13:35	**Close of Meeting**	

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M. R. Raupach and J. G. Canadell

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WHAT IS CAUSING THE RECENT HIGH CO_2 GROWTH?

R. Francey*, P. Krummel, C. Allison and P. Steele

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Abstract

Recent enhanced growth rates of atmospheric CO_2 were reported by Francey [2005] and Canadell *et al*., [submitted]. We explore the possible contributions of interannual (ENSO) and volcanic forcing to the high CO_2 growth, and use the long term CO_2 and $^{13}C/^{12}C$ [Allison and Francey, 2006] Cape Grim records to comment on the relative oceanic and terrestrial contributions to the changes.

Reference

Francey, R. J., Recent record growth in atmospheric CO_2 levels. *Environmental Chemistry*, 2(1): 3-5, doi: 10.071/EN05013, 2005.

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Allison, C. E., and R. J. Francey, Verifying Southern Hemisphere Trends in Atmospheric Carbon Dioxide Stable Isotopes, J. Geophys. Res. (in review).

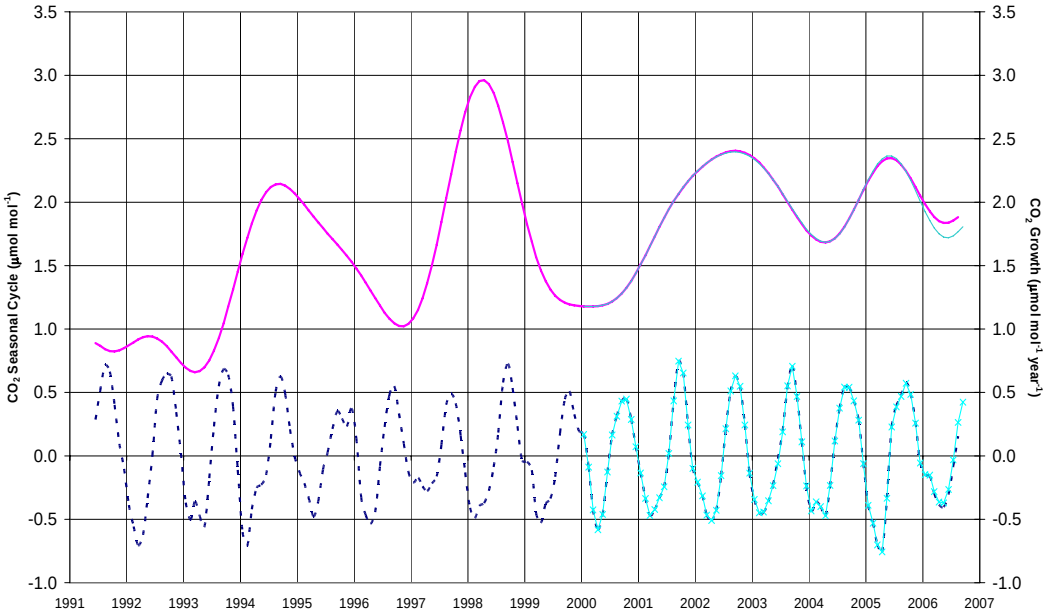


Figure 1. Recent growth in the Cape Grim CO_2 record, compared to the seasonal cycle.

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THE GLOBAL CARBON CYCLE: DRIVERS, DYNAMICS AND VULNERABILITIES

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Abstract

For most of the earth's planetary history, the global carbon cycle has played a central part in the coevolution of earth system and a carbon-based biosphere. Humans are recent but now major participants in this coevolution. Increasing human use of energy and resources is not fundamentally limited by trophic mechanisms, unlike the natural limits which have kept top predators in balance with other trophic levels in the past. Consequently we are entering a new planetary ecology, with the potential to shift the entire earth system into uncharted territory. It is appropriate to assess the vulnerabilities of the earth system to probable changes – recognising that humans are not only observers but also participants in the system. Two major kinds of vulnerability arise from the present dynamics of carbon-climate-human interactions. The first is biophysical: how will the exchanges of carbon between major pools (atmospheric, terrestrial, oceanic) alter under the influence of current and projected earth system changes, and how will they feed back on climate? The second kind of vulnerability stems from human resource use (primarily fossil fuel consumption and land use change) and associated human behavioural norms.

This talk will present recent data on trends in fossil-fuel emissions of CO_2, and new analyses of links between ENSO, volcanic activity and the terrestrial and ocean sinks of CO_2. Implications for the CO_2 airborne fraction will be drawn.

Finally, the talk will assess the growing gap between behavioural scenarios that are "expected" (likely or predicted) and 'stabilising' (required to stabilise the earth system in the new, human-dominated planetary ecology). Strategies for closing this gap include technical, economic, policy and cultural elements.

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PERFORMANCE OF THE LOFLO CONTINUOUS CO_2 ANALYSERS: RECENT RESULTS FROM CAPE GRIM AND MACQUARIE ISLAND

M. van der Schoot[1*], P. Steele[1], R. Francey[1], D. Spencer[1], L. Porter[1†], S. Baly[2], C. Rickard[2], B. Wastine[3] and M. Schmidt[3]

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[2]*Cape Grim Baseline Air Pollution Station, Australian Bureau of Meteorology, Smithton, Tasmania*
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Abstract

The CSIRO-developed LoFlo CO_2 analyser is a high precision and continuous atmospheric CO_2 analysis system [Da Costa and Steele, 1999]. Compared to conventional systems it exhibits improvements in measurement precision, at the same time reducing consumables and the requirement for operator intervention. There is potential for the system to greatly improve atmospheric monitoring traceability and network comparability [Francey and Steele, 2003].

A LoFlo analyser at Cape Grim Baseline Air Pollution Station is the central element in a planned Southern Ocean regional atmospheric CO_2 network (currently includes LoFlo instruments operating at Cape Grim, Macquarie Island and Amsterdam Island). This network is being established to resolve the small atmospheric CO_2 spatial gradients and the possible changes of CO_2 fluxes in this important region [Matear and Hirst, 1999].

An 'overlap' experiment was conducted at Cape Grim (July to November 2005), involving two individually calibrated LoFlo analysers (identified here as LoFlo 2A and LoFlo 2B, each one operating with its own suite of calibration gases). The seven high-pressure, CO_2-in-dry air calibration standards used for LoFlo 2B were calibrated at the WMO Central CO_2 Calibration laboratory at NOAA ESRL/GMD [Zhao *et al*., 1997]. The seven-cylinder calibration suite of LoFlo 2A was calibrated intensively against the LoFlo 2B calibration suite. The analysers continuously monitored marine boundary layer air from a shared single air intake. The results demonstrate very good agreement between the two instruments. The overall result is highly encouraging, and supports an expectation that it will be possible to propagate a central calibration scale with improved precision with an immediate application in the Southern Ocean CO_2 network. We present the results from this overlap experiment, in addition to preliminary results from the recent LoFlo atmospheric CO_2 measurements made simultaneously at Cape Grim and Macquarie Island.

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Da Costa G A, and L. P. Steele, A low-flow analyser system for making measurements of atmospheric CO_2, in *Report of the ninth WMO Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurements*, R. J. Francey (editor), (Environmental Pollution Monitoring and Research Programme/Global Atmosphere Watch, 132; WMO/TD; no. 952), Secretariat of the World Meteorological Organization, Geneva, Switzerland, 16-20, 1999.

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Acknowledgements

The authors gratefully acknowledge important contributions from: P. Krummel, R. Langenfelds, B. Petraitis, R. Howden, J. Bennett, H. Davies, I. Morrissey and C. Smith from CSIRO Marine and Atmospheric Research, Aspendale, B. Tilbrook from CMAR, Hobart, and Fiona Phillips, Greg Stone, Peter Mantel and Tim James from the Australian Bureau of Meteorology, Macquarie Island.

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THE ATMOSPHERIC AND SOIL GAS $^{14}CO_2$ PROGRAM AT ANSTO

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Abstract

In 2002, ANSTO and CSIRO Atmospheric Research undertook a pilot project to assess the possibility of measuring the ^{14}C of CO_2 in the residual air from 0.5L GASLAB flasks, following the usual suite of GASLAB measurements. Additionally, we measured ^{14}C of CO_2 in breakseals collected at the Cape Grim Baseline Station (Smith 2002 & 2003). These results were promising, but highlighted the need for larger air samples if high precision results are required.

Following a hiatus, there is renewed interest in further developing this capability at ANSTO. One new area of application is the potential for 14CO2 analyses of soil gas and air to monitor geosequestration programs, such as that been undertaken by the Cooperative Research Centre for Greenhouse Gas Technologies (CO2-CRC) in the Otway Basin, Western Victoria. We report on the technical development of 14C of CO2 at ANSTO and discuss some of the applications of this capability.

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Smith, A. M., R.J. Francey, I. Levin, Q. Hua, U. Zoppi, D.M. Etheridge and A.A. Williams, Monitoring contemporary Southern Ocean atmospheric $^{14}CO_2$ by AMS, *18th International Radiocarbon Conference*, 1st - 5th September 2003, Wellington, New Zealand.

Smith, A. M., Accelerator Mass Spectrometry: an overview of the technique and of small-mass 14C Antarctic projects at ANTARES, in Cape Grim Baseline Air Pollution Station [CGBAPS] Annual Science Meeting [abstracts], 7-8 November 2002, Aspendale, Victoria.

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RADON-222 OBSERVATIONS IN THE CAPE GRIM BASELINE SECTOR IN 2001-2005

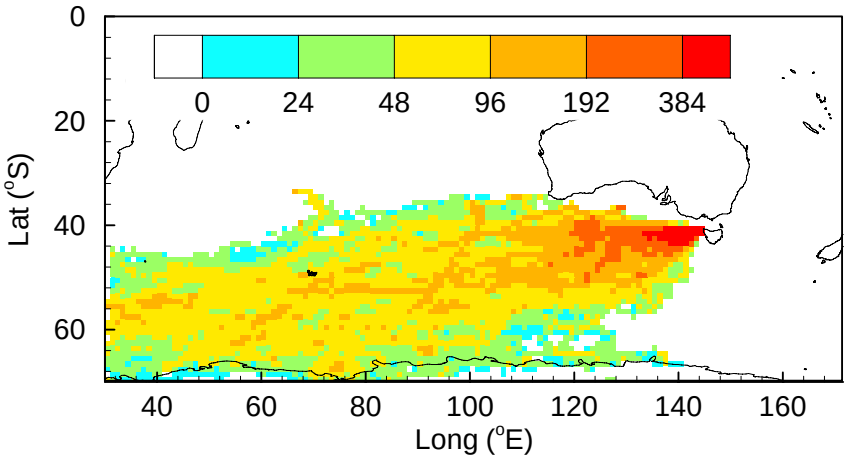
W. Zahorowski*, S. Chambers, J. Crawford and S. Werczynski

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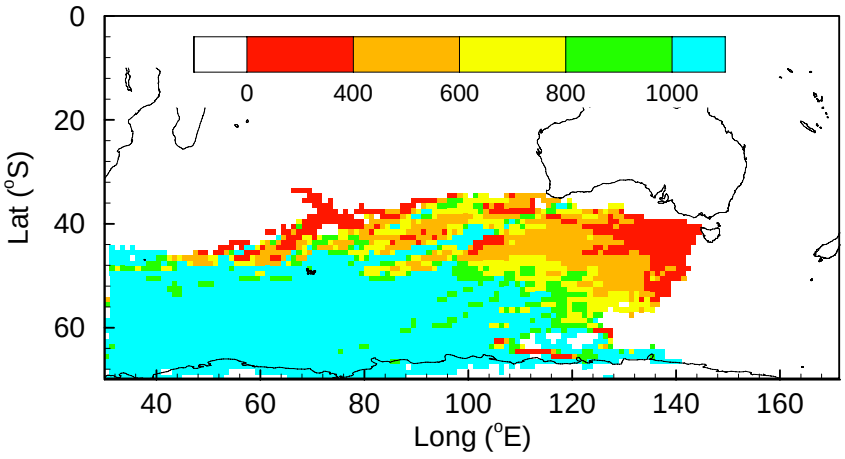
Abstract

A distinctive feature of radon concentrations recorded in Cape Grim's baseline sector is their dependence on the length of time the local wind direction has persisted within that sector. It can be shown that hourly radon concentrations measured during periods when baseline conditions had persisted for between 2 to 4 days, the corresponding air parcels represent the least perturbed oceanic air.

We explore various properties of these persistent baseline events in the 2001-2005 radon dataset by utilising horizontal and vertical projections of their corresponding 10 day back trajectories. Both seasonal and inter-annual trends are analysed. Examples of the analysis included below show contour maps (based on values centred in 1°x1° grid cells) depicting the degree to which oceanic areas potentially affect the composition of oceanic air analysed at Cape Grim (top panel) and the air parcels' median height (bottom panel).



Top panel:
Back trajectory density function for baseline sector observations at Cape Grim. The contour map indicates the number of times a 1°x1° grid cell has been traversed by a baseline sector event trajectory.



Bottom panel:
Estimate of median air parcel heights based on values centred in 1°x1° grid cells derived from 10 day back trajectories corresponding to baseline events.

Both plots show contributions from baseline events persisting for between 2 and 4 days in the sector during the composite Southern Hemisphere spring (2001-2005).

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DATA FILTERING APPROACHES FOR SURFACE OZONE TIME SERIES FROM CAPE GRIM AND ASPENDALE

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[2]*Environment Protection Authority Victoria, Centre for Environmental Sciences, MacLeod, Victoria*

Abstract

The surface ozone monitoring system has been operating at Cape Grim sin 1982 with near 100% data capture. A comprehensive time series filtering algorithm was developed and tested in 1986 to identify and remove bad data while retaining all valid data. This algorithm has been applied to the Cape Grim time series to the present. Surface ozone concentrations are also routinely monitored at air quality stations operated by the Victorian Environmental Protection Authority in the urban airshed, at CSIRO Aspendale in the Bayside Air Quality Monitoring Station. The short-term and diurnal variability ozone concentrations in urban air is considerably more complex than in Rural/background air a poses additional challenges to the development of data filtering algorithms for quality control (QC). In this paper we reanalyse the performance of the QC methodology at Cape Grim and compare it to the options appropriate for the more dynamic time series observed in the Melbourne Airshed.

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CURRENT STATUS OF THE 2006 ANTARCTIC OZONE HOLE

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Abstract

During each spring in the Southern Hemisphere a stratospheric ozone hole forms over Antarctica, due primarily to the fast catalytic destruction of ozone by chlorine and bromine radicals released from the breakdown of ozone depleting substances such as chlorofluorocarbons (CFCs) and halons. The levels of chlorine and bromine radicals are enhanced with respect to non-polar regions of the stratosphere by fast heterogeneous chemistry on polar stratospheric clouds (PSCs). The hole has grown in area and depth over the past two decades, but its size varies from year to year due to variations in meteorology, solar activity and the aerosol loading of the stratosphere.

One of the longest running global satellite borne total column ozone datasets is the TOMS (Total Ozone Mapping Spectrometer) series, which has been flown on a succession of satellite platforms, beginning with Nimbus 7 (1978-1993), Meteor 3 (1991-1994) and ending most recently with Earth Probe (1996-2005). This long-term dataset is one of several that have traditionally been used each year by scientists to estimate the size and depth (or severity) of the spring-time Antarctic ozone hole.

On July 15 2004, the Earth Observing Satellite (EOS) Aura was launched by NASA into a near polar, sun-synchronous orbit with a period of approximately 100 minutes. Onboard Aura are several dedicated atmospheric chemistry instruments, including the Ozone Monitoring Instrument (OMI). OMI will continue the TOMS record for total ozone and other atmospheric parameters related to ozone chemistry and climate. The NASA TOMS Version 8 algorithm has been applied to the OMI data to ensure continuity of the long-term data record.

In the presentation we will show the development and current status of the 2006 ozone hole based on the OMI satellite data. To ascertain any calibration or other differences between the TOMS and OMI instruments, a comparison of the ozone hole minima and area metrics using both datasets for 2005 will also be shown. Given these results, we will then compare the 2006 ozone hole metrics from the OMI data with the historical TOMS data.

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NEW INDICES FOR CLIMATE FORCING AND OZONE DEPLETION

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Abstract

For the past 30 years, the U.S. National Oceanic and Atmospheric Administration (NOAA) has monitored climate-forcing and ozone-depleting atmospheric gases. These global measurements have provided input to climate and ozone assessments (e.g., the quadrennial IPCC Climate Reports and WMO/UNEP Ozone Assessments). Recently, efforts to make these data more useful and available have been undertaken through release of the NOAA Annual Greenhouse Gas Index (AGGI), http://www.cmdl.noaa.gov/aggi, and the Ozone Depleting Gas Index (ODGI) http://www.cmdl.noaa.gov/odgi. These indices are designed to enhance the connection between scientists and society by providing a normalized standard that can be easily understood and followed. The contribution of these long-lived gases to climate forcing and ozone depletion are well understood by scientists; nevertheless, the language of scientists often eludes policy makers, educators, and the general public. The atmospheric chemical indices are designed to help bridge that gap. Data are obtained through continuous measurements at baseline climate observatories at Pt. Barrow, Alaska; Mauna Loa, Hawaii; American Samoa; and the South Pole. In addition, flask air samples are collected through global networks, including an international cooperative program for carbon gases. The concepts of radiative climate forcing and equivalent chlorine are used to build the greenhouse gas and ozone-depleting indices, respectively.

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CHANGES IN RADIATIVE FORCING AND OZONE DEPLETION DRIVEN BY CHANGES IN TRACE GAS COMPOSITION OF THE BACKGROUND ATMOSPHERE, FROM PRE-INDUSTRIAL TIMES TO THE PRESENT

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Abstract

Measurements of the major greenhouse gases (CO_2, CH_4, N_2O, HFCs, PFCs, SF_6) and ozone depleting chemicals (CFCs, HCFCs, halons, CH_3Br, CH_3CCl_3, CCl_4) have been made at Cape Grim, Tasmania, since 1976 and on air samples from Antarctic firn and ice since pre-industrial times. From the resultant data describing the long-term concentration trends in the background atmosphere, changes in the radiative forcing (the major driver of climate change) and equivalent chlorine (the major driver of ozone depletion) of the background atmosphere can be made. These will be discussed and compared to long-term changes in temperature in the lower atmosphere and ozone changes in the stratosphere.

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KNOWN AND UNEXPLORED ORGANIC CONSTITUENTS IN THE EARTH'S ATMOSPHERE

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Ecosystem Sciences Division, University of California, Berkeley, California, USA

Abstract

Recent research, when considered as a whole, suggests a substantial fraction of both gas phase and aerosol atmospheric organics have not been, or have very rarely been, directly measured. Even though our knowledge of them is limited, the compounds we refer to clearly influence the reactive chemistry of the atmosphere and the formation, composition, and climate impact of aerosols. A review of the global budget for organic gases shows that we cannot account for the loss of approximately half the non-methane organic carbon entering the atmosphere. We suggest that this unaccounted for loss most likely occurs through formation of secondary organic aerosol (SOA), indicating an order of magnitude larger source for this aerosol than current estimates. A major challenge in the coming decade of atmospheric chemistry research will be to elucidate the sources, structure, chemistry, and fate of these clearly ubiquitous yet poorly constrained organic atmospheric constituents.

Here we review current knowledge about atmospheric organic constituents through the following questions:

i) What atmospheric organic compounds do we know about and understand?

ii) What organic compounds could be present as gases and in aerosols?

iii) What evidence exists for additional organic compounds in the atmosphere?

iv) How well do we understand the transformations and fate of atmospheric organics?

We conclude by suggesting opportunities for future research directions.

Reference

Goldstein, A. H. and I. E. Galbally, Known and unexplored organic constituents in the Earth's atmosphere, Invited feature article, *Environmental Science and Technology*, accepted for publication 18 October, 2006.

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THE UOW FTIR TRACE GAS ANALYZER: PROGRESS REPORT PERFORMANCE AND MEASUREMENTS AT LAUDER NEW ZEALAND

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Abstract

In the past 2 years we have developed "2G", the second generation FTIR trace gas analyser. Like its predecessor, the analyser is able to measure CO_2, CH_4, CO, N_2O and H_2O vapour simultaneously with high precision in ambient air, as well as $\delta^{13}C$ in CO_2 (in dried air) and δD in H_2O. The new instrument is based on a new FTIR interferometer, the Bruker 'IRcube', and has several advantages:

- TE-cooled IR detector – no need for liquid nitrogen
- Tight purge, only minimal purge gas required (0.1L min-1 requires 1 x G cylinder every 2 months)
- Nafion + $MgClO_4$ airstream drying, very low drying agent consumption
- More compact and 'shippable' – works out of the box.
- Minimal operator intervention.

The first unit has been operating at NIWA Lauder lab in NZ since July 2006 making continuous 10 minute-average measurements. Sample measurements from this dataset will be presented to illustrate the performance and data quality. Typical accuracy and precision are summarized below.

We are currently building 3 further units, one for the TCCON/OCO CO_2 remote sensing site in Darwin, one for transects on the Ghan railway (also available for general use such as trials at Cape Grim), and a custom version to measure δD in atmospheric water vapour (for ANSTO).

Table 1. Typical short term precision and 24 hr drifts (indicative values only)

Species	Short term precision (1σ, minutes)	Drift (24 hours)^
CO_2	<0.1ppmv	<0.5ppmv
CH_4	< 1 ppbv	<1 ppbv
CO	1ppbv	1ppbv
N_2O	<0.2ppbv	<0.2 ppbv
$\delta^{13}C$-in-CO_2	0.1‰	<0.5‰
δD in H_2O vapour	< 1‰	1‰

^ current improvement is focused on improving calibration drift

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THE AGAGE GC-MS-MEDUSA SYSTEM - RECENT IMPROVEMENTS

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Abstract

The Medusa gas chromatograph-mass spectrometer (GC-MS) automated instrument systems have been developed for the Advanced Global Atmospheric Gases Experiment (AGAGE) network of baseline atmospheric trace gas measurement stations, including for Cape Grim, where Medusa measurements began in January 2004. The Medusa instruments employ a custom-designed cryogenic trace gas trapping and pre-concentration system, customised control of the Agilent capillary-column gas chromatograph and quadrupole mass spectrometer, and integrated software for instrument control and operating diagnostics, data processing and management. They are currently configured to measure more than 40 atmospheric trace gas species (including CFCs, HCFCs, HFCs, PFCs, halons, chlorocarbons, bromocarbons, one iodocarbon, SF_6, and hydrocarbons) in a 2-litre air sample, with an analysis time of one hour. By alternating between ambient air sample and standard air calibration measurements, the Medusa systems measure 12 ambient air samples per day. The Medusa instruments were developed at the Scripps Institution of Oceanography (SIO), and have subsequently been refined as a result of our accumulated experience from the field operation of six AGAGE instruments. After a brief overview of the Medusa system and its operation, these refinements will be described, and some examples of Medusa data will be presented.

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MEASUREMENT OF SELECTED ATMOSPHERIC TRACE GASES USING GAS CHROMATOGRAPHY AND THE VALCO PULSED DISCHARGE IONISATION DETECTOR

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Abstract

In CSIRO's GASLAB, and at the Cape Grim Baseline Air Pollution Station, packed column gas chromatography (GC) has been used for many years as a technique for making measurements of atmospheric trace gases. For measurements of methane, the detector of choice has been the flame ionisation detector (FID). For GC measurements of carbon dioxide, the FID has also been used as the detector, but a high temperature (400C) catalytic conversion is required of the column-separated carbon dioxide to methane. Carbon monoxide and hydrogen have been measured using the Trace Analytical heated mercuric oxide detector, while nitrous oxide has been measured using the electron capture detector (ECD). While these detectors have proven to be reliable in these applications over many years, some limitations are becoming apparent.

In this presentation, the experiences so far in trials of the Valco pulsed discharge helium ionisation detector (PDHID), as a potential replacement for the FID, ECD, and mercuric oxide detector, in measurements of methane, carbon dioxide, carbon monoxide, hydrogen, and nitrous oxide by packed column GC will be described. Briefly, the PDHID has the advantage of being highly sensitive, and effectively behaves as a universal detector. But the universal response has introduced difficulties which are not so severe with the other detectors. In particular, the large (and tailing) chromatographic peaks for nitrogen and oxygen present challenges for improved column separation for those species eluting soon after the oxygen and nitrogen. The strong response of the PDHID to oxygen and nitrogen make the technique particularly sensitive to leaks anywhere in the GC system. The response of the PDHID to the noble gases present in the atmosphere requires very good column resolution to avoid interferences with the targeted species. Good temperature control of the detector and key plumbing components is required for best results.

Results will be presented for measurements of hydrogen, which show great promise. Hydrogen elutes prior to oxygen and nitrogen on the selected packed columns, and so is not subject to the difficulties of the tailing oxygen and nitrogen peaks. Precisions (repeatabilities) of 0.1% have been achieved with hydrogen mixing ratios of approximately 500 parts per billion in dry air. Linear response over a 20-fold range in hydrogen mixing ratios has been found.

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EMISSIONS OF GREENHOUSE GASES AND OZONE DEPLETING CHEMICALS FROM THE RYE LANDFILL SITE

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Abstract

Landfills are potentially significant urban sources of non-CO_2 greenhouse and ozone depleting gases. Flux chamber experiments commenced in mid-2006 at the Rye landfill site, 60 km south of Melbourne, to estimate the emissions of these gases form a typical landfill site. As expected, CH_4 dominates the non-CO_2 greenhouse gas emissions, but many other trace gases are seen escaping from the landfill. The emissions are highly variable spatially, and depend on the type of soil cover. Some emissions associated with the commercial production of mulch will also be discussed.

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GLOBAL EMISSIONS OF HALONS FROM AGAGE AND NOAA DATA

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Abstract

Halons are a very significant source of the bromine that plays a major role in stratospheric ozone depletion at mid-to-high latitudes. Halons have been measured since the mid-to-late 1990s at Cape Grim and other global sites in both the NOAA flask sampling program and the AGAGE *in situ* GC-MS program. The AGAGE and NOAA global data will be reviewed and compared. Estimates of global emissions of halons from both the NOAA and AGAGE data will be discussed.

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ANALYSIS OF RADON-222 OBSERVATIONS IN THE CAPE GRIM MAINLAND SECTOR IN 2001-2005

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Abstract

Conventionally, Mainland events at Cape Grim are defined by local wind directions higher than 280° and lower than 90°. We explored both horizontal and vertical projections of air parcel trajectories corresponding to hourly Mainland events thus defined in the 2001-2005 dataset. We observed that Mainland event trajectories can be further subdivided as follows: (a) events that cross the mainland (45%); (b) events entirely over water (34%); (c) events that cross Tasmania (13%); and (d) others (8%), which cross both the mainland and Tasmania. We analysed how this partitioning of Mainland events changes seasonally and annually, and found distinctive seasonal trends.

Using back trajectories we calculated the Potential Source Contribution Functions of each category of Mainland event on a 1°x1° grid and analysed the resulting contour maps to further investigate their seasonal and annual footprints, heights, and radon distributions. Figure 1a shows an example of the footprint of category (a) Mainland events in the 5-year composite spring. Such maps define geographic areas which, notwithstanding other factors including regional source functions, contribute in various degrees to atmospheric species' concentrations measured at Cape Grim.

We also explored radon concentration distributions corresponding to the above four categories of Mainland events. The example in Figure 1b shows radon concentration distributions for all category (b) Mainland events in 2001-2005 as a function of local wind direction. There is a clear trend to higher radon concentrations as the local wind direction swings from West to East. Such distributions provide a measure of the influence of the Australian mainland and Tasmania on radon concentrations in marine perturbed air in Bass Strait.

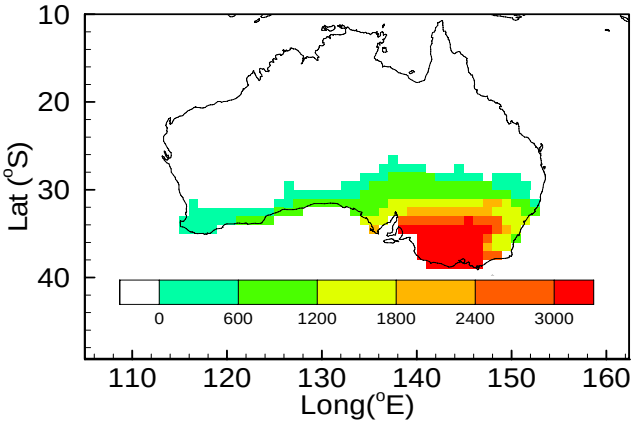


Figure 1a. Back trajectory density function (or footprint) for category (a) Mainland sector observations at Cape Grim. Plot indicates the number of times a 1°x1° grid cell has been traversed by a Mainland sector event trajectory during composite Southern Hemisphere spring (2001-2005).

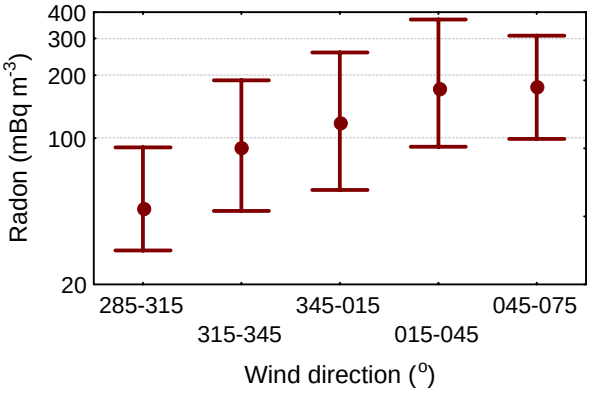


Figure 1b. Radon concentration distributions (medians and quartile ranges) in category (b) Mainland sector events as a function of direction in which they approach Cape Grim in 2001-2005.

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HOURLY VERTICAL RADON-222 GRADIENT ESTIMATES FROM A 50M TOWER AT LUCAS HEIGHTS

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Abstract

Vertical radon profiles can be used to quantify mixing and exchange of air in the lower atmosphere. The Australian Nuclear Science and Technology Organisation has recently developed a comprehensive system for measuring vertical radon profiles throughout the atmospheric boundary layer and lower free troposphere up to about 3000m above ground level. The system comprises continuous tower-based measurements of hourly radon gradients at two sites (Lucas Heights, NSW and Cabauw, the Netherlands), as well as airborne measurements from a radon sampler designed to be mounted on light aircraft such as motorised gliders. The airborne system is complemented by a laboratory-based radon rig equipped with 24 counting channels.

Our ultimate aim is to contribute to improved parameterisation schemes for vertical transport processes in regional and global models using radon as the tracer of choice of these processes.

We report results from the first year of hourly observations of the vertical radon gradient from a 50m tower at Lucas Heights. The lower and higher inlets on the tower are mounted at 2m and 50m, respectively. Due to the time scale of interest, the gradient is estimated using two independent radon detectors (Figure 1a) rather than a multiplexing system. An example of the resultant time series is included in Figure 1b, which shows two consecutive periods where large radon gradients are observed as a result of the nocturnal boundary layer depth decreasing to below 50m.



Figure 1a. The 2-50m radon gradient in the surface layer is characterised using a pair of 1500L detectors at Lucas Heights.

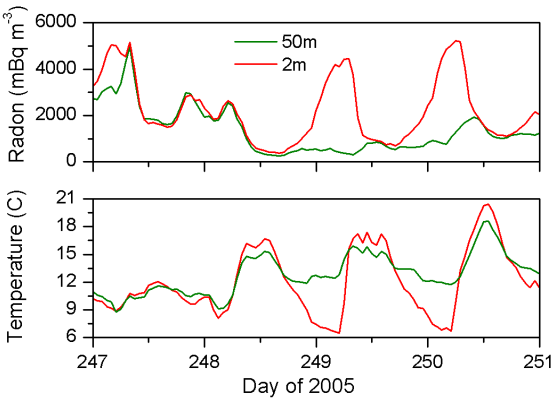


Figure 1b. Changes in wind speed and thermal stratification often result in the depth of the stable nocturnal boundary layer reducing to less than 50m above ground level resulting in a large radon gradient.

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A NETWORK OF COLLOCATED RADON-222 DETECTORS AND FINE PARTICLE SAMPLERS IN THE GREATER SYDNEY REGION AND CAPE GRIM

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Abstract

The first Australian system comprising a fine particle sampler and a radon detector has been in operation at Cape Grim since 1992. We established and operated similar systems at each of three stations in East Asia during the Aerosol Characterisation Experiment in 2001-2003.

Earlier in 2006 we completed commissioning a new network of radon detectors at four sites in the greater Sydney region. These detectors are also collocated with fine particle samplers and, together with the system at Cape Grim, will provide a unique opportunity for a comprehensive multi-year evaluation of atmospheric pollution and location of its sources in the most populated region in Australia. The measurement sites were selected based on the following criteria: (a) locations progressively further from the coast and associated oceanic influence; (b) a combined footprint that ensures adequate coverage of the study domain; and (c) an established multi-year record of fine particle sampling. The resulting collection of sites is shown in Figure 1a. An example installation of a radon detector and fine particle sampler is shown in Figure 1b.

We present details of the system and discuss the radon observations made in the first few months of operation of the new system.



Figure 1a. Network of collocated radon detectors and fine particle samplers in the greater Sydney region.



Figure 1b. Collocated radon detector (left) and fine particle sampler (right) at Muswellbrook, NSW.

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PARTICLE FORMATION AT CAPE GRIM: IS KELP IMPORTANT?

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Abstract

During February 2006 a 4 week SOLAS campaign focusing on new particle formation in the clean marine boundary occurred at the Cape Grim Baseline Air Pollution Station, Tasmania.

Additional measurements during the campaign included boundary layer profiling, DOAS measurements, a suite of particle measurements, measurements of gaseous volatile organic precursor compounds including methyl halides and DMS and the concentration of atmospheric oxidants including ozone and NOx. Data on marine biological activity along 5km boat transects along 270° off Cape Grim and from the adjacent beach were performed. DOAS and particle number measurements were also made on the beach.

During the campaign baseline conditions dominated, interrupted only by the passage of one front and a smoke plume from a local bushfire. Particle formation events and their precursors were difficult to detect in baseline air either at the Station, 94 m above the ocean surface, or on the beach. The smoke plume showed a significantly different signature in gaseous species and concentration and particle size distributions and composition.

In an effort to understand the limiting factors in new particle formation flux chamber studies were performed and further flux chamber work and a marine ecological survey of the waters below the Cape Grim Station are planned for late November.

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THE MARINE METHYL IODIDE SOURCE AT CAPE GRIM

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Abstract

Iodine from a coastal marine source is thought to be a significant contributor to particle formation processes from work done at Mace Head. The importance of iodine at Cape Grim is of great interest, and was the subject of the 'Precursors to Particles' campaign, February 2006. A significant component of the iodine source at Cape Grim is the biological production and emission of methyl iodide.

Ongoing work characterising the biological source of methyl iodide that is detected at the station is presented here, including measurements made during the P2P campaign. The source of methyl iodide from kelp was found to be significant, and there is indirect evidence that it may contribute to new particle formation processes.

This source is highly localised and variable, depending at least partially on tide. Other controlling environmental variables on kelp production remain unidentified. Measurements of production from phytoplankton are also presented, including work done from inshore to coastal oceans and the open Indian Ocean southwest of Tasmania. The large scale distribution of the marine methyl iodide source are shown, and the implications for atmospheric processes are discussed.

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THE IMPORTANCE OF GROUND STATIONS, SUCH AS CGBAPS, IN ASSESSING AEROSOLS AS A SOURCE OF MICRONUTRIENTS TO THE SOUTHERN OCEAN - A PROSPECTIVE PROJECT

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Abstract

The Southern Ocean is seen as not being biologically productive to its full potential; it is often described as a 'high-nutrient, low-chlorophyll' region.

One of the main reasons for this is the deficiency of iron, and possibly other trace metals (micronutrients), in surface waters that hampers phytoplankton primary production. Current research is assessing the distribution of iron and its cycling in the Southern Ocean. The delivery of iron to surface waters is either through vertical advection (upwelling) of iron-rich deeper waters, or via wind-blown terrigenous dusts. Current estimates suggest that the former is greater than the latter in the Southern Ocean, but the significance of dust transport is yet to be reliably evaluated in the Australian region. We are planning to collect and analyse aerosols to the south of Australia to investigate this pathway. In this presentation, we shall outline current research and the prospective program for the study of aerosols.

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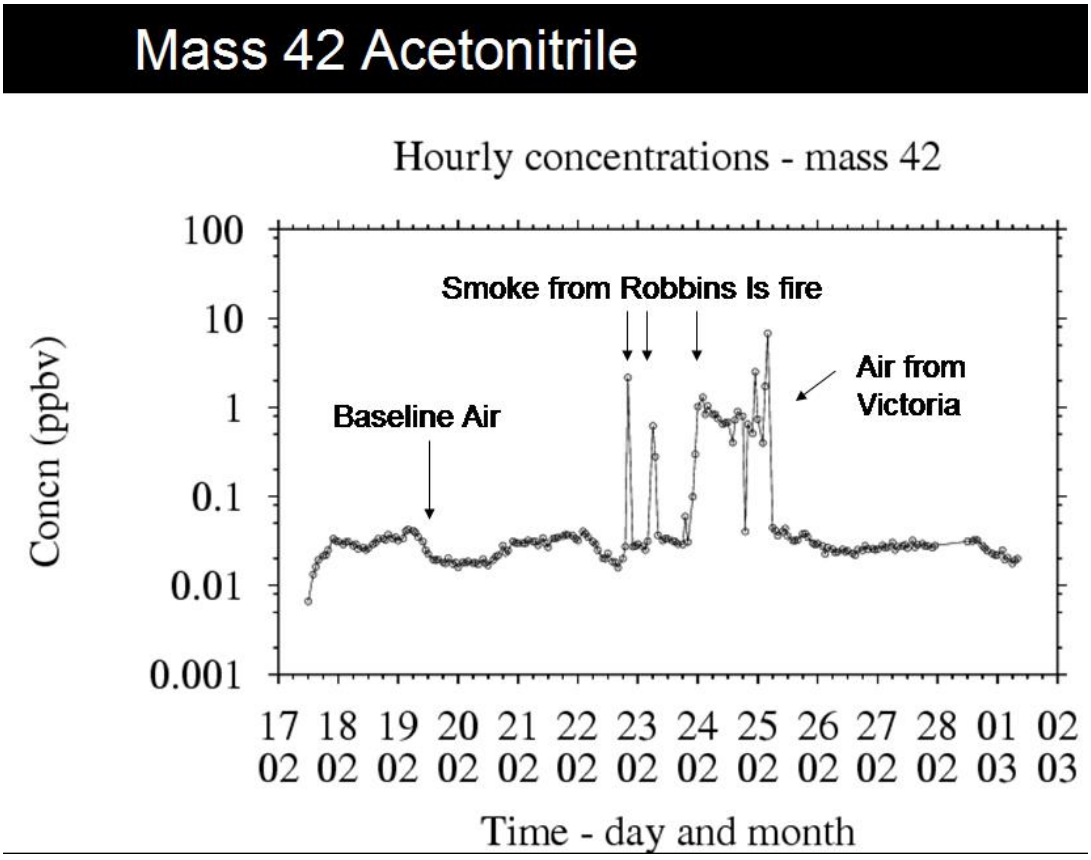
VOCs, OZONE AND NITROGEN OXIDES DURING THE PRECURSORS TO PARTICLES CAMPAIGN

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Abstract

During the Precursors to Particles (P2P) Campaign in February 2006 measurements were made of volatile organic compounds (VOCs) at Cape Grim using Proton Transfer Reaction Mass Spectrometry (PTR-MS), as well as by active adsorption tube sampling followed by gas chromatography mass spectrometry analysis. Successful measurements of fifteen VOCs were made by PTR-MS during the period 17th February to 1 March 2006. Approximately 8 days of clean air data were obtained (not necessarily all baseline), along with 4 days when a smoke plume from the Robbins Island fire and air from Victoria was present. An analysis of these exciting results will be presented. A sample of the data is shown below.



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OCEANIC INFLUENCES ON THE WATERS NEAR CAPE GRIM

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Abstract

The main oceanographic systems influencing the waters off the northwest coast of Tasmania are described. These include the background mean circulation, coastally trapped waves, seasonally varying currents, ENSO, decadal changes and a long term trend.

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DEVELOPMENT OF A CONTINUOUS OXYGEN ANALYSER SYSTEM AT CAPE GRIM

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Abstract

We have developed a continuous oxygen analyser system based on a commercially available differential fuel-cell analyser to make measurements of atmospheric O_2 variations, with a measurement resolution at the parts-per-million level. Atmospheric O_2 measurements complement CO_2 measurements and have proven to be valuable constraints on global carbon budgeting, marine productivity, and oceanic transport processes. A comparatively simple and fully computer controlled gas handling design was chosen with the intent to develop a robust analysis system with low operating costs. One main feature of this new analyser system compared to other existing O_2 analysers is low gas flow rates, which extends the life of calibration gases in high-pressure cylinders and facilitates the propagation of O_2 standards. By implementing frequent calibrations and active pressure, flow and temperature control, the analysis system has a 1-sigma precision of about 5 per meg (≈ 1 ppm) for a 2-minute measurement. We describe the measurement technique and gas handling procedures and present the first two months of data from the Cape Grim Baseline Air Pollution Station to illustrate the performance of the O_2 analyser.

Acknowledgements

Engineering support from Craig Smith, Ian Morrissey, and Jamie Harnwell of CSIRO Marine and Atmospheric Research is gratefully acknowledged in the construction and testing of the system. Support from the Cape Grim staff in the operational phase is also gratefully acknowledged.

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PFC EMISSION FACTORS FROM GLOBAL AND AUSTRALIAN ALUMINIUM PRODUCTION

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Abstract

Measurements at Cape Grim and on air samples from the Cape Grim air archive and from Antarctic firn have resulted in the most comprehensive record to date of the accumulation of PFC-14 (CF_4) in the southern hemisphere atmosphere. The data are used to derive global and regional emissions of PFC-14, which are then combined with aluminium production data to produce PFC emission factors for the globe and for SE Australian smelters.

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IDENTIFYING SEASONAL CYCLES OF SOME ATMOSPHERIC TRACE SPECIES BY TIME SERIES ANALYSIS OF MEASUREMENTS MADE ON THE CAPE GRIM AIR ARCHIVE

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Abstract

The Cape Grim Air Archive has proven to be a very valuable resource for determining multi-decadal trends of many atmospheric species since the first archive sample was collected in 1978. But many atmospheric species exhibit both a long-term trend and a seasonal variation. Described in this presentation are the results of time series analysis techniques, applied to measurements of selected trace species in the Cape Grim Air Archive, to investigate whether both a trend and a seasonal variation can be reliably estimated. These results are compared to those from periods when high-frequency measurements at Cape Grim are available.

The methodology is explored further by the analysis of synthetic time series, to gain insight into the influence of both the relative sparsity (3-4 samples per year) of the Cape Grim Air Archive samples, and the uncertainty ascribed to each measurement.

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AN UPDATE ON THE RECENT TREND OF ATMOSPHERIC METHANE

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Abstract

In a recent paper, [Bousquet *et al*., 2006] used an inversion model of atmospheric transport and chemistry to investigate the variability of atmospheric methane (CH_4) over the period 1984-2003, constrained by measurements of CH_4 from 68 sites worldwide. The findings of this paper will be briefly described, with a particular emphasis on the explanation for the stabilisation of atmospheric CH_4 levels during the 1999-2003 period.

Measurements from flask air samples measured in CSIRO's GASLAB, and the AGAGE *in situ* measurements show that the atmospheric CH_4 abundance has continued to remain effectively stable since 2003, with early hints of a decline at Cape Grim in 2006. These results will be presented, with some analysis and comment.

Reference

Bousquet, P., P. Ciais, J. B. Miller, E. J. Dlugokencky, D. A. Hauglustaine, C. Prigent, G. R. van der Werf, P. Peylin, E.-G. Brunke, C. Carouge, R. L. Langenfelds, J. Lathiere, F. Papa, M. Ramonet, M. Schmidt, L. P. Steele, S. C. Tyler, and J. White, Contribution of anthropogenic and natural sources to atmospheric methane variability, *Nature*, 443, 439-443, 2006.

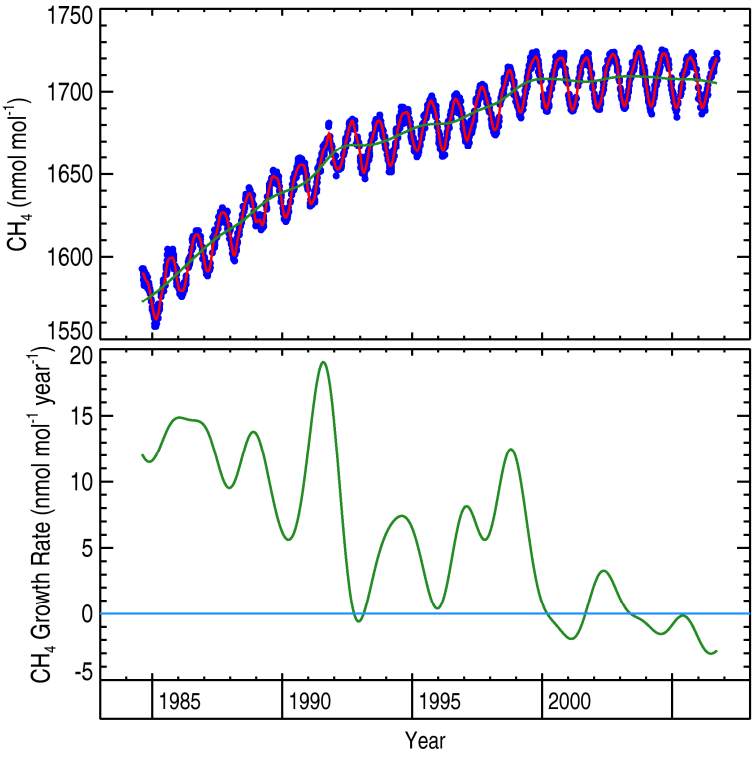


Figure 1. The top panel shows the CSIRO CH_4 flask record from Cape Grim. The blue points are individual flask measurements, the red line is a smooth curve fit to the data and the green line is the long-term trend curve fit. The bottom panel shows the corresponding instantaneous growth rate for CH_4 at Cape Grim.

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IN SITU MEASUREMENT OF HALOCARBON SPECIES AT ASPENDALE

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Abstract

In February 2005 the ADS-GCMS (adsorption/desorption system gas chromatograph/mass spectrometer) system that had been operating at Cape Grim since 1997 [Sturrock *et al.*, 2001] was installed at CMAR's Aspendale laboratory. Since then, the ADS-GCMS has been used to analyse air from the Melbourne region approximately every 4 hours. We will present results from the first 18 months of the ADS-GCMS operation at Aspendale and compare them with results obtained from the Medusa-GCMS system that replaced the ADS-GCMS system at Cape Grim. As an example, Figure 1 below shows measurements of the refrigerant HFC-134a at Aspendale and at Cape Grim for the first 9 months of 2006.

Reference

Sturrock, G. A., L. W. Porter, and P. J. Fraser, *In situ* measurement of CFC replacement chemicals and other halocarbons at Cape Grim: The AGAGE GC-MS program, in *Baseline Atmospheric Program (Australia) 1997-1998*, edited by N. W. Tindale, N. Derek, and R. J. Francey, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia, 43-49, 2001.

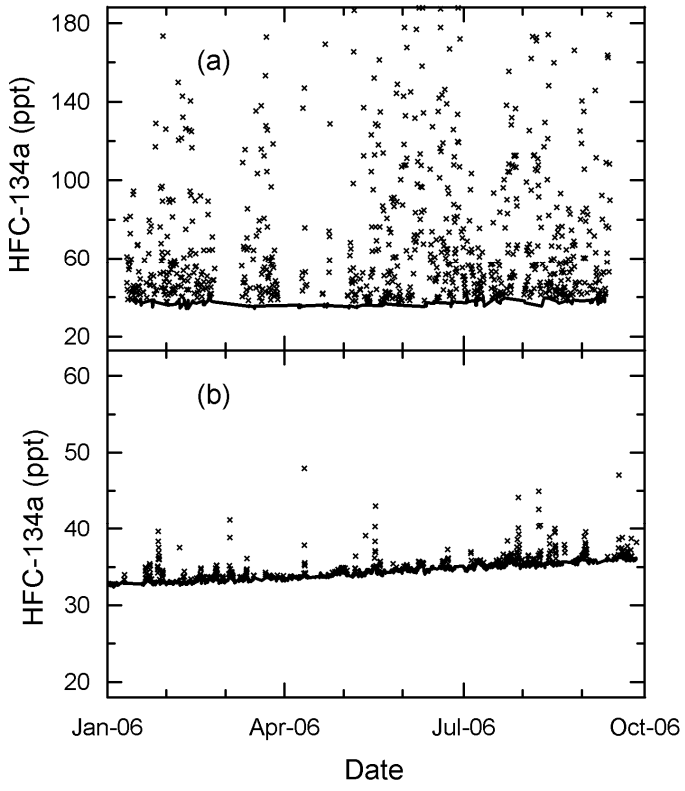


Figure 1. HFC-134a concentration for 2006 measured at (a) CMAR Aspendale using the ADS-GCM system, and (b) Cape Grim using the Medusa-GCMS system. The solid lines connect 'baseline' values; the crosses represent 'non-baseline' values.

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Wealth from Oceans Flagship

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Department of Environmental Science, Policy and Management
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Environment Protection Authority Victoria
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www.epa.vic.gov.au

Global Carbon Project – International Project Office
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Laboratoire des Sciences du Climat et de l'Environnement, Gif sur Yvette, France

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National Institute of Water and Atmospheric Research,
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www.niwa.co.nz/flash

NOAA Earth System Research Laboratory,
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School of Earth and Atmospheric Sciences,
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