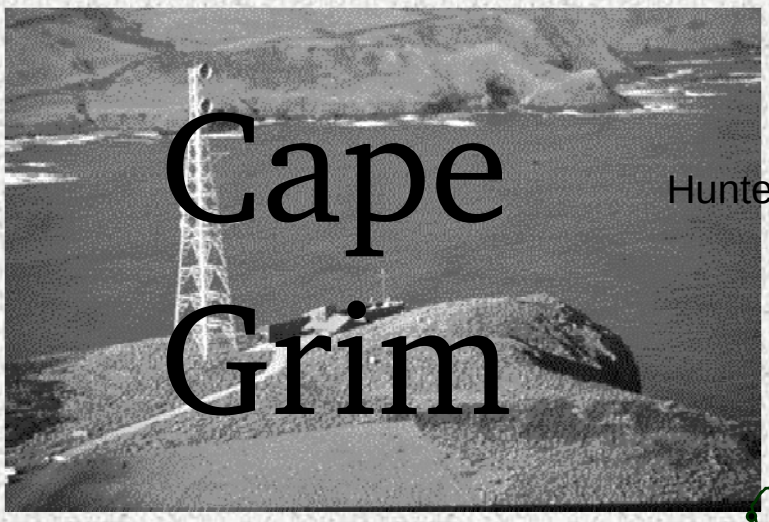
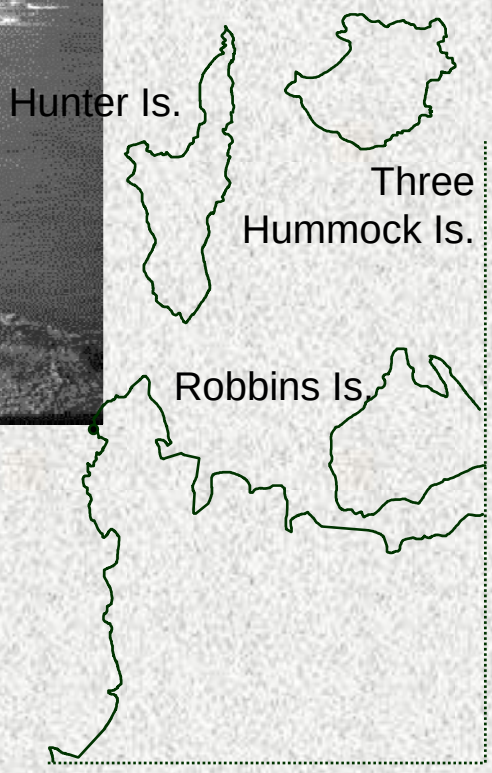
Cape Grim
Baseline Air Pollution Station
Annual Scientific Meeting





3-4 November, 1999
CSIRO Atmospheric Research,
Aspendale, Victoria

Edited by Neil Tindale & Nada Derek

Bureau of Meteorology

CSIRO

Cape Grim Baseline Air Pollution Station
Annual Meeting, 1999

Wednesday, 3 November		
Chair	***Neil Tindale***	
09:00	Convenors / Hosts	General information on arrangements etc.
09:10	Peter Rayner	Using continuous CO_2 data from Cape Grim to estimate Australian CO_2 fluxes
09:40	David Garton	Ion Beam Methods for Fine Particle Characterisation
10:10	Reinout Boers	Clouds and radiation at Cape Grim
10:40	**Morning Tea**	
11:00	Roger Francey	A New Global Quality Control for Long-Lived Trace Gas Measurements
11:20	Paul Krummel	The Vital Role of Data Management in Studies of Atmospheric Trace Species
11:45	Bronwyn Dunse	Investigation of Urban and Regional Emissions of Trace Gases
12:10	Ying-Ping Wang	Estimating Net Primary Productivity of the Australian Continent
12:35	**Lunch**	
Chair	***Roger Francey***	
13:30	Lisa Cooper	Comparing Trace Gas Measurements from Flasks Collected at Cape Grim and Analysed at Different Laboratories
14:00	Stewart Whittlestone	Air Mass Characterisation at Cape Point
14:30	Eva Kowalczyk	Recent Simulations of Trace Gas Transport using C-C Model and DARLAM
15:00	Jill Cainey	The Use of Sulfur Isotopes to Assess the Gas to Particle Conversion Mechanism of Atmospheric Sulfur Species
15:30	**Afternoon Tea**	
15:50	Arndt Meier	Total column amounts, isotopic ratios, and information on trace gas profile variations retrieved from solar infrared spectroscopy
16:20	Henry Granek	Cape Grim Photochemical Boundary Layer Box Model: Recent Developments
16:50	Mick Meyer	Auditing Instrument and System Performance and Data Quality in Surface Ozone Monitoring Systems
17:20	Darren Spencer	Atmospheric Air Dryer System for Cape Grim's New Low Flow CO2 Analyser
17:50	Grant Da Costa	Cape Grim's New Low Flow CO_2 Analyser: Results of Operational Trials at Aspendale
18:20	**Close of Papers**	
18:30	**Poster Wine and Cheese Evening**	**CSIRO-Atmospheric Research Canteen**

Thursday, 4 November		
Chair	***Paul Fraser***	
09:00	Convenors / Hosts	General information on arrangements etc.
09:10	Ian Galbally	Comparison Of The Regionally Averaged Surface Exchange Rates Of Ozone And Radon Made Through Atmospheric Concentration Observations.
09:40	Stephen Wilson	Aerosol Optical Depth at Cape Grim (1985 - 1999)
10:10	Colin Allison	Instrumental Effects on Stable Isotope Measurements of Atmospheric CO_2
10:40	**Morning Tea**	
11:00	Laurie Porter	Methodology of the Cape Grim GC-MS
11:30	Paul Fraser	Review of Montreal Protocol Trace Gas Measurements at Cape Grim, Tasmania
12:00	Paul Fraser	Review of Kyoto Protocol Synthetics Measurements at Cape Grim, Tasmania
12:30	Michelle Cox	Regional and Background Measurements of Halomethanes at Cape Grim, Tasmania
13:00	**Lunch**	**Chicken and champagne lunch! Ladies, a hat please for 'Ladies Day'**
Chair	***Stephen Wilson***	
14:00	David Griffith	Position-dependent fractionation of ^{15}N in sources and sinks of atmospheric N_2O.
14:30	Fred Turatti	Isotopic analysis of atmospheric N2O by FTIR spectroscopy: ^{15}N, ^{18}O and positional dependence
15:00	David Etheridge	Cape Grim Methane Isotopic Record Extended into the Pre-Nuclear Era
15:30	**Afternoon Tea**	
Chair		
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16:20	Manuel Nunez	A Variable Sky Platform for Analysis of Erythemal UV Radiation
16:50	Kevin Rosman	Preliminary results of sampling Cape Grim baseline-sector aerosol for lead concentration and isotopic composition
17:20	John Gras	Cape Grim Particle Program Review 1999
18:20	**Close of meeting**	
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Using Continuous CO_2 Data from Cape Grim to Estimate Australian CO_2 Fluxes

Peter Rayner

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

Atmospheric inversions use information on spatial and temporal concentration gradients to infer estimates of sources. Typically we use monthly mean concentrations and infer estimates of monthly mean sources. One limitation to this approach is the rate of atmospheric diffusion so that concentration signatures from small regions may not be observable in monthly mean data. In this talk we investigate the ability of highly time-resolved data to estimate the spatial structure of monthly mean sources over Australia. In particular we show that the difference in arrival times of signals at cape grim can provide a useful constraint on regional sources, pointing the way to an automation of the commonly used trajectory methods. Finally we comment on the demands such an approach make on models of atmospheric transport.

Ion Beam Methods for Fine Particle Characterisation

David Garton, & David Cohen

Australian Nuclear Science and Technology Organisation, Menai, NSW 2234

Brian Weymouth

Cape Grim Baseline Air Pollution Station, Smithton, Tasmania 7330

John Gras

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

To better understand the contribution of fine particles (PM2.5) and their effect on global climate change, the composition of fine particles from natural, urban and industrial sources must be measured.

Cape Grim provides a unique platform to observe these sources of fine particles from natural baseline sea air to air more influenced by urban and industrial activities. The low background site provides the opportunity to monitor small increases in particle levels that may not be seen at sites located nearer to populated areas.

To sample the individual sources the Australian Nuclear Science and Technology Organisation (ANSTO) has developed an air sampling unit that can sample fine particles from up to four selected sectors. These sectors are separated by their unique source characteristics which are distinguished by their relative radon levels, condensation nuclei and wind direction. The four fundamental sources are from 'Aged' and 'Normal' baseline, 'City Continental' and 'Non-city Continental'.

The fine particle collection and analysis is based on 8 years of air sampling experience from over 50 sites including Cape Grim. Using nuclear analysis techniques from the ANSTO accelerators, fine particle air samples are characterised by the measurement of their elemental composition and relative concentrations.

Clouds and Radiation at Cape Grim

Reinout Boers & Stuart Young

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Bruce Forgan

Bureau of Meteorology, Melbourne, Victoria 3001

Abstract

The radiative balance at the surface is governed by atmospheric parameters among which clouds are the most influential, but also the most variable. Since the upgrade of the radiation equipment at Cape Grim and the installation of the mini-lidar last year, it is now possible to study some of the fundamental links between radiation and clouds. The shortwave transmittance is mostly controlled by the fractional cloudiness which can be measured by the lidar and the microwave radiometer. The downwelling infrared irradiance is controlled by cloud base height. During the presentation we will show first results of a study of these links at Cape Grim.

A New Global Quality Control for Long-Lived Trace Gas Measurements

Roger Francey, Paul Steele & Colin Allison

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Peter Tans & Ken Masarie

National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory Boulder, Colorado, USA

Abstract

The presentation describes new Global Quality Control for Long-Lived Trace Gas Measurements.

The Vital Role of Data Management in Studies of Atmospheric Trace Species

Paul Krummel & Paul Steele

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Brian Weymouth

Cape Grim Baseline Air Pollution Station, Smithton, Tasmania 7330
Bureau of Meteorology, Melbourne, Victoria 3001

Abstract

The important role of effective data management in the operation of the Cape Grim Baseline Air Pollution Station has long been recognised. Advances in both computer technology and telecommunications technology have permitted, even demanded, changes in the way that some issues of data management are addressed.

Over the past year, some important upgrades have been initiated in aspects of the management of Cape Grim and related data at CSIRO Atmospheric Research (CAR). One of these was our access to a network server (Windows NT) with adequate disk storage capacity. All raw and semi-processed flask data from analytical instruments in GASLAB (gas chromatographs and mass spectrometers) are now backed up to either the central (UNIX) file server or the network server, on a nightly or fortnightly basis. The installation of the network server has also allowed us to begin compiling a central repository of Cape Grim and related data. Routine, automated backups of these data (to digital linear tapes) provide a high level of security. Files are accessible to CAR Cape Grim staff and are 'read only', preventing inadvertent or malicious alterations. Data files have been compiled using common formats wherever possible, and a selection of date/time styles, making them particularly user-friendly. Files can be easily imported into spread-sheet applications, and IDL routines are provided for each data set. The maintenance of effectively duplicate information at both Cape Grim and Aspendale is part of an agreed strategy for long-term security of the data records, and supplements the database developments at Cape Grim.

AGAGE data have been transferred electronically from Cape Grim to La Jolla and then to Aspendale on a nightly basis for about 3 years. A recent development is the implementation of automated transfers and processing of other data from Cape Grim to Aspendale. Presently, only CO_2 'baseline hours' (transferred monthly), back trajectory and hourly averaged meteorological, CO_2 and CN data (transferred daily) are being handled in this way. The time and cost savings of such methods make them attractive for most data sets. The existence of duplicate data sets at Aspendale could also help reduce the need for data requests directly to Cape Grim staff. The current status of the Cape Grim data holdings at Aspendale will be described.

Effective data management and good software tools make the science easier to do. We will attempt to demonstrate this with some case studies of significant short-term changes in CO_2 concentration at Cape Grim. The meteorology during the periods of these case studies will be examined, as well as corresponding changes in some other trace species.

Investigation of Urban and Regional Emissions of Trace Gases

Bronwyn Dunse

Department of Chemistry, University of Wollongong, Wollongong, NSW 2522
CSIRO Atmospheric Research, Aspendale, Victoria 3195

Paul Steele, Paul Fraser & Peter Hurley

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Stephen Wilson

Department of Chemistry, University of Wollongong, Wollongong, NSW 2522

Abstract

The AGAGE multi-detector (FID, ECD's, MRD) trace gas data set (consisting of ten trace species) from Cape Grim for the years 1994 to 1998 is being used for a study of emissions of these trace gases from the Melbourne region. The observed correlations between the trace species during episodes of Melbourne pollution at Cape Grim, and an independent estimate of annual emissions of carbon monoxide from the Melbourne region are used to estimate emissions of other species.

The estimated emissions for N_2O by this correlation method are considerably higher than inventory estimates. Possible sources of N_2O in Melbourne have been investigated. Results from flask sampling around Melbourne allow some suggestions to be made about which sources may be responsible for the higher N_2O emission estimate obtained in this study.

The emission and transport of trace gases from the Melbourne region to Cape Grim is being investigated using The Air Pollution Model (TAPM). TAPM uses the Bureau of Meteorology (BoM) Limited Area Prediction system (LAPS) analysis data to provide the synoptic conditions. Emissions inventory data in the form of spatially distributed source functions for species such as carbon monoxide have been obtained from the Victorian EPA. These emissions have been gridded and are released into the model to study the transport of trace gases from Melbourne to Cape Grim. Preliminary results from model runs will be presented.

Estimating Net Primary Productivity of the Australian Continent

Ying-Ping Wang

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Ray Leuning

CSIRO Land and Water, FC Pye Laboratory, Canberra, ACT 2601

Abstract

Various models of terrestrial ecosystems have been used to estimate the net primary productivity (NPP) of the whole Australian continent, and the results from these models vary between 1 and 2.8 Gt C yr^{-1}. Because these estimates of NPP have not been directly verified, and because the assumptions made in the models and the data sets used to calibrate those models are different, it is quite difficult to reconcile the differences in the estimated NPP by different models. Here we incorporated a process-based model of terrestrial ecosystems into an atmosphere transport model (DARLAM) and used the combined model to calculate the expected hourly CO_2 concentrations at Cape Grim. The initial estimate of NPP for Australia was between 1 and 1.25 Gt C per year for the period 1990 to 1995, but the resultant calculated surface CO_2 concentrations at Cape Grim were significantly lower than observed. Using an inverse technique to match the modelled and observed surface CO_2 concentrations at Cape Grim, our revised estimate of NPP for Australia was between 0.8 and 1.1 Gt C yr^{-1} for the period 1990 to 1995. Caveats of the approach will be discussed.

Comparing Trace Gas Measurements from Flasks Collected at Cape Grim and Analysed at Different Laboratories

Lisa Cooper, Roger Francey, Paul Steele, Ray Langenfelds,
Darren Spencer, Colin Allison & Paul Krummel

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Ken Masarie

National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado, USA

Abstract

A flask air-sharing or Intercomparison Program (ICP) commenced between NOAA/CMDL and CSIRO GASLAB in 1991. Flasks filled at Cape Grim as part of the routine sampling network are sent to CSIRO's GASLAB for trace gas analyses before being forwarded to the originating laboratory. (The initial stimulus came from the GASLAB strategy of minimising the sample size required for multi species measurement, which in turn was developed for the ice core program). Now GASLAB is carrying out similar intercomparisons with 7 international laboratories, with mixed results. Comparisons are not always frequent enough to determine differences at the required precision for global inversion studies. Recent software developments have improved the diagnostic aspects of the program. However, they are much more effective when the data transfers and comparisons are automated, which is the case for three laboratories now.

The future evolution of the ICP program will be explored in the context of the GLOBAL HUBS proposal a new Global Quality Control for Long-Lived Trace Gas Measurements.

Air Mass Characterisation at Cape Point

Ernst Brunke

South African Weather Bureau, Stellenbosch 7599, South Africa

Stewart Whittlestone & Wlodek Zahorowski

Australian Nuclear Science and Technology Organisation, Menai, NSW 2234

Abstract

A new radon detector equipped with a calibration system was installed at the baseline atmospheric observatory at Cape Point, South Africa in February 1999. Analysis of the first few months of data have shown that a broad range of air mass origins can be present in both the baseline and continental wind sectors. Baseline sector air generally has higher radon levels, averaging about 800 mBq m^{-3} than at Cape Grim, where the average is about 100 mBq m^{-3}. While this may be partly due to curving air paths entraining South African air into the baseline sector, back trajectories show that transport over South America can lead to radon levels as high as 600 mBq m^{-3} after a transit time of one to two weeks. In this respect the Cape Point air masses resemble those at Mauna Loa Observatory, where radon levels are rarely below 200 mBq m^{-3}, and transit from Asia can occur in less than 10 days. A preliminary assessment has been made of radon in conjunction with other trace gases in the baseline, urban (Cape Town) and continental wind sectors.

On its own, wind sector selection achieves only limited characterisation of the air samples. It is clear that a much improved characterisation of air masses will be achieved by including carbon monoxide and radon in the selection criteria.

Recent Simulations of Trace Gas Transport using C-C Model and DARLAM

Eva Kowalczyk & John McGregor

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

Considerable progress has been made in the development of the Conformal-Cubic Model (C-C Model) since the last Cape Grim meeting. The C-C Model is a global grid-point primitive equations model with semi-Lagrangian numerics and provision for grid stretching. The talk will describe simulations of transport of radon and CO_2 for a stretched grid over Australia. Comparisons between the results from C-C Model, DARLAM and observations of radon and CO_2 from Cape Grim will be presented. Some recent experiments with the latest version of DARLAM will also be presented during the second part of the talk.

The Use of Sulfur Isotopes to Assess the Gas to Particle Conversion Mechanism of Atmospheric Sulfur Species

Jill Cainey & Mike Harvey

National Institute of Water & Atmospheric Research, Kilbirnie, Wellington, New Zealand

Abstract

The emission of dimethylsulfide (DMS) from the remote oceans of the world is suggested to result in the production of new cloud condensation nuclei (CCN) in the form of sulfate aerosol. This increase in CCN numbers could result in an enhancement of clouds, affecting global albedo. To date it is this indirect effect of sulfate aerosol and clouds that cause some of the biggest uncertainties in modelling the impact of greenhouse gases. Observations of the atmospheric sulfur cycle indicate that most marine sulfur is incorporated into existing particles, via heterogeneous processes, resulting in no net change in the number of CCN. To increase CCN numbers homogeneous conversion must occur. Sulfur isotope studies can be used to identify the relative importance of the heterogeneous and homogeneous processes, since fractionation occurs between the gas phase, sulfur dioxide, and the aerosol sulfate. The heterogeneous process favours the heavier sulfur isotope, while the homogeneous favours the lighter isotope. By concurrently monitoring sulfur dioxide and aerosol sulfate at Baring Head, this shift in the $\delta^{34}S$ value can be determined and used to assess the role of DMS-derived sulfate in climate modification.

Total Column Amounts, Isotopic Ratios, and Information on Trace Gas Profile Variations Retrieved From Solar Infrared Spectroscopy

Arndt Meier, David Griffith, Cirilo Bernado, Stephen Wilson,
Ian Jamie, Fred Turratti & Frances Phillips

Department of Chemistry, University of Wollongong, Wollongong, NSW 2522

Abstract

Since June 1995, solar infrared spectra have been recorded on a continuous basis at Wollongong University (34.45°S, 150.88°E, 30 m above sea level). Solar FTIR spectroscopy is a valuable contributor to long-term monitoring. Its inherent, long-term stability and the re-assessability of the raw data at any time in the future, as well as the high number of trace gases measured simultaneously, add vitally to its importance.

We will give an overview of the trace species currently retrieved from these spectra with an emphasis on results relevant to Cape Grim. Besides the 'classical' retrieval of total column amounts we will highlight most recent developments in the data retrieval that allow us to quantify isotopic ratios for select species. Case studies will include D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$, and $^{15}N/^{14}N$ ratios. Though the current quality of the spectroscopic data available from laboratory measurements limits our absolute accuracy at present, the precision is good enough to observe significant signals.

We do not see our isotopic measurements as a potential replacement for mass spectroscopy approaches, but as a complement. We can separate molecules of same mass but different symmetry (e.g. $^{15}N^{14}N^{16}O$ versus $^{14}N^{15}N^{16}O$, while mass spectrometers can achieve higher absolute accuracy for the sum of the isotopomers (e.g. the different mass 46 N_2O molecules).

Finally, we show that common dynamical changes, such as variations in the tropopause altitude, are readily seen in the line shape of absorption lines. We use this information to improve our assumed volume mixing ratio profiles. It is demonstrated that even simple profile corrections improve the accuracy of both the retrieved total column amounts and the corresponding tropospheric volume mixing ratios considerably.

Cape Grim Photochemical Boundary Layer Box Model: Recent Developments

Henry Granek, Greg Ayers, & Rob Gillett

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Rebecca Johns

School of Chemistry, University of Tasmania, Launceston, Tasmania

Abstract

The initial version of a photochemical box model 'tailored' to conditions encountered at Cape Grim was produced in 1989, aimed at providing a hitherto lacking tool for evaluating oxidation processes central to the marine atmospheric sulfur cycle derived from oxidation of dimethylsulfide (DMS). The initial model contained only twelve kinetic coefficients, and was focussed solely on ozone photolysis followed by production of OH and HO_2 radicals, and formation of hydrogen peroxide. Ozone levels were prescribed, as were virtually all other important physical and chemical boundary conditions. Nevertheless, the model did a remarkably good job of reproducing features of the observed diurnal and seasonal cycles in hydrogen peroxide levels measured at Cape Grim.

In the decade since this initial work the model has been developed and applied to a variety of increasingly complex photochemical problems. The model currently contains almost five hundred kinetic coefficients applied to almost two hundred chemical species, and has applications to the ozone-nitrogen oxides photochemical cycle, peroxy radical/peroxides cycles (including organic peroxides), DMS and other sulfur oxidation processes, methane oxidation processes including formaldehyde formation, and short-chain hydrocarbon oxidation processes. In addition to being developed chemically, the model has been generalised in a temporal sense to enable easy modelling of complete annual periods at virtually any chosen time resolution. It has also been generalised in a spatial sense, such that subject to availability of necessary boundary conditions it may be run for any location in the Southern Hemisphere.

In this presentation the features of the current model will be described, with model capabilities illustrated by a range of results from runs carried out at Cape Grim and two other locations.

Auditing Instrument and System Performance and Data Quality in Surface Ozone Monitoring Systems

Mick Meyer, Ian Galbally & Simon Bentley

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

The surface ozone monitoring system has been in continuous operation at Cape Grim since 1982. Using the operational experience gained from this system, two more surface ozone monitoring systems were subsequently installed in tropical sites; at Charles Point, NT, in 1993, and at the WMO GAW station at Bukit Koto Tabang, West Sumatra in 1995. When the Cape Grim system was designed, there were no international ozone standards directly relevant to background air monitoring systems. However in recent years the WMO has developed a suitable standard and has instituted a program of regular independent audits of surface ozone systems in GAW stations. The first audit was performed in July 1999 at Bukit Koto Tabang and found the system conformed to the standard. In this paper we discuss the performance characteristics of the instruments and systems at all three stations in the light of this current standard, and review the statistical properties of the resultant data stream with respect to the data reduction procedures currently in operation.

Atmospheric Air Dryer System for Cape Grim's New Low Flow CO_2 Analyser

Darren Spencer, Grant Da Costa & Paul Steele

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

High Precision measurement of atmospheric CO_2 by NDIR requires extremely low levels of water present. With the new CO_2 analyser achieving improved precision and lower flow rates of sample gas, a drying system was required which matched this design philosophy.

To achieve this goal, an alternative to the existing cryo trap system was chosen. The requirements for an improved drying system are:

- small volume
- less maintenance
- low cost
- a more robust, portable system for field applications.

The new drying system consists of a Nafion dryer with magnesium perchlorate mop up to achieve a dew point of -76°C (1 ppm H_2O) at the operational flow rate of 15scc min^{-1}.

Nafion is a proprietary copolymer made by DuPont. The material is extremely selective for transporting water molecules through the membrane to a dry purge gas. The manufacturer claims no loss of CO_2 from the sample across the membrane to the purge gas. However, at the precision to which we are measuring, there is some CO_2 transfer across the Nafion membrane.

This talk will discuss testing of the dryer system using a dry baseline test atmosphere. Sensitivity of the CO_2 measurement to CO_2 concentration gradients and differential pressure across the Nafion membrane will be examined and quantified.

Cape Grim's New Low Flow CO_2 Analyser: Results of Operational Trials at Aspendale

Grant Da Costa, Paul Steele & Darren Spencer

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

The new CO_2 analyser has been carrying out in situ measurements successfully at Aspendale since February 1999. This operational trial has allowed the performance of the system to be verified. A set of calibration procedures, atmospheric measurement procedures and data processing strategies have been developed to make use of the unique capabilities of the system.

The talk will begin with a brief recap on the features of the new system. Next will follow the results of the operational trial, under the following headings:

1. Calibration-related issues and calibration performance
   - ♦ New calibration procedures.
   - ♦ Long term stability of the analyser.
   - ♦ Use of the system for detecting drifting tanks.
   - ♦ Precision when operating in calibration mode.
   - ♦ The ongoing issue of high-pressure regulators altering the concentration of resident CO_2.
2. Atmospheric measurement issues and performance.
   - ♦ The new operating strategy for atmospheric measurements.
   - ♦ The abolition of working standards.
   - ♦ Data processing and correction methods.
   - ♦ Reference tank and calibration tank lifetimes.

The issue of alteration of CO_2 concentration by the Nafion drying system will be discussed in a separate presentation by Darren Spencer.

If time permits, the presentation will conclude with a remote-controlled live demonstration of *in situ* measurements, along with a data processing demonstration.

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Methane Emissions From Cattle Using Long-Path FTIR Spectrometer and Tracer Method

Chih-Hsiang Hsu & David Griffith

Department of Chemistry, University of Wollongong, Wollongong, NSW 2522

Andy Reisinger & Martin Manning

National Institute of Water and Atmospheric Research, Kilbirnie, Wellington, New Zealand

Abstract

Methane emissions from a herd (23 to 50) of yearling cattle were measured, between September 4 and 19, 1999, on a dairy farm in Battersea, south Wairarapa, New Zealand (41° 12' S, 175° 42' E).

The measurements were carried out on a paddock of a dairy farm. The paddock had an open fetch of 500 m towards the north/north-west and south, and shelter belts within 150 m towards the west and east. A 6 m mast was set up at the south end of the paddock. The mast contained measurement devices for wind speed (at 0.5, 1, 2, 4 m), temperature (at 1 and 4 m), relative humidity (at 1 and 4 m), sonic wind/temperature (at 2 m), and gas inlets for the FTIR spectrometer (at variable heights between 0.5 and 6 m, as well as upwind of cattle on certain occasions). A digital camera was used to monitor cow positions at 10 minute intervals. A caravan containing the FTIR instrumentation, PCs for logging meteorological data and a GC with PC for SF_6 measurements was placed about 40 m away, south-east of the mast.

Figure 1 shows the setup where yearling cows were confined to a narrow grazing strip upwind of the mast (strip width 5-10 m, distance from mast 15-25 m). N_2O was released from 11 capillary tubes connected to a N_2O cylinder at distances of approximately 4 m, thus covering a total strip length of 40 m.

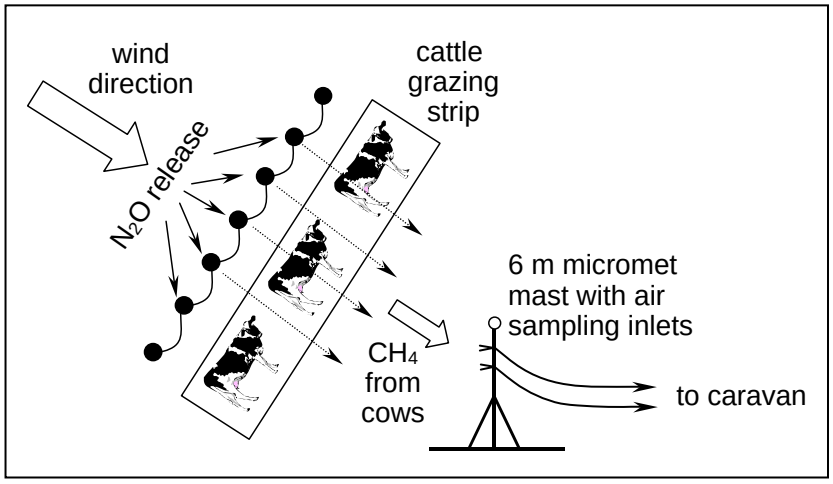


Figure 1. Schematic configuration for cattle CH_4 emission measurement using a tracer technique. The same arrangement was also used for the mass-balance approach.

Since the release rate for N_2O is known, the correlation between CH_4 and N_2O allows the calculation of the CH_4 flux according to:

$$F_{CH_4} = F_{N_2O} \cdot \frac{\Delta CH_4}{\Delta N_2O} \quad (1)$$

where Δ signifies the concentration relative to the upwind (background) value. Three such experiments were carried out for various numbers of cows and mast distances. Figure 2 shows the concentrations of N_2O and CH_4 measured during 16 September 1999. A good linear correlation between the observed N_2O and CH_4 concentrations can be seen. The slope between the CH_4 and N_2O concentrations is 10 (ppb / ppb). Together with the known release rate for N_2O (0.94 l/min) and the total number of cows (23) in the paddock, this translates into an emission rate of 24.5 litres of CH_4 per cow per hour according to (1).

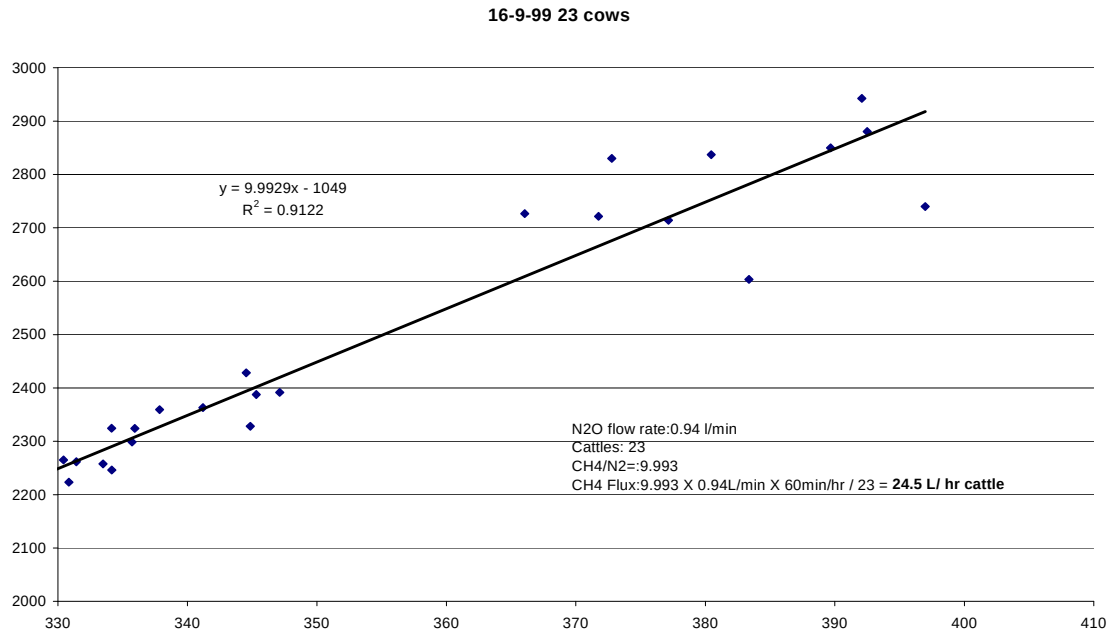


Figure 2. Correlation between CH_4 and N_2O for the time period plotted in Figure 3 at all heights.

The emission rate derived from the 3 days of separate measurements, on the 9th, 11th and 16th of September, were found to be very consistent. The hourly emission rates for the 3 days were 25, 25, and 24.5 litres CH_4 per hour per cow. The consistency of these rates, despite the variation in total numbers of cows and distances from the mast, suggests that the measurement system is a robust method for estimating CH_4 emissions on a small scale. It is also worth pointing out that the sensitivity of the instrumentation would allow the measurement of much smaller emission rates.

Measurements of Atmospheric Trace Gas Composition at Charles Point, N.T., 1996 - 1998

Ian Jamie & David Griffith

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Abstract

A Fourier Transform Infrared (FTIR) spectrometer was installed at the Charles Point Atmospheric Monitoring Station, 30 km west of Darwin in northern Australia. From August 1996 to December 1998 the instrument was used to monitor the near-ground atmospheric volume mixing ratios (vmr) of CO_2, CH_4, CO, N_2O and $\delta^{13}CO_2$. These measurements will be used in an attempt to address the large uncertainties in the contribution of tropical savanna biomass burning to the Australian greenhouse gas budget.

The instrumentation consisted of a 1 cm^{-1} resolution FTIR spectrometer, 22.1 m optical pathlength sample cell, InSb detector, gas handling hardware with computer control for unattended operation. Samples are taken every 30 minutes. Quantitative analysis was achieved using synthetically derived calibration spectra and Classical Least Squares fitting. Conversion to an absolute scale was obtained through the measurement of a well characterised standard (traceable to a primary standard).

The high temporal resolution has allowed the detection of correlations between the mixing ratios of the species on a daily or shorter time-scale and of seasonal trends. During a calendar year there was a general decrease in the mixing ratio of the species, from roughly January to April, and then an increase May through to December (Figure 1). This trend is overlaid with acute changes on the order of hours or days.

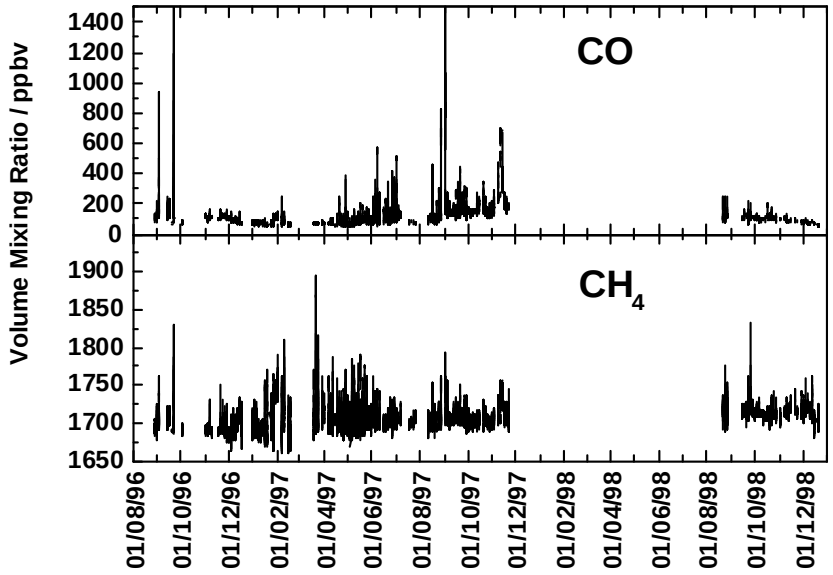


Figure 1. CO and CH_4 volume mixing ratios at Charles Point, N.T., 1996 – 1998.

The seasonal trend matches well with the change from Wet Season (maritime, clean air) to Dry Season (terrestrial and biomass burning affected air).

The mixing ratios were seasonally detrended by subtraction of a spline fit to weekly minimum mixing ratios. The result is equivalent to an excess mixing ratio, i.e., the variation in mixing ratio from 'background' values. The ratio of CO and CH_4 excess mixing correlates well with seasonal effects (Figure 2).

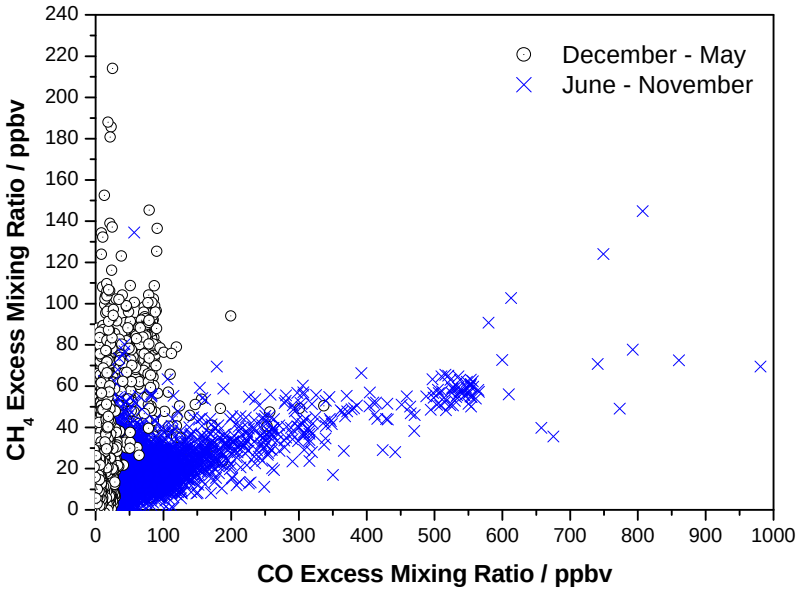


Figure 2. The correlation between the excess mixing ratio of CO and CH_4 at Charles Point.

The June - November data show a correlation that corresponds well with the arrival of air at Charles Points that has been in contact with biomass burning events. The December - May data show little or no correlation.

Teaching Atmospheric Chemistry

Stephen Wilson & David Griffith

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Abstract

As part of the 'strategic link' between Cape Grim and the University of Wollongong we have been considering methods for increasing student interest and exposure to the research carried out at Cape Grim. One option that is currently being developed is based on students in the 3rd year Environmental Chemistry course analysing Cape Grim data to produce estimates of trends and annual cycles, and to interpret this in terms of what is known. A possible list of species is presented below.

This will allow students to look at the real issues of data analysis and interpretation, as well as see how these measurements fit within the current understanding of the atmospheric fate of these species.

Examples of what this might look like will be presented, and it is hoped that this will act as a catalyst for discussion and invitations/offers of assistance!!

Species	Source of data
CO_2	Cape Grim
N_2O	Cape Grim
CO	Cape Grim
CH_4	Cape Grim
CFC's	Cape Grim
Aerosols (CN/CNN)	Cape Grim
Aerosol optical properties	Cape Grim
Ozone	Cape Grim
NOx	Cape Grim + ?
HCl/ HF	UoW FTIR data

Observations of OH, HO_2, Hydrocarbons and Formaldehyde and Modelling Studies from SOAPEX2

Nicola Carslaw, David Creasey, Geoffrey Evans, Dwayne Heard, Maxwell Hunter, James Lee, Alastair Lewis & Michael Pilling

School of Chemistry, University of Leeds, Leeds, UK

Abstract

Using a variety of experimental techniques, a number of measurements were made by the Leeds group during the Southern Ocean Atmospheric Photochemistry Experiment (SOAPEX2), at Cape Grim Baseline Air Pollution Station (CGBAPS), in January and February 1999. The aim of SOAPEX is to understand the local fast photochemical processes which occur throughout the atmosphere and which determine the distribution of atmospheric trace constituents on a range of scales from local pollutants to globally distributed greenhouse gases. Diurnal profiles of OH and HO_2 were recorded, with 30 second resolution, on 25 and 6 days, respectively, using laser-induced fluorescence detection at low pressure (the FAGE technique). The maximum noon-time values for OH and HO_2 were $4x10^6$ and $2x10^8$ molecule cm^{-3}, respectively. A comprehensive suite of non-methane hydrocarbons (23 species, C2-C7) were measured continuously at hourly intervals for over 5 weeks, using an automated GC-FID instrument. Formaldehyde measurements were made at ca. 20 minute intervals using a gas chromatograph equipped with a helium ionisation detector (HID), which displays a better response to oxygenated hydrocarbons than FID. Representative data will be shown for all these species during baseline and non-baseline conditions. A zero-dimensional box model has been constructed using the Leeds Master Chemical Mechanism, in order to describe the chemistry at Cape Grim. The predictions of the model for OH are compared to observations, although the comparison is preliminary as some of the required input data are unvalidated.

Observations of Halogen Species in the Southern Hemisphere during SOAPEX2

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Abstract

Tropospheric oxidants control the conversion of trace gas pollutants to soluble compounds, which can subsequently be removed from the atmosphere by depositional processes. The tropospheric oxidising capacity is governed largely by the abundance of hydroxyl (OH) radicals, nitrate (NO_3) radicals and O_3, which provide primary loss mechanisms for the removal of many trace gases. Reactive halogen species (RHS) have been shown to influence tropospheric oxidation processes in polar regions, where they are strongly inferred in rapid ozone depletion events. Halogen atoms react directly with O_3 forming XO (where X = Cl , Br and I) radicals. The recent observation of IO at mid-latitudes has demonstrated the impact of RHS on the oxidising capacity of the non-polar troposphere. Sources of inorganic halogen species included natural (oceanic biogenic production) photolabile polyhalomethanes such as bromoform ($CHBr_3$) and diiodomethane (CH_2I_2). We present measurements of halogen species including the iodine oxide radical and a number of organohalogen compounds, made in the remote marine boundary layer during the Southern Ocean Atmospheric Photochemistry Experiment (SOAPEX2) in January/February 1999.

Oxidised Nitrogen Compounds in the Marine Boundary Layer of the Southern Hemisphere Measured During SOAPEX 2

Graham Mills, Neil Brough, Tim Green, Jon Baker, Lucy Carpenter & Stuart Penkett

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Measurements of oxidised nitrogen including C_1 and C_2 alkyl nitrates, PAN, NO_x and NO_y were made at Cape Grim during SOAPEX II. In baseline air, NO levels peaked at about 5 pptv during mid-morning, with NO_2 showing only a small variation from a 24 hr hour average of about 15 pptv. The source of NO_x in clean oceanic air is uncertain. PAN levels were not above 3 pptv during baseline conditions and decomposition could not explain the observed NO_x levels. Methyl and ethyl nitrate concentrations were both elevated in clean oceanic compared to polluted air, and over a factor of 3 higher than measurements made in the clean northern hemisphere. These atmospheric observations suggested an oceanic source. However, our preliminary conclusion from analysis of coastal seawater samples is that the ocean was undersaturated. Baseline levels of methyl and ethyl nitrate were approximately 20-30 and 4-5 pptv, respectively, representing a combined fraction of NO_y similar to that of modelled HNO_3 levels. Even though their concentrations were high, the alkyl nitrates did not significantly impact baseline NO_x levels, due to their long lifetimes. Preliminary NO_y data suggested a deficit in the oceanic oxidised nitrogen budget, other than from observed NO_x, PAN, C_1 and C_2 alkyl nitrates and calculated HNO_3.

The Aerosonde as an Atmospheric Chemistry Sampler

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Greg Tyrrell

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Abstract

The Aerosonde is a small robotic aircraft for long-range environmental monitoring and surveillance. It has been developed especially for meteorological and environmental reconnaissance over oceanic and remote areas, and in harsh conditions for which its economy and flexibility will allow routine operations on a much wider scale than has been possible in the past. The Aerosonde robotic aircraft was developed from the start with very strong user input. To ensure that the user input remained at a high level, we programmed an extensive series of field missions into the overall development effort.

As a result, over 800 hours of Aerosonde flight operations were undertaken in Australia, the United States, Canada and East Asia in the period 1995-1998. These extensive operations have provided a valuable experience base for establishment of the Aerosonde operational facility. Aerosonde Robotic Aircraft provide a full service for the operation of Aerosonde-class robotic aircraft. Operations has added over 200 flight hours in 1999.

The operations at Cape Grim were undertaken in support of the SOAPEX II field campaign. This was the first operations for the Phase I Aerosonde in 1999 and was conducted as a collaboration between the Bureau of Meteorology, CSIRO and Aerosonde Robotic Aircraft. The specific goal was to make serial soundings from the surface to 3000 m in the vicinity of Cape Grim to provide meteorological data during flights covering five days, including one 24-hour mission, in support of the chemistry observations that were the feature of SOAPEX II. The mission objectives were achieved during 7 flights totaling of 64 hours. No aircraft were lost during the exercise although some minor problems were reported. The Aerosonde crew worked with the field scientists to provide soundings at requested sites during that time.

Plans to further the Aerosonde as an atmospheric chemistry sampler are currently underway with NASA to develop small, lightweight chemistry instrumentation. Envisaged operations are of Aerosonde flights within a volcanic plume in order to make *in situ* measurements of ambient conditions, including temperature, pressure, and humidity, with the additional possibilities of deploying a new electrochemical SO_2 concentration sensor and a particulate collector and number-density counter.

Results from the SOAPEX II flights will be presented along with plans to further Aerosonde capabilities as a chemistry sampler.

Long-lived Halogenated Compounds in the Stratosphere

William Sturges, David Oram & Stuart Penkett

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Paul Fraser

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Andreas Engel

Institute für Meteorologie und Geophysik, J. W. Goethe Universitat Frankfurt, Germany

Abstract

Stratospheric air was collected using a balloon-borne cryogenic whole air sampler at both mid-latitudes and in the Arctic. This device collects up to fifteen samples from the tropopause to above 30 km. Analyses of a wide range of halocarbons were made using a gas chromatograph-high resolution sector mass spectrometer. In this abstract we present selected results for some very long-lived halocarbons measured in the stratosphere. In the poster these are compared with tropospheric trends obtained from air archived at Cape Grim, Tasmania.

Figure 1 shows the altitudinal profiles from one of the balloon flights over France. The concentrations in a high-pressure standard collected by NOAA-CMDL at 3100 m in the Colorado Mountains in 1994 are shown for comparison (except for CHF_3, which is anomalously high in the standard). The lower-most balloon samples closely resemble the concentrations in the NOAA standard, reflecting the essentially tropospheric nature of the bottom of the profile. Declining concentrations with height arise both from stratospheric loss processes (where these exist) and from tropospheric growth, bearing in mind that the mean age of stratospheric air generally increases with height.

The shortest-lived compound of those shown is CFC-114a, a less abundant isomer of the much longer-lived (300 y) CFC-114, as clearly demonstrated by their very different gradients. CFC-115 is longer lived in the atmosphere at 1,700 y. SF_6, which is now quite widely used for dating stratospheric air, has a lifetime of 3,200 y. Fluoroform (CHF_3), despite an only moderately long tropospheric lifetime (230 y) has a steep gradient in the stratosphere, which is itself largely accounted for by its tropospheric growth rate.

CFC-13, c-C_4F_8, and C_2F_6 have lifetimes of 640, 3,200, and >10,000 y respectively. The latter compound is of interest as a potential alternative age tracer to SF_6, due to its longer lifetime, absence of sinks in the upper atmosphere, and essentially linear tropospheric growth as shown by the Cape Grim record. The poster will show that the SF_6 trend deduced from C_2F_6-dated stratospheric air from four balloon flights matches the observed tropospheric trend well, although there is a slight tendency towards higher SF_6 values in mid-latitudinal profiles compared with Arctic profiles for equivalent C_2F_6 ages.

An interesting 'new' compound has been tentatively identified as SF_5CF_3. The concentrations shown in Figure 1 are highly approximate from comparison with SF_6 peak areas. This compound appears to be extremely long-lived and to be growing in the atmosphere. Also measured in more recent profiles, as shown in the poster, is C_3F_8. This also shows a steep stratospheric gradient (long lifetime) and a positive tropospheric trend.

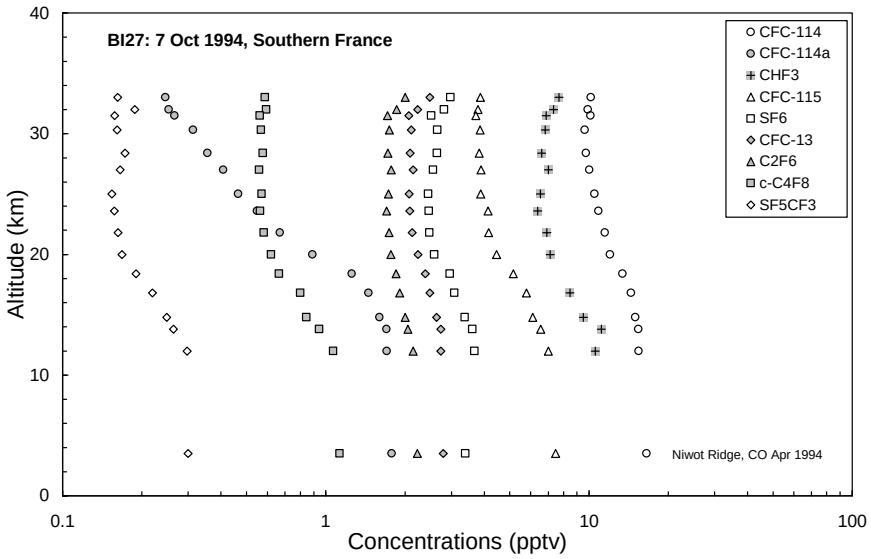


Figure 1. Stratospheric profiles of selected long-lived halocarbons from a balloon launched at Aire sur l'Adour, France.

Identification and Transport of Air Masses at Cape Grim During SOAPEX2 Field Campaign

Neil Tindale

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Bureau of Meteorology, Melbourne, Victoria 3001

Arthur Downey

Bureau of Meteorology, Melbourne, Victoria 3001

Abstract

Conceived as a study of basic tropospheric photochemistry, SOAPEX2 (Southern Ocean Atmospheric Photochemistry Experiment 2) specific goal was to study aspects of the oxidative capacity of the unperturbed atmosphere of the Southern Hemisphere at Cape Grim. Unfortunately conditions at Cape Grim during January - February, 1999, were anything but typical. Non-baseline, dry, north-easterly flow across the state was predominant and true baseline conditions were only fleetingly seen. Although frustrating for the SOAPEX2 experimenters, the anomalous flow did provide an interesting opportunity to look at air mass source regions during SOAPEX2 and at how the trajectory system portraits atmospheric flow.

Air Mass Origin: a Climatology

Arthur Downey

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Abstract

The trajectories vary seasonally and interannually. In constructing a climatology we hope to be able to make observations about different air mass origin patterns and possibly explain concentration variations in some of the constituent data. The trajectories used in this study are 96 hour daily back trajectories terminating at Cape Grim at 1500hrs local time. There is almost a complete data set for 1984 to 1993, when the system changed and so it was the data for these years that was used rather than the more recent but smaller data set. The accuracy of the trajectories is linked with natural variability. At 96 hours we estimate an average error of 350km (this equates to an average error of 1 ms^{-1}). This is in line with other published results [Kahl and Sampson, 1986]. The position of the subtropical ridge plays an important part in the pattern or shape of the trajectories. Figure 2 shows the long term average position of the ridge over the region during winter summer and respectively [Young and Holland, 1996]. The Figure shows the expected contrast between the land and the see with the ridges movement far more pronounced over land. From thermal considerations, the maximum north and south positions of the ridge occur about a month after the mid summer and mid winter months. It is a time averaged feature and so it does not tell us much about the passage of systems other than in winter, with the ridge further to the north, we would intuitively expect the trajectories arriving at Cape Grim to be more westerly than in summer. If we look at the long term monthly average percent of time the there is 'baseline' flow then the summer minimum and broad winter maximum more or less bear this out (though the maximum of the long term monthly means is October at 39%). If we look at the averages by year for January and July (Figure 4), we can see that it is quite variable though and that in July there can be over 50% baseline time or as little as 15%.

Too look at how the trajectories vary by month we constructed a climatology in which the number of hours every trajectory is within a 5 degree box is summed. These totals are then analysed by contouring. The picture these reveal is interesting and, too some degree, at odds with some of the observations above. In winter, the trajectories appear to have a bias northward and have a little less westerly component when compared to summer. This is fairly consistent with only small changes from month to month. A partial explanation may be the more frequent passage of frontal systems in winter leads to a more variable wind field.

Non Methane Hydrocarbon Measurements at Cape Grim

Loretta Kivlighon, Ian Galbally & Ian Weeks

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

Cape Grim surface air samples collected since November 1998 have been analysed by GC-FID for C_2 and C_3 hydrocarbons. Vertical profiles (150 m to 7000 m) of these compounds have been measured since January 1999.

Surface air measurements revealed seasonal cycles for ethane, propane and acetylene with a minimum around April and a maximum around November. Seasonal cycles for ethene and propene were not evident. Cape Grim overflight data showed higher concentrations of ethane in the upper troposphere compared with surface air.

This paper will review the southern hemispheric budget of ethane and its relationship to the observed seasonal cycle of ethane at Cape Grim. The sources estimated are biomass burning, vehicle exhaust, natural gas production, soil emissions and oceanic emissions.

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Comparison Of The Regionally Averaged Surface Exchange Rates Of Ozone And Radon Made Through Atmospheric Concentration Observations

Ian Galbally & Mick Meyer

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Wlodek Zahorowski & Stewart Whittlestone

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Abstract

We have analysed simultaneous observations of ozone and radon in air 10 m above the surface at the coastal site at Cape Grim, Tasmania, and related these concentrations to varying duration of time of the trajectories of these air parcels over land before they arrive at the Cape Grim station. We present a model where under selected conditions, the ratio of the regional exchange rates of the two gases at the underlying land surface is uniquely related to the ratio of the atmospheric concentrations of the two gases. This model is applicable to many gases, not only ozone and radon, and can be used either to determine an unknown exchange rate or verify an exchange rate that has been determined by the other means. In the case of ozone and radon, the exchange rates of both are known from other means, and this study serves to examine the consistency of that knowledge and reveal new aspects of the seasonal and long term variation of these exchanges.

Aerosol Optical Depth at Cape Grim (1985 - 1999)

Stephen Wilson

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Bruce Forgan

Bureau of Meteorology, Melbourne, Victoria 3001

Abstract

A 4-wavelength sunphotometer has been operating at Cape Grim since 1985. This data set has recently been completely reanalysed, using a variety of calibration methods. This analysis has quantified a number of changes that have occurred to the instrument during this period. This paper will then present a summary of the resulting record of aerosol optical depth, highlighting the impact of Mt. Pinatubo, local wind speed and the seasonal cycle in aerosol optical depth.

Instrumental Effects on Stable Isotope Measurements of Atmospheric CO_2

Colin Allison & Roger Francey

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Abstract

Time series of atmospheric carbon dioxide (CO_2) concentration and stable isotopic composition ($\delta^{13}C$ and $\delta^{18}O$) are used to provide constraints for carbon exchange. However, at the high precision required for the global isotopic measurements instrumental effects can lead to significant errors in the measured isotopic composition.

Our recently published CAR CG92 scale for stable isotope measurements of CO_2 adequately compensates for many of the instrumental effects that affect measurements of flasks from our global sampling network [*Allison and Francey*, 1999]. However, we have since observed another effect that is not adequately treated by the CG92 scale. This effect has been termed 'scale contraction' and its effects are most pronounced on our pure CO_2 standards and the Cape Grim *in situ* stable isotope program. This paper will describe the scale contraction and the new procedure developed to compensate for it. The effects of this new procedure on the CG92 scale and the wider implications of the scale contraction for merging data from other laboratories will be explored.

Allison, C. E. and R. J. Francey, $\delta^{13}C$ of atmospheric CO_2 at Cape Grim: The *in situ* record, the flask record, air standards and the CG92 calibration scale, in *Baseline Atmospheric Program (Australia) 1996*, edited by J. L. Gras, N. Derek, N. W. Tindale and A. L. Dick, pp. 45-56, Bureau of Meteorology and CSIRO Atmospheric Research, Melbourne, Australia, 1999.

Methodology of the Cape Grim GC-MS

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Simon O'Doherty & Peter Simmonds

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Abstract

An automated gas chromatograph-mass spectrometer (GC-MS) was installed at Cape Grim in September 1997, for *in situ* measurements of a range of natural and anthropogenic atmospheric halocarbons. A custom built absorption-desorption system (ADS), developed at the University of Bristol, is coupled to a Hewlett Packard HP6890 GC and HP5973 MSD.

Two litre air samples are collected and pre-concentrated by the ADS, before injection onto the GC-MS. Ambient air and alternate standard gas samples are analysed every two hours giving six calibrated measurements per day of some twenty-five compounds.

A review of the technical details of the system will be presented and some of the operational experiences discussed.

Review of Montreal Protocol Trace Gas Measurements at Cape Grim, Tasmania

Paul Fraser, Georgina Sturrock & Michelle Cox

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Nada Derek, Paul Krummel & David Etheridge

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Laurie Porter

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Abstract

Halocarbon chemicals, whose global consumption are subject to control by the Montreal Protocol, are CFCs (chlorofluorocarbons), chlorinated solvents (methyl chloroform, carbon tetrachloride), halons, HCFCs (hydrochlorofluorocarbons) and methyl bromide. There are a number of flask, including the air archive, and *in situ* measurements projects at Cape Grim that are designed to research the short and long term temporal behaviour of these species and to estimate their global and regional emissions.

A brief review of these projects will be presented and implications for recovery of the stratospheric ozone layer discussed.

Review of Kyoto Protocol Synthetics Measurements at Cape Grim, Tasmania

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Abstract

HFCs (hydrofluorocarbons), PFCs (perfluorocarbons) and sulfur hexafluoride (SF_6) are included in the Kyoto Protocol because of their very large climate forcing potential on a molecular basis and their potential effect on long term climate change. All of the major HFCs (CHF_3, CH_2FCF_3, CH_3CHF_2), SF_6 and one of the two major PFCs (CF_3CF_3) are currently measured at Cape Grim, either *in situ* or by flask sampling. Although the other major PFC (CF_4) is not currently measured at Cape Grim, data have been obtained from Antarctic firn air and these will be presented.

All of the available Kyoto Synthetics data will be reviewed and some estimates made of regional emissions. Implications for future climate forcing and plans for *in situ* measurements of all Kyoto synthetics at Cape Grim will be discussed.

Regional and Background Measurements of Halomethanes at Cape Grim, Tasmania

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Abstract

Chlorine and bromine species are the major catalysts for the significant, anthropogenically-enhanced, stratospheric ozone destruction that has occurred over the past two decades. The synthetic chemicals that provide the major halogen sources are the chlorofluorocarbons (CFCs) and halons. However, approximately 20% of stratospheric chlorine and 50% of stratospheric bromine are derived from halomethanes, largely methyl chloride (CH_3Cl) and bromide (CH_3Br), which have both natural and anthropogenic sources. The atmospheric behaviour, sources and sinks of these halomethanes are not well understood.

In an attempt to reduce the uncertainties associated with these species, an *in situ* measurement project for CH_3Cl, CH_3Br, CH_2Cl_2 (dichloromethane) and $CHCl_3$ (chloroform) was established at Cape Grim in late 1997, using state-of-the-art GC-MS instrumentation developed at the University of Bristol as part of the global AGAGE (Advanced Global Atmospheric Gases Experiment) program.

In this paper, the temporal behaviours of these species in the background atmosphere are described and low level trajectories are used to investigate the pollution episodes and to help identify possible source regions. Trajectories from two high resolution regional climate models (DARLAM – Division of Atmospheric Research Limited Area Model (CSIRO) – and LAPS - Limited Area Prediction System (BMRC)) are compared.

Positionally-Dependent Fractionation of ^{15}N in Sources and Sinks of Atmospheric N_2O

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Abstract

Nitrous oxide is a linear, asymmetric molecule with the structure N-N-O, which allows the possibility that isotopic fractionation of ^{15}N may differ between the terminal and central N atoms in atmospheric source and sink processes. For example, Yung and Miller [1997] proposed that the stratospheric photolysis rates of $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ (and indeed all N_2O isotopomers) should differ due to their different vibrational zero point energies and the consequent different overlap of their absorption spectra with the solar UV spectrum. For $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ the fractionation factors are predicted to vary by several tens of ‰. We have confirmed this positionally-dependent fractionation effect by FTIR isotopic analysis of samples of N_2O laser-photolysed between 193 and 211 nm; detailed method and results will be presented by Fred Turatti in the accompanying paper.

We have also measured vertical profiles of ^{15}N fractionation in stratospheric N_2O by analysis of solar FTIR limb spectra taken from a stratospheric balloon platform. These data also demonstrate the positionally dependent ^{15}N fractionation. The positional asymmetry is an effective tracer for N_2O stratospheric photolysis exposure and should prove useful in both budget and stratospheric transport studies.

On the input side of the ledger, biological denitrification and nitrification are major global sources of atmospheric N_2O. We will briefly discuss the biochemical pathways for N_2O production and show very preliminary evidence that positionally dependent ^{15}N discrimination is also significant in these processes.

The ^{15}N positional asymmetry provides an additional, independent isotopic constraint on atmospheric budgets of N_2O and provides a label for specific source and sink processes. In this sense it is similar to mass-independent fractionation. Positional dependence should become a useful tool in improving our understanding of the global budget of N_2O.

Yung, Y. L., and C. E. Miller, Isotopic fractionation of stratospheric nitrous oxide, *Science*, *278*, 1778-1780, 1997.

Isotopic Analysis of Atmospheric N_2O by FTIR Spectroscopy: ^{15}N, ^{18}O and Positional Dependence

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Abstract

The study of the isotopic composition of atmospheric trace gases has proven valuable in constraining budget estimates for key greenhouse gases, like CO_2. We have developed a high resolution Fourier transform infrared (FTIR) spectroscopy technique that enables measurement of the full isotopomeric composition of N_2O. We demonstrate that the isotope ratios $\delta^{15}N$, $\delta^{18}O$ and $\delta^{17}O$ can be measured to a precision of ±1.0 ‰, ±2.5 ‰ and ±4.4 ‰, respectively (1 σ). More importantly, FTIR allows discrimination of the two symmetry isotopomers $\delta^{14}N^{15}N^{16}O$ and $\delta^{15}N^{14}N^{16}O$, to a precision of ±0.6 ‰ and ±1.4 ‰, respectively. The difference between these two quantities ($\delta^{15}N^{14}N^{16}O$ - $\delta^{14}N^{15}N^{16}O$) is measured to a precision of ±0.8 ‰, and this quantity is proving to be a sensitive marker of the history of the N_2O sample.

This talk will describe the analytical technique, its strengths and limitations. Measurements of laboratory photolysed N_2O samples will be presented which show a clear symmetry discrimination in the N_2O destruction process. Plans for characterising positional asymmetry of tropospheric N_2O and its sources will be discussed.

Methane Isotopic Record Extended into the Pre-Nuclear Era

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Abstract

An expedition to Antarctica in 1997-98 retrieved hundreds of litres of air from the firn layer of the Law Dome ice sheet. The oldest samples have a mean air age of about 1940 AD. The samples were dated using measured tracers, including the radiocarbon $^{14}CO_2$ bomb pulse, and with a model of firn air diffusion. The samples allowed us to significantly extend the isotopic records of atmospheric methane, initially constructed from Cape Grim air and younger firn air samples [Etheridge *et al.*, 1998; Francey *et al.*, 1999].

Methane isotopic determinations in conjunction with mixing ratio measurements provide constraints on estimates of the global methane budget. ^{14}C, in particular, carries information on fossil sources. The large volumes of air available in firn gave us the unique opportunity to determine the $^{14}CH_4$ levels before nuclear emissions.

Etheridge, D. M., L. P. Steele, R. J. Francey, and R. L. Langenfelds, Atmospheric methane between 1000 AD and present: Evidence for anthropogenic emissions and climate variability, *J. Geophys. Res.*, *103*, 15,979-15,993, 1998.

Francey, R. J., M. R. Manning, C. E. Allison, S. A. Coram, D. M. Etheridge, R. L. Langenfelds, D. C. Lowe, and L. P. Steele, A history of $\delta^{13}C$ in atmospheric CH_4 from the Cape Grim Air Archive and Antarctic firn air. *J. Geophys. Res.*, *in press*, 1999.

Anomalous Increase in Atmospheric Methane During 1998

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Abstract

The global atmospheric methane burden has increased by a factor of 2.5 from pre-industrial times to present. This increase is responsible for –20% of the change in direct radiative forcing due to anthropogenic greenhouse gas emissions. Recent CMDL measurements show that the globally averaged methane growth rate has decreased from –14 ppb yr^{-1} in 1984 to –5 ppb yr^{-1} in 1997. Our globally averaged atmospheric CH_4 mole fractions and trends were combined with the CH_4 atmospheric lifetime of 8.9 years in a global mass balance equation to show that the decreasing growth rate of CH_4 can be explained as a chemical system approaching steady-state on a time-scale comparable to the CH_4 lifetime, where CH_4 emissions and [OH] remained nearly constant over the period of our measurements (1983-1997) [Dlugokencky *et al.*, 1998]. Based on this result, it might be concluded that there will be little future change in methane's contribution to the greenhouse effect. This is a dangerous conclusion, because the details of the global CH_4 budget are poorly known and future rates of change in CH_4 emissions cannot be predicted. During 1998, the zonally averaged CH_4 increase in the latitude band 30-90EN was 18 ppb, the largest increase observed for that latitude zone since CMDL measurements started in 1983. It is likely that this increase was due to increased natural emissions of CH_4 due to anomalously high temperatures observed in N. America during 1998 and is only temporary, but it emphasises the strong link between this potent greenhouse gas and climate.

Dlugokencky, E. J., K. A. Masarie, P. M. Lang and P. P. Tans, Continuing decline in the growth rate of atmospheric methane, *Nature, 393*, 447-450, 1998.

A Variable Sky Platform for Analysis of Erythemal UV Radiation

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Abstract

We introduce a timer-controlled variable sky-view platform (or VSP) for use with the erythemal UV-Biometer (Solar Light Company Inc.). The Biometer is housed within a vertically mounted 'shading' cylinder. A hydraulic system provides up and down movement to the Biometer thus allowing the sensor to view changing portions of the sky.

The VSP design, electronics and construction materials provides high precision usage under all weather conditions. In particular it is well adapted for continuous routine measurements of direct and diffuse UVB irradiance from a single sensor, therefore avoiding problems in matching calibrations from two different sensors.

Raw data from the VSP allows us to estimate the direct and diffuse UV irradiance for all solar zenith angles. A parameterisation of the diffuse component into variable portions of the sky for varying sky zenith angles is also possible. This task has previously been accomplished using radiance detectors with tracking systems, an expensive and time-consuming process that is not well suited for routine measurements.

An analysis of the latter component allows for investigation of the UV sky-radiance distribution. This has important applications in the areas of aerosol and cloud radiation climatology.

Preliminary Results of Sampling Cape Grim Baseline-Sector Aerosol for Lead Concentration and Isotopic Composition

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Abstract

An investigation of Pb isotopes in air at Cape Grim began in 1994. The aim was to analyse baseline air, and for this reason samples were collected from the Telecom tower to minimise the collection of local soil dust. In a preliminary study, non-baseline air from a 315° - 060° sector, was sampled in March-May, 1994. Samples were collected on 37 mm diam., 0.47 μm pore-size, cellulose acetate filters that were mounted in polystyrene monitors and housed in individual PVC rain-shelters. The measurements, made by IDMS and TIMS, gave Pb concentrations of 20-100 pg m^{-3} and a $^{206}Pb/^{207}Pb$ ratio ~ 1.10 which was slightly higher than in Melbourne (~1.07) and Hobart (~1.07) air. The small amount of Pb collected on the filters under non-baseline conditions prompted a review of the sample collection and analysis procedures.

An improved monitor-enclosure was developed through a series of prototypes to give a model that was reliable, clean and could be easily serviced. The final instrument, constructed from polyethylene and teflon, pneumatically opens to receive baseline air. Up to four filters can be mounted on the Tower, while sampling is fully controlled from the ground. The use of monitors and filters made from teflon as well as improved cleaning and handling procedures have led to a significant improvement in the quality and reliability of the measurements. Sampling of baseline-sector air began in Feb. 1999 and collection has been continuous until now. Each filter collects air for approximately one month, giving a 5-400 m^3 sample of baseline air. Figure 1 shows that over this period the Pb concentration has varied from ~2 to 68 pg m^{-3} (mean 11 pg m^{-3}) and the $^{206}Pb/^{207}Pb$ ratio changed from 1.12 to 1.16, with evidence of higher ratios in winter than in late summer and autumn. The lowest concentrations, e.g. 0.6 ± 0.6 pg m^{-3}, are comparable with the lowest reported on the Antarctic continent (1.4 ± 2.4 pg m^{-3}, Gipps Ice Rise: Dick, *Geochim Cosmochim. Acta 55*, 1827-1836, 1991). There is no apparent trend in Pb concentration with time. The Pb arriving early in the year is slightly more radiogenic than aerosol Pb on the Australian mainland or in Hobart, which suggests there is some dust in the samples. Preliminary measurements have been made of other elements to independently estimate the soil dust contribution and support the final interpretation of the isotopic data.

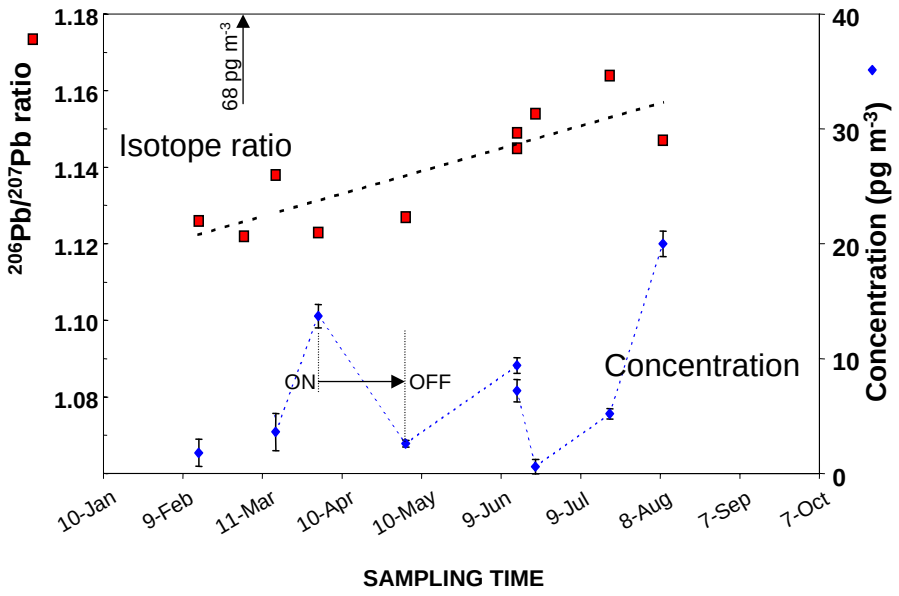


Figure 1. Plot of the $^{206}Pb/^{207}Pb$ isotope ratios and Pb concentrations in baseline air collected at Cape Grim during 1999.

Cape Grim Particle Program Review 1999

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Abstract

This presentation will give an overview of the Cape Grim particle program, comprising the history of particle measurements in the program, a number of the more important findings and technical aspects of the instrumentation and measurements. I will also discuss the rationale behind the measurement program and possible future directions. The written review will include a publication/presentation bibliography.