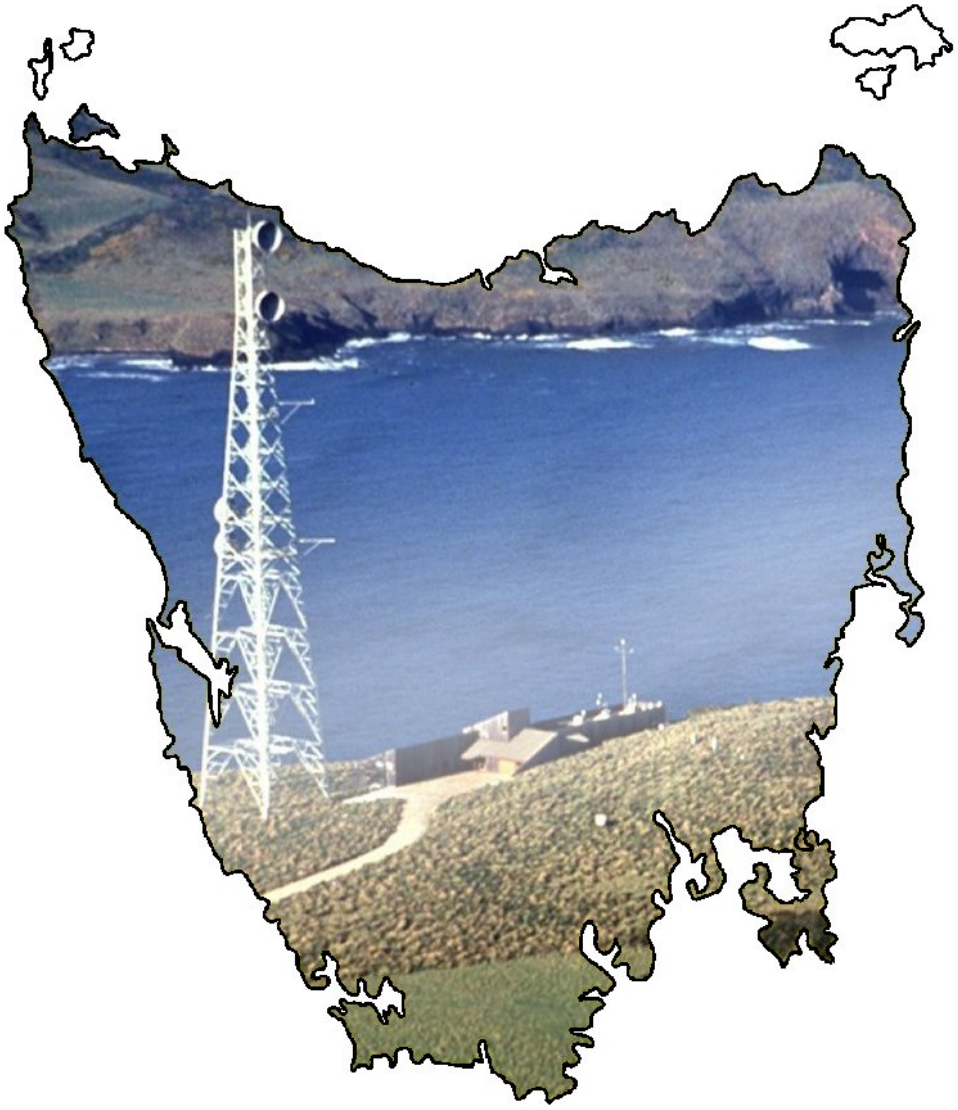
Cape Grim Baseline Air Pollution Station
Annual Science Meeting 2008

27 – 28 November 2008

ABSTRACTS



Edited by

Paul Krummel & Nada Derek

CENTRE FOR AUSTRALIAN WEATHER AND CLIMATE RESEARCH
CSIRO MARINE AND ATMOSPHERIC RESEARCH
ASPENDALE, VICTORIA

Cape Grim Baseline Air Pollution Station
Annual Science Meeting 2008

Centre for Australian Weather and Climate Research
CSIRO Marine and Atmospheric Research
Aspendale, Victoria

27 – 28 November 2008

Thursday, 27th November		
Chair	***Paul Krummel***	
09:00	**Convenors**	**General information on arrangements etc.**
09:05	**Helen Cleugh**	**Welcome and opening of meeting**
09:15	Roger Francey	Changes in global atmospheric CO_2 growth
09:40	Ken Masarie	CarbonTracker and the critical role of ongoing comparison experiments
10:05	Zoë Loh	Laboratory assessment of wavelength scanned-cavity ringdown spectrometers
10:30	**Morning Tea**	**Provided**
11:00	David Etheridge	Results from two years of atmospheric monitoring at the CO2CRC Otway CO_2 storage project
11:25	Zoë Loh	Comparing atmospheric CO_2 measurements made at Aspendale by a LoFlo CO_2 Analyser system and a Picarro WS-CRDS System
11:50	John Gorman	Cape Grim meteorology program: Review
12:40	**Lunch**	**Own Arrangements**
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14:15	Matt Tully	Interannual variability in springtime ozone buildup over the Australian region
14:40	Roger Dargaville	Developing a coupled chemistry-climate modelling capability for Australia
15:05	Ian Galbally	C_2 and C_3 VOCs in the atmosphere over the Australasian region of the southern hemisphere
15:30	**Afternoon Tea**	**Provided**
16:00	Martin Cope	A model of sea salt aerosol for Cape Grim - preliminary investigations
16:25	John Gras	Southern Ocean aerosol - just how biogenic is it, and what about CLAW?
16:50	Melita Keywood	Organic composition of clean marine aerosol at Cape Grim
17:15	Paul Krummel	AGAGE software – instrument control, data processing and display demonstration
17:30	Close of Papers	
18:30	**Meeting Dinner**	**Ficelle – 196 Como Parade, Parkdale**

Cape Grim Baseline Air Pollution Station
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Friday, 28th November		
Chair	***Melita Keywood***	
09:00	Convenors / Hosts	
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09:30	Paul Steele	A serendipitous addition to the air archive
09:55	Paul Fraser	Refrigerant emissions from the Melbourne road transport fleet
10:20	David Etheridge	Deployment of a programmable flask sampling unit at the Otway geosequestration pilot project
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11:40	Wlodek Zahorowski	A new application of Radon-222 for clustering of atmospheric pollution events
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Changes in Global Atmospheric CO_2 Growth

R. Francey*, C. Trudinger, M. van der Schoot, P. Krummel, L. Steele and R. Langenfelds

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Abstract

Measured annual growth of atmospheric CO_2 slows over the period 2001-2007, contrary to expectations from reports of accelerating global emissions and declining Southern Ocean sink. The atmospheric measurements question the reliability of reported emissions and/or requiring significantly increased post-2000 sinks.

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CarbonTracker and the Critical Role of Ongoing Comparison Experiments

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Abstract

CarbonTracker is a combined observing and modeling system that estimates CO_2 uptake and release at the Earth's surface over time. CarbonTracker uses high-precision atmospheric CO_2 observations to optimize derived surface flux estimates that are based on our current understanding of CO_2 exchanges between the atmosphere, ocean and terrestrial biosphere. We believe CarbonTracker is capable of producing reliable flux estimates and uncertainties on regional scales but a much denser observing network than currently exists is needed. The observing system will require a cooperative international effort from both the ground-based and remote-sensing communities. The major challenge in creating a defensible cooperative observing system is to ensure that independent measurements can be merged without introducing systematic biases. Since 1992, CSIRO and NOAA have been routinely comparing independent measurements from weekly air samples collected at the Cape Grim Baseline Observatory. This ongoing experiment, without doubt, improves the quality of both CSIRO and NOAA measurements but also clearly demonstrates the challenges of establishing and maintaining comparability of carbon cycle and related trace gas measurements to the levels recommended by the World Meteorological Organization. Comparison results suggest that CSIRO and NOAA CO_2 measurements are comparable to within 0.2 ppm. Recently, CSIRO and NOAA researchers have worked together to include data from the CSIRO High Southern Hemisphere observing network into the most recent update of CarbonTracker (carbontracker.noaa.gov). We look to further strengthen our collaboration through research opportunities resulting from CarbonTracker. This presentation will highlight the ongoing CSIRO/NOAA comparison experiment, summarize the impacts of the CSIRO CO_2 data on CarbonTracker results and describe recent efforts to enhance the carbon cycle measurement community's ability to assess data comparability.

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Laboratory Assessment of Wavelength Scanned-Cavity Ringdown Spectrometers

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Abstract

Two wavelength scanned-cavity ringdown spectrometers have been purchased and tested in the laboratory. One instrument measures the dominant isotopologues of carbon dioxide ($^{12}C^{16}O^{16}O$) and methane ($^{12}CH_4$); the second measures both the $^{12}C^{16}O^{16}O$ and $^{13}C^{16}O^{16}O$ isotopologues of CO_2. Features of their performance will be described.

The robustness, long-term stability and precision of both instruments are encouraging, indicating that cavity ringdown based techniques are likely to become integrated into global atmospheric monitoring networks. However, as these instruments make isotopologue specific measurements, linking these measurements to current international mole fraction calibration scales presents some new challenges. This presentation will outline a calibration strategy devised to link isotopologue specific measurements to existing calibration scales.

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Results from Two Years of Atmospheric Monitoring at the CO2CRC Otway CO_2 Storage Project

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Abstract

An atmospheric monitoring station has been established at the onshore Otway Basin in south western Victoria. The measurement program is designed to monitor the CO2CRC Otway Project, Australia's first CO_2 geological storage facility, and to develop atmospheric monitoring strategies for future industrial scale CO_2 storage projects. Continuous records of CO_2 concentration from a CSIRO LoFlo analyser and CO_2 land-air fluxes from an eddy-covariance flux tower have been obtained for almost 2 years. Other greenhouse gas concentrations and CO_2 isotopes have been measured at approximately monthly intervals in flask air samples. Soil CO_2 fluxes have been surveyed several times per year. Together, these data provide information on the carbon dynamics of the region which can be used to constrain ecosystem models such as CSIRO's CABLE, as well as provide a baseline for the detection of potential CO_2 emissions due to leakage from the storage reservoir.

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Comparing Atmospheric CO_2 Measurements made at Aspendale by a LoFlo CO_2 Analyser system and a Picarro WS-CRDS System

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Abstract

As part of the testing and evaluation of a newly acquired Picarro wavelength-scanned cavity ringdown spectrometer (WS-CRDS) analyser system designed to measure atmospheric CO_2 and CH_4, the analyser was used to measure ambient air at Aspendale during those times when it was not being used for other tests. A LoFlo CO_2 analyser system is also operated at Aspendale on a similar basis, where it measures ambient air when it is not occupied with other tasks. The ambient air measured by both of these analysers is drawn from a common air intake which extends above the roofline of the building.

Over a period of several months, a useful data set has been accumulated to allow a thorough comparison of the performance of the two analysers. The very encouraging results of this investigation so far will be presented.

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Cape Grim Meteorology Program: Review

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Abstract

The Meteorology Program is pivotal to the interpretation of most of the data collected at Cape Grim. More than any other program, the aims are coupled to the needs of others.

The activities fall into three parts:

1. Collecting sufficient high quality data to allow characterization of the atmospheric conditions at Cape Grim and to build a climatology for the site to allow interpretations of other measurements.
2. Air mass origin studies.
3. Measurement and modeling of boundary layer conditions and micrometeorology that affect atmospheric chemistry and composition at Cape Grim.

The program was last reviewed in 1997. This review will note the history of the program and the changes that have taken place since the last review. It will also review the achievements of the program and discuss its success in meeting its three aims.

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Ground Level Ozone in the 21st Century: the Royal Society Report and Observations from a Cape Grim Perspective

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Abstract

Tropospheric ozone has five functions of relevance to the human environment. It

- contributes to the ozone shield against biologically harmful ultraviolet radiation,
- is a greenhouse gas and helps maintain the current global climate,
- is the primary source of hydroxyl radicals, a key component of atmospheric chemistry,
- is the seed to activate photochemical smog reactions in cities, and it
- has a direct biological impact on humans and vegetation.

Ozone has a strong infra red adsorption feature at 9.6 microns wavelength. There is evidence for an increase in tropospheric ozone from the pre-industrial period from about 1750 to the present. The IPCC states that tropospheric ozone is the third most important greenhouse gas after CO_2 and CH_4. This effect is due to the direct role of tropospheric ozone in infrared adsorption. As well, there is an indirect effect due to the role ozone has within the chemistry of the troposphere which dictates the lifetime of CH_4 and other climatically active atmospheric constituents.

Ozone has an important role in the cleansing power of the troposphere. Ozone is the major primary source of hydroxyl radicals in the background atmosphere. Hydroxyl radicals along with ozone and nitrate radicals (formed from NO_2 and ozone) are the main initiators of the oxidation of reduced compounds such as CH_4, VOCs, organic sulfides and amines in the troposphere. Without these three initiators, the troposphere would be a toxic soup of reduced compounds.

Urban photochemical smog starts each day from its precursors. Ozone is formed from an ozone depleted airmass rich in NOx and VOCs, where under the influence of sunlight, NO_x is initially oxidised to NO_2 and then ozone rapidly grows to become the dominant pollutant. Any increase in the tropospheric ozone that surrounds a city will have two effects on the daily maximum ozone experienced in and downwind of the city. Firstly, because there is a higher ozone concentration in the air advected into the polluted airshed, there will be greater night-time titration of NO to NO_2, with the resultant effect that the ozone production will start earlier in the day because of the higher initial NO_2 concentration and a higher daily maximum ozone concentration will be achieved. Furthermore the air entrained from aloft during the day will have higher ozone levels, directly boosting the the ozone maximum. Due to these two processes it is possible that increases in background ozone levels are amplified in urban airsheds and will contribute to exacerbate the existing urban smog levels.

Tropospheric ozone has a number of deleterious effects on vegetation, materials and human health. Ozone has been shown to lead to increased airway resistance and airway inflammation. In epidemiological studies, ozone has been linked with premature mortality and hospital admissions and emergency room visits for respiratory causes. Because of these effects on human health, there exists the various national air quality standards and objectives for ambient ozone concentrations. Ozone has a damaging effect on vegetation, and recent studies indicate that increasing tropospheric ozone may have a substantial indirect greenhouse effect by its action on limiting plant growth and thus carbon storage in the biosphere.

There is evidence from observations and modelling studies that ozone in the troposphere has increased as a result of increases in human produced ozone precursor emissions over the period from the pre-industrial era circa 1750 to the present (around 2000 CA). Observational evidence is primarily based on European records where the measurement methodology used in the 19th century is reproducible and is traceable to current ozone measurement techniques. In Europe concentrations of ozone doubled between the late 19th and late 20th century. More recently the IPCC reviewed 9 modelling studies, and concluded that there had been an increase of global tropospheric ozone by around 36% from the pre-industrial period to the present.

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It is clear from the planned development of many of the worlds economies and the projected changes in fossil fuel usage that NO_x, CO and VOC emissions will rise. The most extreme projection indicated a 30 ppb increase in tropospheric ozone, a 60% increase on the present or a 5% per decade compound rate of increase. However the effects of a warmer wetter climate are to promote ozone loss, and the increases for either the same or a lesser emissions scenario and including a climate-chemistry coupling suggest an 11 to 33 % increase by 2100.

Recently the Royal Society has issued a Science Policy Report covering these and related areas. The Report will be discussed and a Southern Hemisphere perspective presented.

References

"Ground-level ozone in the 21st century: future trends, impacts and policy implications" Science Policy Report 15/08, The Royal Society, October 2008, 132p.

Galbally, I. E., C. P. Meyer, and S. T. Bentley, Trends in near-surface ozone at Cape Grim and in the Southern Hemisphere troposphere [electronic publication], in *Towards a new agenda*: *17th International Clean Air & Environment Conference proceedings*, Hobart, Tasmania, Clean Air Society of Australia and New Zealand, Hobart, Tasmania, 2005.

Interannual Variability in Springtime Ozone Buildup over the Australian Region

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Abstract

Results of ongoing investigations into patterns of interannual variability in total column ozone as measured by the Bureau of Meteorology's Dobson network over the Australian region are presented. At all latitudes, total column ozone increases during winter and spring, reaching an annual maximum in September-October, however, except in Darwin, there is significant interannual variation in the magnitude of the springtime maximum. Particularly in Melbourne, ozone anomalies during the months of winter and spring are well correlated with each other and persist to a considerable extent into the following summer and autumn, but not then into the next winter.

Using multiple linear correlation analysis, it is found that much of the variation in springtime ozone can be accounted for in terms of hemisphere-wide processes, such as the Quasi-Biennial Oscillation (QBO), variations in planetary wave forcing as represented by the Eliassen-Palm (EP) flux, the 11-year solar cycle and stratospheric chlorine loading.

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Developing a Coupled Chemistry-Climate Modelling Capability for Australia

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Abstract

Modelling studies of the Antarctic Ozone Hole have shown that on decadal timescales, ozone variability affects the position and strength of the polar vortex [Arblaster and Meehl, 2006; Miller *et al*., 2006; Perlwitz *et al*., 2008] and that the Southern Annual Mode (which is affected by the polar vortex) plays an important role in the climate of southern Australia [Cai and Cowan, 2006, 2008; Frederiksen and Frederiksen, 2007; Hendon *et al*., 2007]. However, no studies to date have directly estimated the impact of the ozone trends on the climate of southern Australia, in part due to the lack of modelling capability.

In this presentation we explain the links between stratospheric ozone variability and southern hemisphere climate, especially the Southern Annual Mode. We will show results from the CCMVal coupled chemistry-climate model inter-comparison [Eyring *et al*., 2006] compared to observations of ozone from OMI and TOMS remote sensing instruments, and also from ozone balloon flights from Melbourne and Macquarie Island. Results show that there is a broad range of behaviour from the models, and that while some aspects of the seasonal cycle of stratospheric ozone are well represented, generally the models have significant shortcomings.

We present plans and progress on the coupling of the UK Chemistry and Aerosols (UKCA) model into the Australian Community Climate and Earth Systems Simulator (ACCESS). This model will allow studies looking at the impact of ozone trends on climate, and also the impact of global climate change on the dynamics and chemistry of the stratosphere. We will briefly discuss the potential for using the Cape Grim CFC/halocarbon measurement records to update and improve the emission scenarios for ozone depleting gases.

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C_2 and C_3 VOCs in the Atmosphere over the Australasian Region of the Southern Hemisphere

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Abstract

A number of studies have been undertaken in Australia and surrounding regions to investigate VOCs in background air. This presentation will concentrate on the studies of C_2 (ethane, ethene and acetylene) and C_3 (propane and propene) hydrocarbons measured in background air from Cape Grim and overflights, Charles Point NT, various aircraft campaigns and studies of sources in urban and rural locations.

The VOC measurements at Cape Grim are: *in situ* and overflight flask sampling during two periods from November 1995 – March 2000 (Ye, Kivlighon, Galbally and Weeks, CSIRO); *in situ* sampling and GC-FID analyses January and February 1999 (Lewis *et al*., University of Leeds); *in situ* sampling and GC-MS analyses October 2004 – ongoing (Krummel, Fraser, Steele, Porter, CSIRO, AGAGE); air archive analyses and GC-MS analyses 1978 – present (Krummel, Fraser, Steele, Porter, CSIRO, Miller SIO/NOAA); *in situ* sampling and PTR-MS analyses 2006 – ongoing on a campaign basis (Galbally, Lawson CSIRO).

VOC flask sampling was conducted at Charles Point NT (1997-98), in Perth and from Indonesian fires (1997-98), and continuous sampling has been conducted in the Latrobe Valley and Melbourne.

The focus of the interpretation will be on understanding the cycle of ethane on baseline marine air. The seasonal cycle of ethane shows a autumn minimum and spring maximum in concentration. The ethane mixing ratios in the free atmosphere above Cape Grim are higher than those observed at the Station. The combined ethane data when over-plotted (baseline flasks from 1998-2000, the *in situ* Medusa from 2004-2006 and the air archive from 1984 – 2006) show good agreement during the autumn minimum with more variability in the spring maximum. There is a strong biomass burning influence on ethane at Cape Grim, evident from the correlation of ethane excursions with acetylene. The ratio of the excursions (ethane/acetylene ~2) is consistent with the ratios observed both on the ground at Charles Point and from aircraft sampling of smoke in the NT and Indonesian fires. There appears to be a consistent residual (uncorrelated with acetylene) component of the ethane at Cape Grim and in the free atmosphere. This component could be either aged biomass emissions (where acetylene disappears before ethane) or ethane from non-burning sources such as leakage in gas and oil production. The contribution of ethane emissions from urban centres to the background atmosphere is evaluated from observations for Melbourne and Perth. A budget with uncertainty analysis is presented for ethane in the Southern Hemisphere.

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A Model of Sea Salt Aerosol for Cape Grim - Preliminary Investigations

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Abstract

Sea salt aerosol is produced by breaking waves, with the dominant mechanism being film and jet drops generated by the bursting of entrained air bubbles [Gong *et al*., 1997]. At high wind speeds (> 9 m s^{-1}), droplets may be produced directly from wave top tearing (spindrift). Sea salt aerosol emissions may also be enhanced by 1-2 orders of magnitude at the coast due to wave-seabed interactions [Leeuw *et al*., 2000]. The size distribution of emitted particles is observed to be bi-modal and spans approximately 0.02-60 μm diameter. Sea salt aerosol may have significant effects on the environment from local to global scales. At the global scale, sea salt aerosol has a direct climate impact through the scattering of radiation, and an indirect effect through contribution to the CCN population in the marine boundary layer. Sea salt aerosol is also a carrier of halogens, some metals and sulfates and therefore plays an important role in the cycling of these species; in ozone production; in the reaction of volatile organic compounds; in the oxidation of heavy metals such as mercury [Seigneur *et al*., 2001]; and is a potential sink for SO_2.

The Cape Grim MAC program has been observing the chemical constituents of sea salt aerosol since 1980. The sampling is undertaken on a 7-day interval using high volume aerosol samplers that collect particles of less than10 μm diameter (at ambient RH). The sampling is conducted at a height of 94 m above sea level (at roof level) in parallel with particle number data, other chemical data (i.e. ozone) and meteorological observations. In combination, these data provide a valuable resource for testing the emission, transport and chemical transformation algorithms of global aerosol transport models [e.g. see Gong *et al*., 1997].

Through the ACCESS project, we are now implementing the UKCA (United Kingdom community atmospheric chemical-aerosol global model- http://www.ukca.ac.uk), a 3-dimensionsal model which will be used by CAWCR in coupled earth system simulations. Part of the implementation process will be the testing of the aerosol sub-model, including the sea salt aerosol scheme. However before this can be undertaken, it is important to have a good understanding of the processes which lead to the sea salt aerosol concentrations observed at Cape Grim. Of particular importance is an understanding of the significance of the processes which lie below the resolvable scale of the UKCA (currently 150-200 km). Examples of these are the elevated location of the sampler, the sub-regional topography and the impact of aerosol generation within the surf zone. In this presentation we will discuss the preliminary application of a high resolution meteorological-chemical-transport model to examine the sensitivity of the Cape Grim sea salt aerosol to these smaller scale processes. This study provides an example of how a synergy of fine scale measurements and modelling may be used to inform the verification and process development of a large scale coupled earth systems model.

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Southern Ocean Aerosol - just how biogenic is it, and what about CLAW?

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Abstract

This presentation is about Southern Ocean aerosol as seen at Cape Grim; it has a particular focus on CCN, and specifically information that can be derived from the extended observation series. This includes some 'climate tracking' findings and some different insights into Southern Ocean sources of both Aitken and CCN particles.

A number of hypotheses have developed over the past few decades relating to CCN. These include that the Southern Ocean atmosphere has minimal anthropogenic pollution and natural processes largely dominate aerosol production, that CCN derive largely from biogenic sources photochemically, and that homeostasis, or biological regulation of the radiation budget (e.g. CLAW) is possibly a controlling factor. Some of these ideas are revisited with the benefit of an extended time series of real-world CCN measurements.

The use of a photochemical tracer indicates that for CCN active at 0.5% supersaturation the non-photochemical source is close to 45 cm^{-3} and about double this for the Aitken mode. This fits well with a primarily wind generated sea-spray origin which is most likely very predominantly sea-salt. Use of marine biogenic process tracer, can explain 91% of the seasonal variance, but still with a significant non biogenic contribution. For the Aitken mode there is no improvement in variance explained over that from photochemistry. Non-biogenic, photochemical CCN, appear to be only around 13 cm^{-3} (annual average) suggesting the DMS-CCN hypothesis still looks sound in an annual cycle sense. But an assumption that the non-biogenic component does not vary seasonally implies that whereas in summer ~65% of CCN are biogenic, in winter the fraction is only ~10%.

Homeostasis, the idea that there is a form of self regulation or a biologically driven negative feedback on radiation budget was made famous by Charlson *et al*. [1987], in what has become known as the CLAW hypothesis. In this form the emission of DMS by marine organisms, after oxidation in the atmosphere become CCN and hence cloud droplets. More radiation produces more DMS, leading to more CCN and thus more cloud droplets, an increased albedo and reduced radiation at the surface. Whilst CCN concentrations at Cape Grim show a strong seasonal coupling to photochemistry there has been a consistent small downward trend over the past 25 years. This CCN trend does not match the interannual variability pattern in the TOMS UV record and would also appear to be reinforcing any regional warming by reducing cloud albedo, thus does not appear to support the idea of homeostasis (e.g. CLAW).

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Organic composition of clean marine aerosol at Cape Grim

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Abstract

With 70% of the Earth's surface covered by oceans, aerosols in the marine boundary layer (MBL) play an important role in climate system, directly by scattering and absorbing radiation and indirectly by acting as cloud condensation nuclei (CCN), thus influencing cloud droplet size distribution, cloud albedo and lifetime. While the submicrometer marine aerosol is dominated by non sea-salt sulfate, which in the unpolluted marine boundary layer is derived from the oxidation of dimethyl sulphide (DMS) emitted by various marine organisms, a large fraction of the submicrometer aerosol over the marine environment can not be accounted for by just sea-salt and non sea-salt sulphate [Quin *et al*. 2000]. Organic compounds may contribute to this missing fraction since the presence of organic compounds in marine aerosol has been known for many years [Lodge *et al*., 1960, Blanchard, 1964, Hoffman and Duce, 1964]. For example, Middlebrook *et al*. [1999] estimated that organic aerosol made up 10% of the aerosol mass under clean marine conditions at Cape Grim during the First Aerosol Characterisation Experiment (ACE 1).

The species that make up the organic aerosol provide information on the sources of the organic compounds, their production mechanisms and their likely interaction with the climate system. We described the non-polar organic species present in PM10 at Cape Grim collected under baseline conditions (August 2002 to October 2003) at the 2007 Cape Grim Science Meeting. The presence of cycloalkanes suggested a biomass burning aerosol source in the marine boundary layer aerosol sampled under baseline conditions, and based on published literature, where air masses have been shown to move from southern Africa to Australia transporting pollutants associated with biomass burning [Pak *et al*., 2003; Edwards *et al*., 2006], we interpreted the presence of the cycloalkanes to indicate long-range transport of biomass burning aerosol to Cape Grim.

In this presentation we investigate 10-day back trajectories for the sampling periods at 100 m, 3 km and 5 km, and show in the 5 km back trajectories that the air masses had passed over land masses such as southern Africa, Madagascar and Western Australia, before arriving at Cape Grim. While there is no indication that the air masses at 5 km directly interacted with the surface at Cape Grim, we investigate the possibility of entrainment of aerosols from the free troposphere as a means of supplying the biomass burning-derived aerosol to the remote marine boundary layer at Cape Grim.

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AGAGE Software – Instrument Control, Data Processing and Display Demonstration

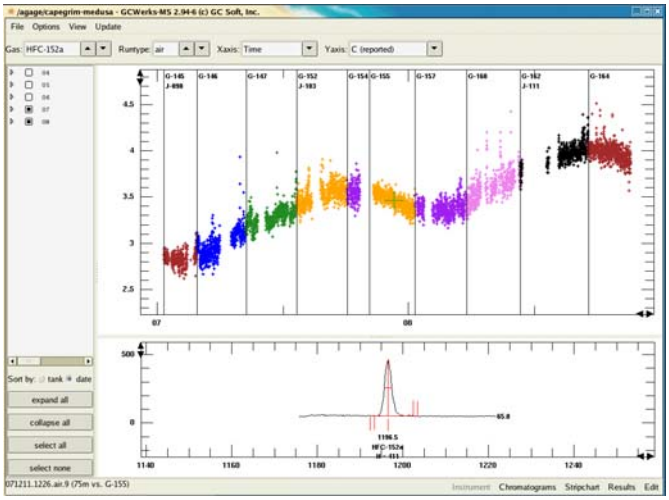
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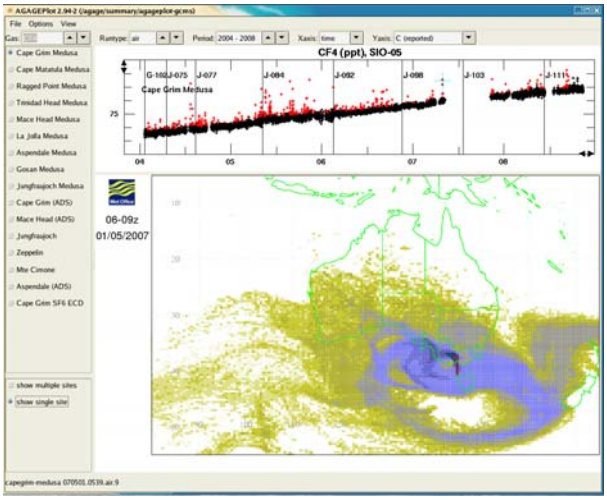
Abstract

During this presentation, the GCWerks software package that was developed by Peter Salameh for the Advanced Global Atmospheric Gases Experiment (AGAGE) program will be demonstrated. GCWerks is powerful software that operates under a Linux operating system and is designed specifically for monitoring applications using gas chromatography (GC) or gas chromatography/mass spectrometry (GC-MS) techniques. Unlike most chromatography data systems, which work best with samples brought to the laboratory, GCWerks is designed for automated instruments in the field and has been refined over many years of use in remote monitoring applications. GCWerks is now available commercially, see http://gcwerks.com/ for details.

An overview of the instrument control will be shown illustrating the powerful and flexible automation features of the software. Then, the powerful data processing elements of GCWerks will be demonstrated, including peak integration, instrument diagnostics and data flagging. It is these features that have greatly aided in the task of keeping on top of the large volumes of data coming in daily from the AGAGE instruments at Cape Grim and Aspendale. Lastly, the AGAGEplot package that was developed to help streamline the data review procedures at the six-monthly AGAGE meetings will be shown. This package allows users to overlay time-series data from multiple sites and/or instruments, and/or plot two species together; it features point and click operation, extensive zoom capability, data point identification, can show data with or without pollution, indicate calibration tank changes etc. AGAGEplot also allows information to be displayed for every data point to aid interpretation, such as, instrument precision and chromatograms, air mass origin maps.



GCWerks screenshot



AGAGEplot screenshot showing air mass origin map

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The Vertical Distribution of Radon in Daytime Terrestrial Boundary Layers

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Abstract

The vertical distribution of the natural radioactive tracer radon-222 through the atmospheric boundary layer (ABL) is a quantitative indicator of exchange and mixing between the terrestrial surface and the lower atmosphere. As an update on our current research in this area, we present time series and high-resolution vertical profiles of radon and meteorological quantities in daytime boundary layers over rural inland Australia, with samplers based on the ground and mounted on motorized gliders. Due to its 3.8-day half-life, there is a steep radon gradient across the top of the ABL in all studied cases ranging from light-wind strong convection to high-wind near-neutral conditions, and from clear skies to moderately developed fair-weather cumulus and stratocumulus. As a consequence of the 'top-down' mixing process, radon displays a range of gradients in the upper mixed layer of the ABL that are sensitive to the degree of exchange (entrainment) across the interface. In the presence of active boundary layer clouds, the venting of air from the sub-cloud layer is strongly enhanced, leading to radon concentrations that remain high within the main part of the cloud layer and only diminish towards its top.

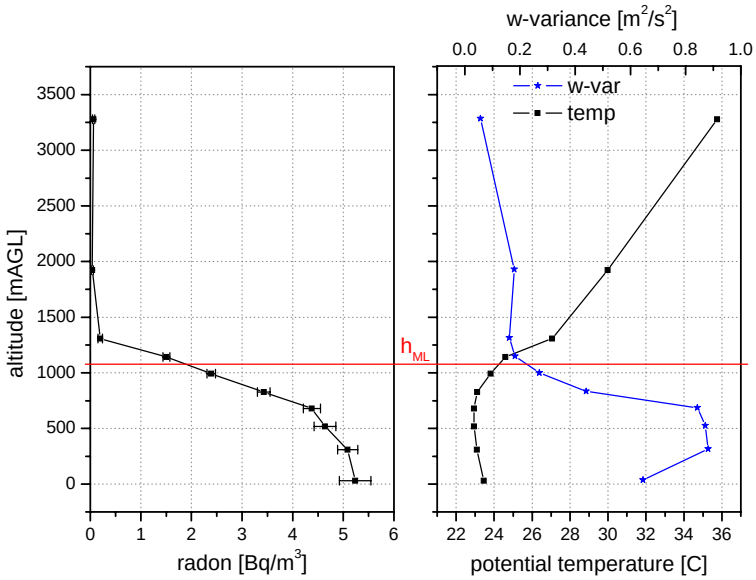


Figure 1. High-resolution profiles of radon concentration, potential temperature and vertical velocity variance in a cloudless convective boundary layer over Goulburn (NSW) on 8 May 2008. The top of the mixed layer (h_{ML}) is marked with a horizontal line. Note the significant vertical radon gradient in the upper part of the mixed layer, indicating strong 'top-down' mixing of very low radon air from above during the entrainment process.

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PFC and other greenhouse gas emission factors from *in situ* measurements at the Kurri-Kurri aluminium smelter

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Abstract

Perfluorocarbons (PFCs) are powerful greenhouse gases released during the production of aluminium. We are developing a low-cost technology (compared to current spectroscopic techniques) to measure PFC emission factors, using high-precision gas chromatography with mass spectrometric detection (GC-MS) to analyse large-volume smelter-exhaust samples, collected over periods of up to a week at individual smelters. The first proof-of-concept experiments were conducted at the Hydro Aluminium Kurri-Kurri smelter in April 2008.

The experiments showed:

- The average CO_2 emission factor was 1.0 tonne CO_2 per tonne aluminium, lower than industry best practice value of 1.4.
- The episodic nature of smelter PFC production was seen, confirming the need for sampling over extended periods.
- A PFC emission factor of 0.1 tonne CO_2-equivalent per tonne of aluminium produced was observed, less then the industry average value of 0.5.
- Minor PFCs, C_2F_6 and C_3F_8, were easily identified, contributing 4% to the overall PFC emission factor; the industry standard is 10%, based on few measurements.
- The PFC hooding efficiency was estimated to be better than 99%.
- Minor emissions of COS, CO, H_2 and N_2O were identified.
- No HFC production was observed.
- The technology works, is inexpensive and potentially more accurate compared to existing spectroscopic technologies.

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Fraser, P., P. Steele, M. Leist, S. Coram and N. Derek, PFC and other trace gas emissions from *in situ* measurements at the Hydro Kurri Kurri aluminium smelter, Hunter Valley, NSW, Report to Hydro Aluminium, Light Metals Flagship, CSIRO Marine and Atmospheric Research, Aspendale, Victoria, May 2008

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Nitrogen Trifluoride and Sulfuryl Fluoride: Two New Greenhouse Gases

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Abstract

Nitrogen trifluoride (NF_3) and sulfuryl fluoride (SO_2F_2) are powerful greenhouse gases that have recently been discovered in the global background atmosphere [Weiss *et al*., 2008; Mühle *et al*., 2008].

Nitrogen trifluoride is used in the electronics industry, often as a replacement for perfluorocarbons (PFCs), in particular in the manufacture of liquid crystal flat-panel displays. SO_2F_2 is used as a replacement for methyl bromide (CH_3Br) in structural fumigation applications.

The first atmospheric observations of NF_3 and SO_2F_2 will be presented, in particular data from Trinidad Head and La Jolla, California, and from Cape Grim, Tasmania, both *in situ* and from the air archive. Atmospheric abundances, growth rates, lifetimes, emissions and Global Warming Potentials (GWPs) will be discussed. Their levels in the atmosphere are low currently, but their growth rates and GWPs are relatively large.

The Kyoto Protocol will be revised later this year, with new emissions targets for the existing 'basket' of gases (carbon dioxide - CO_2, methane - CH_4, nitrous oxide - N_2O, PFCs, hydrofluorocarbons - HFCs, sulfur hexafluoride - SF_6), with potentially new greenhouse gases included and hopefully new signatories from the developed and developing world. NF_3 and SO_2F_2 are being seriously considered by various national governments for possible inclusion in the revised Kyoto Protocol.

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A Serendipitous Addition to the Air Archive

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Abstract

CSIRO and the Bureau of Meteorology have been collecting and maintaining an archive of air collected at Cape Grim, Tasmania, since 1978.

The archive air samples have been analysed at CSIRO for all the important greenhouse and ozone depleting gases. These data have proved invaluable in reconstructing the past chemical composition of the atmosphere as a driver of long-term climate change and ozone depletion [Clerbaux and Cunnold, 2007; Forster and Ramaswamy, 2007].

The only source of Southern Hemisphere baseline air prior to 1978 has been from Antarctic ice and firn. In conjunction with colleagues from the Antarctic Division and from the University of Tasmania, CSIRO have collected and analysed ice and firn air samples from Antarctica for CO_2, CH_4 and N_2O going back two thousand years [McFarling-Meure *et al*., 2006].

There is now an overlap in dates between the oldest archive air samples and the youngest firn air samples. Nevertheless, accurately dated, discrete background air samples older than 1978 are invaluable in reducing the date-concentration uncertainties associated with air samples extracted from firn or ice. The species that are suitable for dating must have been demonstrated to show well-behaved long-term growth trends and long-term stability in pressurized containers.

During October 2008, CSIRO Aspendale was contacted by a local Beaumaris resident (Mr. J. Allport) offering, for research purposes, an old air sample contained in a (steel) SCUBA compressed air tank. Mr Allport indicated that the air sample was from 1970 or earlier, as his diving diary indicated that the last time he used the tank was in 1970 and it had not be refilled since that date.

The tank was filled in 1970 or earlier by a diving service company in Lonsdale Street Melbourne. SCUBA tanks are typically filled using oil free compressors. It is assumed that the air sample was ambient air from the city precinct of Melbourne. Examination of the tank's markings show that it was last hydrostatically tested in February 1968, so the air sample must be from the period 1968-1970.

The tank was about 6 litres internal volume and was measured to contain about 75 bar overpressure of compressed air (450 litres of air at atmospheric pressure). The air was transferred (85%, 385 litres) by pressure equilibration into a previously-evacuated, internally-electropolished 35 litre stainless steel tank. The air sample has been analysed at CSIRO using a variety of instruments.

The results of these analyses will be presented.

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Refrigerant Emissions from the Melbourne Road Transport Fleet

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Abstract

Emissions of refrigerants (HFC-134a – CH_2FCCF_3, CFC-12 – CCl_2F_2), for the Melbourne road transport fleet have been estimated from experiments conducted in the Domain Tunnel from mid-2003 to early 2007. The emissions and their temporal trends will be compared to 'bottom-up' estimates using recommended IPCC methodologies, as employed, for example, in the National Greenhouse Gas Inventory (NGGI).

References

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Deployment of a Programmable Flask Sampling Unit at the Otway Geosequestration Pilot Project

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Abstract

Atmospheric monitoring and verification of geosequestration at the CO2CRC Otway Project includes both continuous *in situ* monitoring, presently of CO_2 concentration only, and discrete sampling into flasks for subsequent multi-species analysis. A limitation of the present discrete sampling regime is the requirement for an operator to collect the sample. At the Otway site, this usually limits sample collection to daylight hours during field experiments. In order to collect samples at other times, a flask sampling system comprising a battery powered compressor and a programmable 12-flask sample package (PFP) has been commissioned for use in field sampling campaigns. With this system, samples are collected according to a sample schedule that can be stored in the PFP before deployment or that can be updated remotely. Results from the testing of the unit and its initial deployment at the Otway site will be presented.

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Time-Integrated Atmospheric Sampling and Analysis

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Abstract

Measurements of trace gases in the atmosphere (or in some process gas streams) mostly fall into two broad categories – continuous (or quasi-continuous) measurements at the site of interest, or the collection of samples in suitable flasks for later measurement in a laboratory. There are some applications where the continuous measurement option is either too costly or logistically impractical. There are also some applications where the flask sampling is too sparse to capture fast variations in trace gas mixing ratios because of practical limitations in the frequency that flask sampling can be carried out.

Time integrated sampling of air (or gas stream) into a suitable flask, with subsequent measurement in a laboratory, offers one possible solution for applications where a time-averaged value for a trace species can provide useful information, but continuous in-situ measurements are not possible. The essence of such an approach has been in use for many years in some programs to measure atmospheric levels of $^{14}CO_2$, where atmospheric CO_2 is chemically extracted from an air stream flowing at a constant rate over a two week period [e.g. Levin *et al*., 2007].

In the technique described here, use is made of stainless steel capillary tubing to achieve relatively low, and constant flow rates of sample into evacuated stainless steel flasks. Achieving a constant flow rate during the sampling period is imperative, underpinning the derivation of true average values of the trace gas mixing ratios. This constraint implies that the pressure of the sample collected in the flask will be sub-ambient, usually requiring a pressurisation with air of known composition, before analysis.

Progress in the development and testing of the technique so far will be described; in particular, the selection and testing of suitable capillaries, and the importance of good, portable pressure sensors (with memory capability).

Results of direct tests of the time-integrated sampling technique applied to ambient air will also be presented, by comparing the average mixing ratios of methane (CH_4) and carbon dioxide (CO_2) determined from the integrated sample with the average mixing ratios determined from continuous measurements made by a Picarro EnviroSense Trace Gas Analyzer over the same period of time. The Picarro analyzer is a continuous trace gas monitor based on Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS).

Whilst initially tested for the measurement of atmospheric greenhouse gases, the integrated sampling technique should be suitable for monitoring many trace gases of interest. For example, in aluminium smelters, the formation and release of perfluorocarbons (PFCs) is known to be strongly episodic. Time-averaged sampling (over periods of 1-2 weeks) for this application has the potential to provide, for the first time, accurate assessments of the contribution of the three major PFCs (CF_4, C_2F_6, C_3F_8) to the overall PFC emission factor.

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A New Application of Radon-222 for Clustering of Atmospheric Pollution Events

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Abstract

Clusters of back trajectories are often used in atmospheric pollution studies to analyse distinct fetch areas and atmospheric transport patterns.

We propose a new, non-Euclidean metric space for generation of back trajectory clusters, which incorporates radon-222 (radon) concentrations measured in air parcels arriving at the receptor site. We have investigated four metric spaces for cluster formation. The first two metrics are defined by horizontal spatial variability of trajectories. Metric 3 includes an explicit trajectory altitude term. Metric 4 contains, apart from horizontal and vertical spatial terms, a non-spatial term derived from radon concentrations.

We demonstrate that inclusion of the non-spatial term improves the overall performance of the resulting clusters applied to aerosol analysis. The performance criterion we adopt is based on an assumption that the better the cluster identifies uniform fetch area and transport patterns, the smaller the resulting intra-cluster variation of its aerosol sample mass. Performance tests, as well as the application of the new metric space are based on a three year long dataset comprising co-located aerosol fine particles ($PM_{2.5}$) collection and hourly measurements of radon-222 concentration at the Hok Tsui site in Hong-Kong. Two examples of performance tests are shown in the figure below.

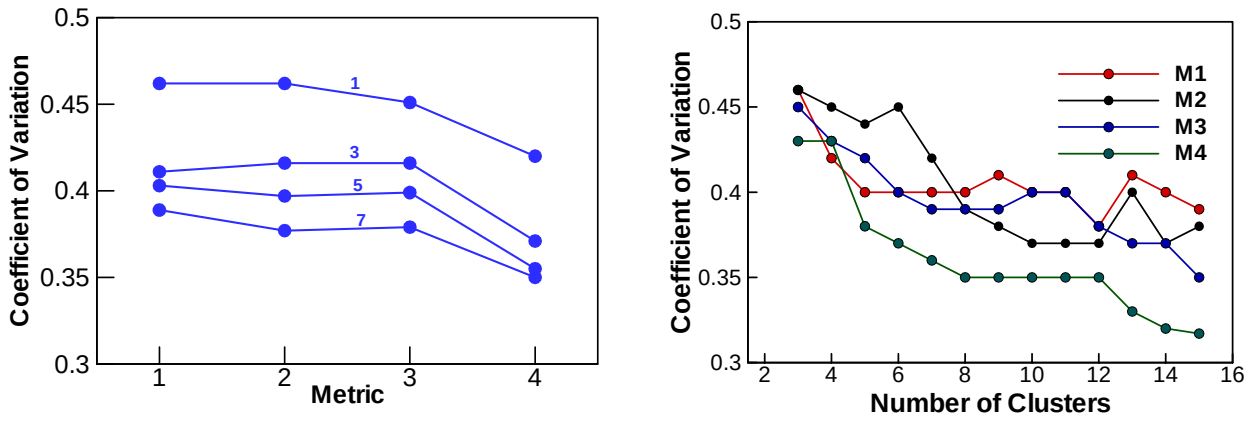


Figure 1. Average coefficient of variation of total aerosol mass for clusters defined using four metrics M1, M2, M3, and M4; for 1, 3, 5 and 7 day back trajectories (numbered, on left panel) and for a number of clusters when 7 day back trajectories are used (right panel).

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Future directions for Spectral Solar Radiation Measurements

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Abstract

Spectral radiation measurements have focussed on characterizing aerosol optical depth (sunphotometers) and UV-B radiation as a driver of photochemistry. Both measurements have had significant successes in the past, but have also had limitations in both equipment reliability and performance.

With sunphotometers one major limitation is calibration at a cloudy site like Cape Grim, and the wear and tear imposed on equipment that is, by its very nature, always outdoors. The limited number of wavelengths measured by classical sunphotometers also limits the amount of information available about aerosol properties. In the case of the UV spectrometer using a rotating grating the slow scan speed of the instrument, while acceptable for the some purposes, limits the ability to extend to other measurement strategies.

Work on the refurbishment of the systems already in place, additional calibration strategies and the assessment of options for replacement spectrometer systems will be presented.

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