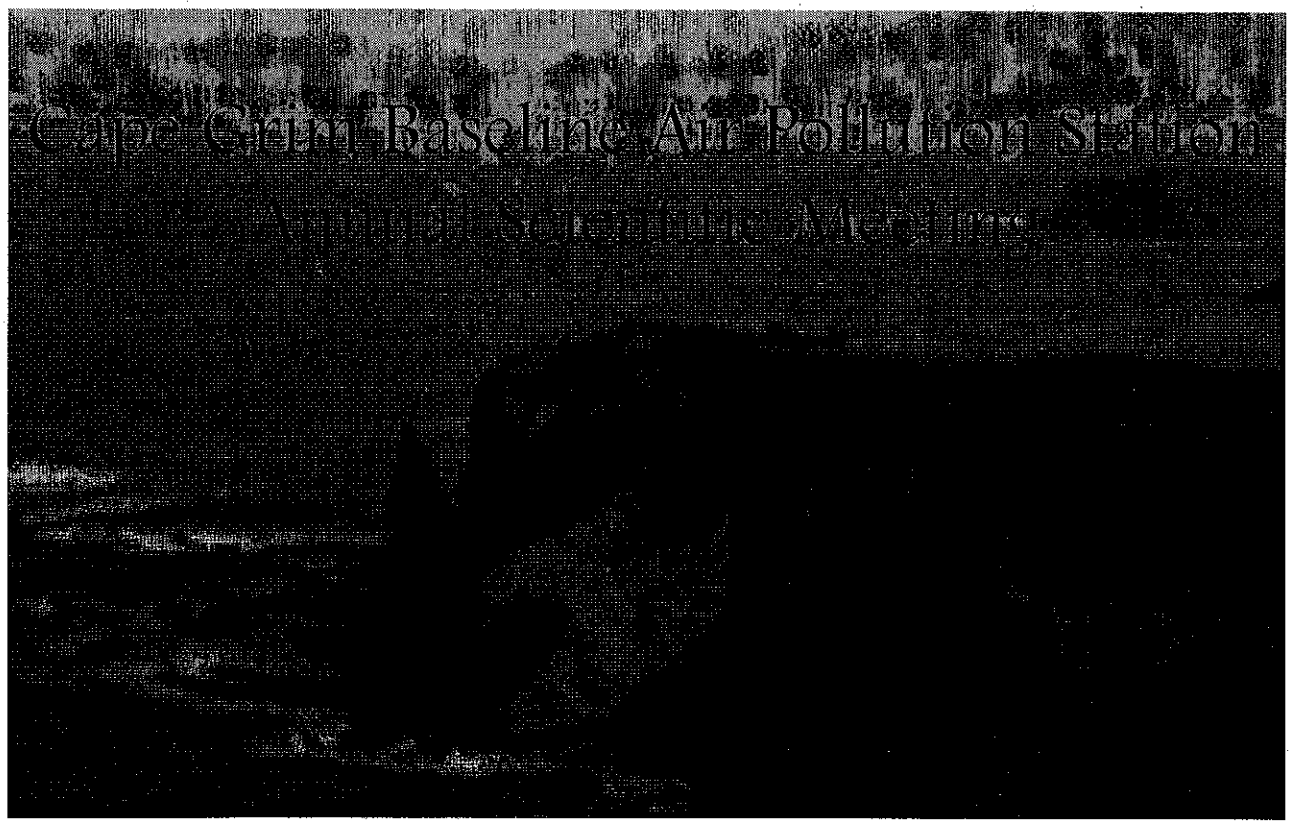
CSIRO

Bureau of Meteorology

CRC



24-25 November, 1997
CRC for Southern Hemisphere Meteorology
Clayton, Victoria

edited by Chad Dick and Nada Derek

Cape Grim Baseline Air Pollution Station

Annual Meeting, 1997

Program

Monday, 24 November

Chair	*Laurie Porter*	
09:00	Conveners / Hosts	General information on arrangements etc.
09:10	John Gras	CCN measurements at Cape Grim during ACE-1
09:35	Chad Dick	The chemical climate during ACE-1
10:00	Rebecca Webb	Nonmethane hydrocarbons in the remote marine boundary layer - some preliminary results
10:25	**Morning Tea**	
Chair	*Chad Dick*	
10:55	Reinout Boers	Retrieval of cloud optical depth and droplet concentration at Cape Grim using a microwave radiometer and a pyranometer
11:20	Frances Phillips	Retrieval of atmospheric ozone from solar spectroscopy between 320 nm and 750 nm
11:45	Lilia Deschamps	UV Index simulations and observations for Cape Grim
12:10	Ian Jamie	Measurement of CO_2, $\delta^{13}CO_2$, CH_4, N_2O and CO mixing ratios at Charles Point, N.T., using Fourier Transform Infrared Spectroscopy
12:35	Fred Turatti	Isotopes, FTIR and methane: why bother?
13:00	**Lunch**	
Chair	*Jane Warne*	
14:00	Gordon Brailsford	An overview of NIWA monitoring activities
14:25	Laurie Porter	CO_2 *in situ* calibrations
14:50	Georgina Sturrock	Progress with the Cape Grim GC-MS
15:15	**Afternoon Tea**	
Chair	*Frances Phillips*	
15:45	Steve Montzka	Observed trends for halocarbons and total anthropogenic chlorine in recent time
16:15	Paul Fraser	HCFC-22 ($CHClF_2$) and HFC-23 (CHF_3) in the Cape Grim air archive
16:40	Chad Dick	The record of chloroform in Cape Grim air
17:05	**Close of meeting**	

18:00 for 18:30	**Dinner**	**Damieri Ristorante Italiano, 259 Springvale Road, Glen Waverley**

Tuesday, 25 November

Chair	*Georgina Sturrock*	
09:00	Stewart Whittlestone	The use of Pb-212 for characterising air samples at Cape Grim
09:25	Paul Steele	The Cape Grim CH_4, CO and H_2 program: Review 1997
10:20	**Morning Tea**	
Chair	*Art Downey*	
10:45	Ray Langenfelds	The Cape Grim Overflights program: Review 1997; and The Cape Grim Archive program: Review 1997
11:45	Gordon Brailsford	Vertical Profile measurements of methane and N_2O over agricultural regions
12:10	Bernard Pak	Quantifying biomass burning contributions in the Cape Grim Overflight dataset
12:35	Ying Ping Wang	Seasonal variation of CO_2 fluxes in the Southern Ocean from 1990 to 1992
13:00	**Lunch**	
Chair	*Steve Montzka*	
14:00	Roger Francey	A 1000 year history of $\delta^{13}C$ in atmospheric CO_2
14:25	Colin Allison	The CG92 calibration scale for $\delta^{13}C$
14:50	Dom Ferretti	The development of a new technique for high precision, N_2O free, isotopic analysis of $\delta^{13}C$ in atmospheric CO_2 from small air samples
15:15	**Afternoon Tea**	
Chair	*Paul Fraser*	
15:45	Peter Rayner	The recent time history of regional carbon sources as deduced from carbon dioxide and oxygen concentration and isotopic composition measurements
16:10	Roger Dargaville	Interannual variability of CO_2 observations and modelled sources
16:35	Grant Da Costa	Recent progress with the new low-flow CO_2 analyser system
17:00	**Close of meeting**	

The CCN activity of atmospheric aerosol

John Gras

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Abstract

From a climate perspective, cloud condensation nuclei (CCN) are arguably the single most import aerosol class. Although the process of cloud nucleation has been understood in principle for many decades, few studies have actually demonstrated an ability to accurately predict nucleation activity from basic aerosol chemical and physical properties. Such a closure experiment was included in ACE-1, the first IGAC aerosol characterisation experiment conducted over the Southern Ocean in late 1995. This talk will discuss the ACE-1 CCN closure study at Cape Grim.

The Chemical Climate during ACE-1

Chad Dick

Cape Grim Baseline Air Pollution Station, Smithton, Tasmania 7330

John Gras

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Alasdair Hainsworth

Bureau of Meteorology, Tasmanian and Antarctic Region, Hobart, Tasmania 7001

Abstract

The Southern Hemisphere Marine Aerosol Characterization Experiment (ACE-1) was carried out in the region to the south and west of Tasmania from 15 November to 14 December, 1995. One of the major reasons for locating the experiment in this region was that baseline data collected at Cape Grim and Macquarie Island could provide long-term records of many of the parameters that were to be measured as part of the intensive experiment. Hence it is of interest to examine the ACE-1 experimental period to determine the extent to which meteorological and chemical conditions in the region were 'typical' for the time of year.

The records of radon, particulates and sulfur species and the general meteorology of the region during the ACE-1 period have been examined. There are several notable anomalies in both the chemical and meteorological records.

Radon concentrations in the baseline sector at Cape Grim were higher during November than average, while December concentrations were close to average. Both condensation nuclei and elemental carbon also appear to have been somewhat elevated in the baseline sector during the ACE-1. Sulfur species seem to have had generally lower than normal concentrations at Cape Grim, particularly during December. In contrast, concentrations of non-sea-salt sulfate at Macquarie Island during ACE-1 were the highest on record for the time of year. The southern part of the ACE-1 area seems to have been more biologically productive (in terms of atmospheric emissions) than the north.

Meteorological conditions were certainly different from average, with more fronts than usual crossing the region, particularly in November. However, anomalies may have been even greater if the experiment had been staged later in the summer. A synoptic pattern set up during December brought a generally southerly air flow over the region, which continued into 1996, leading to one of the coldest summers on record for much of south-eastern Australia.

Non-methane Hydrocarbons in the Remote Marine Boundary Layer - Some Preliminary Results

Rebecca Webb and Barry O'Grady

Department of Chemistry, University of Tasmania, Hobart, Tasmania 7001

Greg Ayers

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Chad Dick

Cape Grim Baseline Air Pollution Station, Smithton, Tasmania 7330

Abstract

A model has been used to simulate annual and diurnal cycles for C2 and C3 hydrocarbons under baseline meteorological conditions at Cape Grim. These modelled cycles compare well with measurements taken at Baring Head, New Zealand, which experiences similar conditions.

An automated system for continuously measuring non-methane hydrocarbons at Cape Grim has been set up by converting the gas chromatograph previously used for dimethylsulfide (DMS). Details of the modifications will be presented along with some initial results from the new system.

Simultaneous Retrievals of Cloud Optical Depth and Droplet Concentration from Solar Irradiance and Microwave Liquid Water Path

Reinout Boers

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Abstract

A 20-month time series of continuous observations of microwave radiation and solar irradiance was used to estimate the cloud optical depth and droplet number concentration at the Cape Grim Baseline Air Pollution Station, Tasmania, (40°41'S, 144°41'E). The data were selected by wind directions. When the air was of 'baseline' origin, i.e., it had travelled over long oceanic distances and was mostly devoid of anthropogenic influences, the retrieved droplet concentration and optical depth were lower than when the air was from 'non-baseline' i.e., continental origin. Therefore the observed variation in cloud microphysical properties reflects the difference between the natural background conditions over the Southern Ocean and continental conditions with elevated droplet counts. Under baseline conditions the retrieved cloud optical depth exhibits a weak but perceptible seasonal cycle that has been previously observed from satellite data with a minimum in the austral winter, and a maximum in the austral summer. The results demonstrate that routine retrievals of cloud microphysical properties are possible using only a pyranometer and a microwave liquid water radiometer.

Retrieval of Atmospheric Ozone by Solar Spectroscopy between 320 nm and 750 nm.

Frances Phillips, Stephen Wilson and David Griffith

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

Abstract

A review of a solar spectroscopic method to retrieve atmospheric ozone will be given. The spectrometers include a high resolution Fourier transform infrared spectrometer, plus two 1024 diode array spectrometers covering the ultraviolet and visible regions from 315 nm to 750 nm. The current optical configuration to transfer solar energy into the ultraviolet and visible spectrometers has been in place for approximately 10 months. During this time the spectrometers have operated on most cloud free days, with data collected on approximately 100 days to date. Recent results on the calibration of the ultraviolet and visible spectrometers using the Langley and the ratio Langley methods will be presented.

Ultra Violet Index: Model Simulations and Observations for Cape Grim

Lilia Lemus-Deschamps and Lawrie Rikus

Bureau of Meteorology Research Centre, Melbourne, Victoria 3000

CRC for Southern Hemisphere Meteorology, Monash University, Clayton, Victoria 3168

Stephen Wilson

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

Abstract

The instantaneous skin damage caused by UV radiation is calculated by the product of surface UV radiation and the erythemal action spectrum (erythemally weighted dose-rate) expressed in terms of UV Index. The UV Index calculations are performed with a simple two-stream radiation code and an ozone scheme using the meteorological fields extracted from the Bureau of Meteorology's operational global numerical weather prediction system (GASP). The UV Index analysis and forecast system was developed by The Cooperative Research Centre for Southern Hemisphere Meteorology and the Bureau of Meteorology.

The global fields of surface UV Index are obtained for each grid point for a solar zenith angle corresponding to local noon for the wavelength interval from 290-340 nm in 1 nm intervals. From the daily global clear sky UV Index fields the Australian region is extracted and interpolated to cities. The results for Cape Grim show that there is good agreement between simulations and observations, with a root mean square error for clear sky UV Index of 0.419. To account for clouds the clear sky UV Index is scaled by an empirical cloud correction factor which depends on cloud cover. The February 1997 monthly cloudy UV Index averages are presented.

Measurement of CO_2, $\delta^{13}CO_2$, CH_4, N_2O and CO Mixing Ratios at Charles Point, N.T., Using Fourier Transform Infrared Spectroscopy

Ian Jamie and David Griffith

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

Ian Galbally

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

D. Parry and G.A. Duff

Northern Territory University, Darwin, Northern Territory 0909

Abstract

A long-path Fourier Transform Infrared (FTIR) spectrometer was installed in the Charles Point Atmospheric Monitoring Station, 30 km west of Darwin, in August of 1996. Since that time it has been used to monitoring the near ground atmospheric mixing ratios of CO_2, CH_4, N_2O and CO, and the $\delta^{13}C$ of CO_2. During the Dry Season, approximately April - October, the prevailing winds bring continental air masses over the station, while maritime air masses are brought over during the Wet Season.

The measurements described here, along with parallel studies, will attempt to address the large uncertainties in Australian biomass burning contribution to the greenhouse gas budget (see Galbally *et al.* [1990]) by providing a measurement of emission levels from acute fire events and by providing an overview of annual cycles and trends in atmospheric mixing ratios. The first objective is achieved through the determination of normalised molar emission ratios, $\Delta X/\Delta Y$, where Δ denotes the excess mixing ratio over non-burning levels. It is usual to take Y as the mixing ratio of CO_2. The second objective is achieved by providing a long term record of atmospheric mixing ratios in the Australian Tropics, something that has not been provided by previous biomass burning studies.

The instrumentation is a development of that described by Esler *et al.* [1996]. It consists of a 1 cm^{-1} resolution FTIR spectrometer, 22.1 m pathlength / 8 L volume sample cell, InSb liquid N_2 cooled detector, gas handling hardware and is computer controlled for all functions. Except for routine replacement of consumables (e.g., liquid N_2, calibration gas), the system is autonomous. Samples are taken every 30 minutes, with every eighth being a calibration gas.

References

Esler, M.B., D.W.T. Griffith, S.R. Wilson and L.P. Steele, Carbon monoxide, nitrous oxide, methane and carbon dioxide - trace gas analysis by Fourier Transform Infrared (FTIR) spectroscopy, in *Baseline Atmospheric Program (Australia)* 1994-95, edited by R.J. Francy, A.L. Dick and N. Derek, pp. 117-119, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia, 1996.

Galbally, I.E., P.J. Fraser, C.P. Meyer, and D.W.T. Griffith, *Australia's Renewable Resources, Sustainability and Global Change*, edited by R.M. Gifford and M.M. Barson, Bureau of Rural Resources and CSIRO Division of Plant Ecology, Canberra, 1990.

Isotopes, FTIR and Methane: Why bother?

Fred Turatti, Stephen Wilson, David Griffith

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

Abstract

Methane is the second most important greenhouse gas. Its current level in the troposphere is 1.7 ppmv, and is increasing at approximately 0.6% yr^{-1}. There is very large uncertainty in the sources of methane. The isotopic ratios $^{13}C/^{12}C$ and D/H in methane can be used to constrain uncertainty in methane emissions, as each methane generating process fractionates the isotopes of methane by different amounts. This talk will show how isotopic measurements of methane can constrain the uncertainty in emissions, and will describe how high resolution FTIR spectroscopy can be used to carry out these measurements. High resolution FTIR offers complementary information to the current analytical technique (Isotope Ratio Mass Spectrometry), namely the ability to easily distinguish molecules of same mass, eg $^{13}CH_4$ and CH_3D.

Atmospheric Trace Gas Measurements by NIWA, Wellington New Zealand

Gordon Brailsford

NIWA Tropospheric Physics and Chemistry group, Wellington, New Zealand

NIWA and its predecessors have been carrying out atmospheric trace gas measurements in the Wellington region for many years. In the 1970's these included CO_2 concentration and isotope measurements at Baring Head with an extension in the 1980's to methane, carbon monoxide and non methane hydrocarbons. More recently the research has extended to include; a site in Suva, an Antarctic programme, the use of a NIWA research vessel in the South Pacific and Container Vessels between Auckland and Los Angeles.

The additional sites and the container ship voyages complement the Baring Head data set. For example small gradients in the $\delta^{13}CH_4$ from the ITCZ to 35°S suggest that seasonal cycles seen in the extra tropical southern hemisphere are driven by the transport of CH_4 enriched in ^{13}C.

To allow the measurement of methane and carbon monoxide samples on our MAT 252 we have modified the inlet system giving higher precision and the ability to retrieve samples for ^{14}C determinations. Current development of continuous flow methods for carbon species ($^{13}CO_2$, $^{13}CH_4$) will allow us to carry out isotope studies on small size samples from both baseline and source conditions. Links between NIWA and DAR have allowed considerable progress to be made on the development of these methods.

The monitoring programmes that NIWA run are now being complemented by some process studies to determine the emission of important greenhouse gases important for New Zealand, methane and nitrous oxide.

In situ CO_2 Analyser Calibration

Laurie Porter and Brian Weymouth
Cape Grim Baseline Air Pollution Station, Smithton, Tasmania 7330
Paul Steele
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195
Stephen Wilson
Department of Chemistry, University of Wollongong, Wollongong, NSW 2522

Abstract

Data from routine fortnightly multipoint calibrations of the Cape Grim CO_2 analyser are re-visited. Variations in analyser non-linearity and drifts in working standards and their implications for interpretation of the ambient data record are considered.

Progress with the Cape Grim GC-MS

Georgina Sturrock and Paul Fraser

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

CRC for Southern Hemisphere Meteorology, Monash University, Clayton, Victoria 3168

Abstract

An automated GC-MS instrument has recently been installed at Cape Grim for the measurement of the principal CFC replacement compounds - the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Alternate ambient air and standard analyses are recorded at a frequency of 2 hours. A 2 litre sample is preconcentrated on an adsorbent filled microtrap held at subambient temperature followed by direct thermal desorption on to a thick film capillary column.

Details concerning the mass spectral quantitation of individual halocarbons and calibration issues are described. Accurate measurement of these trace CFC replacement compounds relies on our ability to prepare gas standards of known concentration. Contamination when preparing calibration standards at the parts per trillion level is greatly enhanced. We aim to reduce this by using a single stage dilution from gravimetrically prepared primary standards. The standard preparation technique, based on a design at the Scripps Institute of Oceanography, and methods of concentration assignment and intercalibration to be used for this programme are covered.

Observed trends for halocarbons and total anthropogenic chlorine in recent time

Stephen Montzka, James Butler, James Elkins, Richard Myers and Thane Thompson
NOAA/CMDL, Colorado, USA
A. Clarke, L. Lock and T. Swanson
CIRES, University of Colorado, Boulder, Colorado, USA

Abstract

At present, the abundance of atmospheric chlorine is declining primarily because of reduced industrial emissions of methyl chloroform and its short lifetime (~5 yr). However, the decline observed for this trace gas is near its theoretical maximum and will soon become smaller. As the abundance of methyl chloroform diminishes, continued increases in other compounds could significantly slow the decline observed for total chlorine and equivalent chlorine. Long-lived halogenated compounds still increasing in the atmosphere include the halons, CFC-12, HCFCs, and HFCs. The global tropospheric abundance of HCFCs and HFCs continues to increase as they gain use as replacements for CFCs, although these gases at present contribute a small amount of Cl to the atmosphere relative to CFCs and chlorinated solvents. The 3 major HCFCs accounted for ~140 ppt of chlorine in the troposphere in mid-1996 (or <5%), and this amount was increasing by approximately 7% per year (10 ppt yr^{-1}). Although HFC-134a was increasing at a rate of 1-1.5 ppt yr^{-1} in mid 1996, it contains no chlorine and does not participate in reactions which deplete stratospheric ozone. More significant are the increases still observed for the halons and CFC-12. These increases continue despite international legislation prohibiting consumption and most production in developed nations over the past 2 - 4 years. Halons are especially important as they contribute significant amounts of bromine to the stratosphere. Our analysis suggests that continuing increases in halons over the next few years will cause the abundance of equivalent chlorine to decline more slowly than predicted by the WMO in the 1994 Scientific Assessment of Ozone Depletion.

HCFC-22 ($CHClF_2$) and HFC-23 (CHF_3) in the Cape Grim Air Archive

Paul Fraser
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195
Ben Miller and Ray Weiss
SIO, University of California at San Diego, California, USA
Jingh Huang and Ron Prinn
Center for Global Change Science, MIT, Cambridge, Massachusetts, USA
David Oram and Stuart Penkett
School of Environmental Sciences, University of East Anglia, Norwich, UK

Abstract

HCFC-22 ($CHClF_2$), the most abundant HCFC in the background atmosphere is released largely from domestic air conditioners. Although emissions of HCFCs are controlled by the Montreal Protocol, they will not significantly affect emissions for several years. This paper will discuss HCFC-22 growth rates as determined from the Cape Grim air archive the data will be compared with industrial estimates of emissions to determine its atmospheric lifetime and the average abundance of OH in the atmosphere.

HFC-23 (CHF_3) is the most abundant HFC in the background atmosphere. It is not used widely in industry, but is produced as an unwanted side product in the manufacture of HCFC-22. This paper will also discuss growth rates for this species as determined from the air archive and will estimates releases for this previously unknown trace gas, which is a very powerful, but low concentration, greenhouse gas.

The Record of Chloroform in Cape Grim Air

Georgina Sturrock and Paul Fraser

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

CRC for Southern Hemisphere Meteorology, Monash University, Clayton, Victoria 3168

Chad Dick

Cape Grim Baseline Air Pollution Station, Smithton, Tasmania 7330

Rebecca Webb

Department of Chemistry, University of Tasmania, Hobart, Tasmania 7001

Abstract

Chloroform ($CHCl_3$) occurs naturally in the atmosphere, being emitted from a number of sources, such as microbial action in soils and in sea-water. In addition, chloroform has a large number of anthropogenic sources. This is of concern as it is potentially harmful to human health and to natural ecosystems, and is also a weak greenhouse gas (global warming potential (GWP) of 5). An additional reason for interest in chloroform is that the main removal mechanism is reaction with the hydroxyl radical (OH), and hence chloroform has the potential to contribute to our understanding of the distribution of this radical.

Despite a number of studies which have examined emissions to the atmosphere, there is considerable uncertainty about the relative strength of these natural and anthropogenic emissions. Most studies have been fairly small scale and have concentrated on individual sources, rather than the global picture.

In this paper we examine the record of chloroform concentrations from the GAGE and AGAGE gas chromatographs, using CO_2 baseline criteria to select data free from local pollution. (This method is superior to the removal of 'pollution episodes', which has been used in the GAGE and AGAGE programs in the past.) There is no evidence for a long-term trend in baseline atmospheric mixing-ratio. A seasonal cycle is apparent in baseline concentrations, with a maximum in late winter/spring, and minimum in late summer. The phase of the cycle matches well with the cycle predicted by a simple photochemical model. However, the amplitude of the real cycle is less than that of the model, and one possible explanation could be the observed seasonal cycle of emissions, which has a peak in summer when photochemical destruction is also at its greatest.

The entire chloroform record from the AGAGE GC has been analysed by wind sector. The resulting pattern shows that the highest concentrations of chloroform come from the Tasmanian sector. This is in contrast to published records of radon, CFC-12 and N_2O, suggesting an abnormally strong Tasmanian source for chloroform. Results from flask sampling in the north-west Tasmanian area allow some suggestions to be made about which sources may be responsible for the unusual pattern of chloroform concentrations.

The use of Pb-212 for characterising air samples at an atmospheric observatory

Stewart Whittlestone and Wlodek Zahorowski,
Australian Nuclear Science and Technology Organisation, Menai, NSW 2234

Abstract

Lead 212 (^{212}Pb) has a half-life of 10.6 hours and is emitted from land. At a baseline atmospheric observatory this makes it useful for determining if a sample has been subject to recent contact with local land. In this application ^{212}Pb is complementary to radon-222 (^{222}Rn), with its 3.8 day half-life. A threshold level can be set for each gas, and samples characterised as 'baseline', 'subject to distant land contact' or 'subject to nearby land contact'.

If the observatory is concerned with the non-baseline samples, it is possible to extend the use of both ^{222}Rn and ^{212}Pb. Both species can be used in principle as quantitative tracers to estimate the flux of a trace gas which is emitted predominantly from land. By studying correlations between radon, ^{212}Pb and the trace gas, it would be possible to make inferences about the distance of the source from observatory on the basis of the difference in half-lives.

For this technique to be viable, the flux of the tracer must be better known than that of the trace gas. It is known that the flux of radon is much less variable in space and time than the source of ^{212}Pb, thoron. In cases where the source is close enough for the differences in half-life to be ignored, radon and ^{212}Pb measurements at an atmospheric observatory can be used in conjunction with radon flux measurements to estimate thoron flux.

This work presents an analysis of radon and ^{212}Pb concentrations at the Cape Grim Baseline Atmospheric Observatory, Tasmania, and fluxes of radon and thoron measured in Tasmania. The accuracy of ^{212}Pb used as a tracer is evaluated.

The Cape Grim Methane, Carbon Monoxide and Hydrogen Programs: Review 1997

Paul Steele

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

The first measurements of atmospheric methane (CH_4) and carbon monoxide (CO) at Cape Grim were made by Paul Fraser in 1978. The first hydrogen (H_2) measurements were made in 1992. This presentation will describe the evolution of three measurement programs, their current status and possible future directions. A bibliography will be available.

The Cape Grim Air Archive and Cape Grim Overflights Programs: Reviews 1997

Ray Langenfelds, Roger Francey, Paul Steele and Paul Fraser
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Abstract

Overviews of both programs will be presented, describing their histories, aims, achievements and future directions.

1. ***Cape Grim Air Archive:*** Archiving of Cape Grim air in high-volume, high-pressure metal cylinders was commenced in 1978. The objective of preserving a record of atmospheric composition anticipated future opportunities to better characterise trends in gases not previously monitored and in those already monitored but with ability to exploit improved technologies. Atmospheric histories of a wide range of species have been reconstructed with most activity occurring in recent years as the archive's age span approaches 20 years. Results have been used to directly infer global trace gas budgets, confirm or improve calibration of higher resolution data sets, characterise modification of air during exchange between atmosphere and linked reservoirs and bridge the gap between contemporary and ice core records.
2. ***Cape Grim Overflights:*** Regular vertical profiling of the troposphere above Cape Grim was commenced in 1989 and remains one of the few ongoing aircraft-based sampling programs in the world today. Since 1989 the program has been bolstered with increased altitude range, higher vertical sampling density and resolution, expanded range and improved precision of trace gas species measurements. Observed variability in the vertical is large compared to surface spatial gradients over the Southern Ocean region. Data are used to constrain relative roles of long-range transport, vertical mixing, surface fluxes and atmospheric chemistry in determining distributions of measured trace gas species, and to assess the spatial representativeness of Cape Grim in the context of zonal or hemispheric mean behaviour.

Vertical Profile measurements of methane and N_2O over agricultural regions

Gordon Brailsford, Tony Bromley, Antony Gomez, Keith Lassey and Neil Gimson.

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

New Zealand has a unique greenhouse gas position: We are the only developed country in which methane (CH_4) is the predominant greenhouse gas emission. Both methane and nitrous oxide (N_2O) are produced by agricultural activities in New Zealand, and together account for over 60% of the greenhouse warming impact of all our emissions. The emission estimates are based on overseas studies in combination with limited local patch scale data. As a response to the need for more robust emission estimates for New Zealand, NIWA has initiated a programme to determine concentration profiles based on aircraft sampling above source regions. These complement a AgResearch-NIWA collaboration measuring methane emissions directly from grazing animals. Our strategy is to couple these measurements to models of airflow across the landscape (based on RAMS) to estimate emissions on a national scale.

The aircraft samples collected up wind and down wind of the source region from close to the surface to the level of the convective boundary layer are analysed for methane and nitrous oxide mixing ratios. To accompany the trace gas profile air sondes are flown before and up to the time of sampling to characterise the air flows leading up to the collections, and to provide data to higher elevations for the (RAMS) modelling. The profile data obtained are compared with model simulations for the study region.

Quantifying Biomass Burning Contributions in the Cape Grim Overflight Data Set

Bernard Pak and Ian Simmonds

School of Earth Sciences, University of Melbourne, Parkville, Victoria 3052

Roger Francey

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Abstract

Since 1991, the Cape Grim Overflight Program [Langenfelds *et al.*, 1996a, b] has been collecting vertical profiles of several trace gas species on a monthly basis. From the climatologies constructed from this data set [Pak *et al.*, 1996], a concerted increase in concentration of most trace gas species was found in August/September. This seasonal maximum could be due to a combination of factors including the seasonality of (i) the transport from northern hemisphere to southern mid-latitudes, and (ii) direct and indirect impact of biomass burning in the tropics.

By comparing transport model simulation results to these trace gas climatologies, it is possible to assess the performance of transport models and deduce possible regional sources and sinks in the Southern Hemisphere. However, preliminary comparison with simulations from the Melbourne University Transport Model could not capture the major peak in carbon dioxide concentrations during austral winter [Pak *et al.*, 1997]. Results from another model have the same discrepancy [Pak *et al.*, submitted]. As the prescribed carbon dioxide fluxes do not have explicit burning sources, it is envisaged that the highly irregular biomass burning signal has to be quantified and removed before assessing the interhemispheric transport.

Since burning products like methane, carbon dioxide, carbon monoxide, hydrogen and nitrous oxide are measured for each of the overflight flask samples, it is possible to look for flasks which yields higher concentrations (compared to climatology) in all or most of these gas species. By excluding these flasks, a new set of trace gas climatologies are constructed and are compared to the ones by Pak *et al.* [1996]. The differences would signify the contributions of biomass burning to the overall trace gas climatology above Cape Grim while the new set of carbon dioxide climatology compares well with simulations.

References

Langenfelds, R.L., R.J. Francey, L.P. Steele, P.J. Fraser, S.A. Coram, M.R. Hayes, D.J. Beardsmore, M.P. Lucarelli, and F.R. de Silva, Improved vertical sampling of the trace gas composition of the troposphere above Cape Grim since 1991, in *Baseline Atmospheric Program (Australia)* 1993, edited by R.J. Francey, A.L. Dick and N. Derek, pp. 45-56, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia, 1996a.

Langenfelds, R.L., R.J. Francey, L.P. Steele, P.J. Fraser, S.A. Coram, M.R. Hayes, D.J. Beardsmore, M.P. Lucarelli, and F.R. de Silva, Flask sampling from Cape Grim overflights, in *Baseline Atmospheric Program (Australia)* 1994-5, edited by R.J. Francey, A.L. Dick and N. Derek, pp. 112-117, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia, 1996b.

Pak, B.C., R.L. Langenfelds, R.J. Francey, L.P. Steele and I. Simmonds, A climatology of trace gases from the Cape Grim overflights, 1992-1995, in *Baseline Atmospheric Program (Australia)* 1994-95, edited by R.J. Francey, A.L. Dick and N. Derek, pp. 41-52, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia, 1996.

Pak, B.C., I. Simmonds and R.J. Francey, Using vertical profiles of CO_2 concentration above Cape Grim to constrain the global carbon budget - the influence of Tropical sources, in Conference Proceedings of the 5th International Carbon Dioxide Conference, pp. 35-36, Cairns, Queensland, 1997.

Pak, B.C., M. Ramonet, P. Monfray, R.J. Francey and I. Simmonds, Comparing 3-D transport model simulations with the Cape Grim overflight CO_2 data, submitted to *Baseline Atmospheric Program (Australia)* 1996.

Seasonal Variation of CO_2 Fluxes in the Southern Ocean from 1990 to 1992

Ying Ping Wang, Eva Kowalczyk, Graeme Pearman and John McGregor
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195
Ian Enting
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195
CRC for Southern Hemisphere Meteorology, Monash University, Clayton, Victoria 3168

Abstract

The southern ocean has been considered as one of the strongest sinks for carbon. So far no direct measurements have been made on the carbon fluxes and only a few of CO_2 partial pressures in the surface water of the southern ocean of south Australia (40° to 50°S), [Tilbrook, unpublished data]. Recently, Monfray *et al.* [1996] found that a larger uptake rate by the southern ocean than other parts of the Austral Indian ocean was required to explain the observed vertical gradients of CO_2 at Cape Grim, Tasmania, Australia using a transport model with relatively coarse resolution (2.5° by 2.5° and 9 vertical levels). Here we present some estimates of the carbon fluxes in the south-west region of the southern ocean (35° to 60°S and 80° to 144°E) using a synthesis inversion and a limited area atmospheric model with relatively high resolution.

Since 1972, CO_2 concentrations near the surface have been measured at Cape Grim by CSIRO Division of Atmospheric Research [Beardsmore and Pearman, 1987]. Monthly samplings of CO_2 up to 10 km in the vertical have also been made by aircraft near Cape Grim since 1990 [Langenfelds *et al.*, 1996]. In this study, we use a 3-D atmospheric model to determine the influence of the south-west sector of the southern ocean on the CO_2 at Cape Grim for a prescribed surface flux, and then infer carbon fluxes using synthesis inversion based on the observed CO_2 at Cape Grim between 1990 and 1992.

The atmospheric model DARLAM was developed in the CSIRO Division of Atmospheric Research [McGregor and Walsh, 1994]. For this study, the Australian land is divided into 9 regions and the ocean into 4 regions. The model was run at 75 km resolution in the horizontal with 18 vertical levels for the domain between 10° and 60°S and 80° and 180°E. The planetary boundary layer is explicitly represented [Kowalczyk *et al.* 1994] and the lowest level of the model is 40 m, as compared to the 70 m height of the *in situ* sampling inlet at Cape Grim. Winds, temperatures and pressure, etc. were prescribed daily from the ECMWF data whilst CO_2 were modelled continuously, but were set arbitrarily to a constant value at the boundaries.

Our interpretation of vertical gradients of CO_2 at Cape Grim is based on a synthesis inversion approach [Enting *et al.*, 1995], in which the source fluxes (S) at time t' and location r', are represented as a linear combination of specified component fluxes (s_j):

$$S(r',t') = \sum_j \alpha_j s_j(r',t') \qquad (1)$$

where the components j represent different processes and/or different spatial regions. The observed concentrations are fitted as a linear combination of the responses as:

$$C(r,t) = \alpha_0 + \sum_j \alpha_j R_j(r,t) \qquad (2)$$

where R_j is the response at time t and location r to the integrated effects of all sources in class j. These responses are calculated using DARLAM, and represent the degree of influence of various regional sources on the CO_2 concentration at Cape Grim. The present analysis is confined to times for which Cape Grim was influenced *only* by sources in the south-west sector of the southern ocean (35° to 60°S and 80° to 140°E). Within the sector over 90% of the area is located between 40° and 55° S. To study the effects of wind speed (u, m s^{-1}), we further partitioned the carbon uptake by the ocean in terms of 6 pseudo-processes with:

$$s_j \propto u^{j-1} \quad \text{for } j=1, \text{ to } 4 \tag{3}$$

$$s_5 \propto \exp(u) \tag{4}$$

$$s_6 = f(T_s) \tag{5}$$

where T_s is the sea surface temperature (K).

Coefficients a_j were estimated by fitting Eqn (2) to monthly segments of hourly Cape Grim CO_2 data, detrended using a spline fit to CO_2 concentration at 3 to 5 km above Cape Grim. This detrending means that we require a_0 close to (but not exactly) zero, since the global-scale transport induces a vertical gradient.

The variances explained by the regression using components s_1 and s_3 are 74%, 85% and 50% for 1990, 1991 and 1992, not significantly different from fits using all 6 components (see Figure 1). When the differences of CO_2 partial pressure between the southern ocean and the atmosphere are largest (December to March), [Tilbrook, unpublished data], the unexplained variance is reduced by including the wind speed-dependent component (s_3), compared to regression using constant flux component (s_1) only. During July and August of 1990, the constant flux component can nearly explain as much variance as all components together, which suggests that atmospheric transport rather than variations of carbon fluxes across the southern ocean most strongly affected the short-term variation of CO_2 concentrations observed at Cape Grim during that period.

Figure 2 shows the inferred seasonal variation of carbon fluxes calculated using Eqn (1) only with two components (s_1 and s_3). Generally the south-west sector is a strong sink in the summer and a weak source between September or October except in 1992. The annual carbon uptake by the south-west sector of the southern ocean is 0.21, 0.12 and 0.20 Gt C yr^{-1} for 1990, 1991 and 1992, respectively. However the rate of carbon uptake may be underestimated, as the mean value of a_0 in the regression was about -0.16, -0.08 and -0.25 ppm for year 1990, 1991 and 1992, respectively.

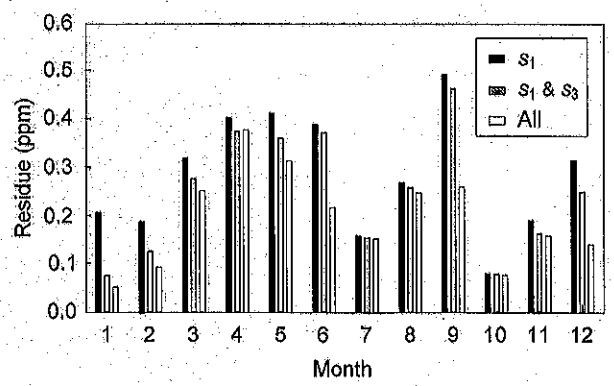


Figure 1. *The unexplained residues by the linear regression (Eqn 2) with one (s_1), two (s_1 and s_3) or all six components for year 1990.*

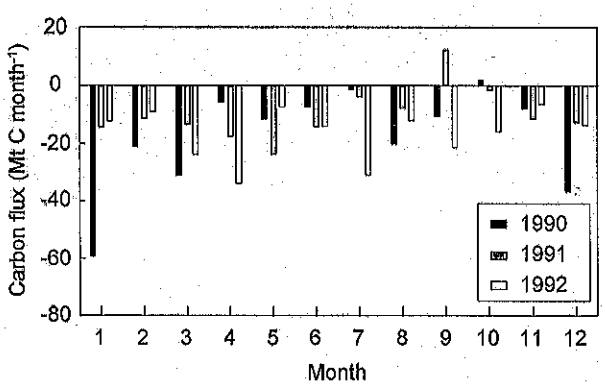


Figure 2. *The inferred seasonal variation of carbon fluxes in the south-west sector of the southern ocean (35° to 60° and 80° to 144°E).*

A 1000 year history of $\delta^{13}C$ in atmospheric CO_2

Roger Francey, David Etheridge, Colin Allison, Vladimir Levchenko and Ray Langenfelds
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Markus Leuenberger
University of Bern, Bern, Switzerland

Elisabeth Michel
LMCE, France

A 1000 year record of $\delta^{13}C$ in atmospheric CO_2 is constructed from the Cape Grim *in situ* record, the Cape Grim Air Archive, firn air from Law Dome and 3 ice cores from Law Dome. Southern ocean ship measurements are necessary to quantify a latitudinal gradient between Cape Grim and the coast of Antarctica. Firn studies are necessary to define the modification of the ice core air during entrapment processes, in particular the temporal smoothing of the ice core results. The biogeochemical implications and applications of the record will be briefly explored.

The CG92 Calibration Scale for $\delta^{13}C$

Colin Allison and Roger Francey
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Abstract

Previously published CSIRO records of $\delta^{13}C$ of CO_2 from Cape Grim have mainly involved *in situ* extraction of relatively large amounts of CO_2 from baseline air, which are returned to Aspendale for isotopic analysis. Since 1991 a parallel program has involved more frequent whole air flask collections which are returned to Aspendale for multi-species trace gas analysis followed by automated extraction of small CO_2 samples and isotopic analysis. Differences between the two $\delta^{13}C$ records expressed relative to the same CO_2 reference gas through the period 1992-1996 are large, up to ~0.1%.

We have documented several unexpected discontinuities in the measured $\delta^{13}C$ of our air standards and the 0.5 litre flask program, not observable in the $\delta^{13}C$ record from the *in situ* program. To address these discontinuities, we have developed an independent calibration strategy for all CSIRO whole-air flask programs which expresses all flask analyses onto a calibration scale which we designate as CG92. When implemented at Cape Grim, CG92 improves the running agreement between the two records towards the 0.01% level.

The Development of a new Technique for High Precision, N_2O Free, Isotopic Analysis of $\delta^{13}C$ in Atmospheric CO_2 from Small Air Samples

Dominic Ferretti

NIWA, Wellington, New Zealand

Abstract

The composition of the Earth's atmosphere has been perturbed by anthropogenic emissions of greenhouse gases and CO_2, a dominant greenhouse gas has increased significantly. Monitoring the isotopic composition of CO_2 ($\delta^{13}C$) reveals invaluable information about the changes taking place within the global carbon cycle. A new technique has been developed for high precision isotopic analysis of $\delta^{13}C$ in atmospheric CO_2. This technique has been termed Continuous Flow, Gas Chromatography-Mass Spectrometry, (ConFlo GCMS).

The technique uses a very small air sample which is loop injected and entrained in a continuous flow of helium onto a packed column. Following chromatographic separation, the sample passes through a thermoelectrically cooled water removal device and is then introduced to the mass spectrometer via a specialised 'open-split' interface. Due to the continuous flow of helium, sample dilution occurs in the GC signal and as a result, less ions are generated than would be for a sample which is analysed by the traditional Dual Inlet method. This traditional method of cryogenic separation before sample introduction has the downfall that an empirical correction in the order of ten times that of the precision required must be made due to N_2O which is trapped along with the CO_2 in the sample to be analysed.

With the development of a specialised inlet system, this new technique delivers N_2O free, high precision isotopic analysis of $\delta^{13}C$ in atmospheric CO_2 from small air samples. As only small samples are required, sample collection is quick and easy and samples do not require any pre-analysis such as cryogenic separation, making the analysis faster and more efficient. The technique is able to repeatedly operate to high levels of precision and will be an extremely valuable tool for monitoring the changing composition of the Earth's atmosphere.

The Recent Time History of Regional Carbon Sources as Deduced from Carbon Dioxide and Oxygen Concentration and Isotopic Composition Measurements

Peter Rayner, Ian Enting, Roger Francey and Ray Langenfelds
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Abstract

We use a time-dependent synthesis inversion to reconstruct spatial and temporal variations in carbon fluxes from 1980 to 1995. The three data sources are the NOAA/CMDL atmospheric CO_2 record and C13 and oxygen records from Cape Grim. The results suggest predominant uptake in the ocean. The tropical land biosphere is almost in balance suggesting large uptake compensating for likely fuxes due to land-use change. The interannual variability of the CO_2 and C13 records suggest large year-year variations in fluxes. There appears to be a strong relationship between tropical fluxes and ENSO with an inexplicable lead of the fluxes over the Southern Oscillation Index.

Interannual Variability of CO_2 Observations and Modelled Sources

Roger Dargaville

School of Earth Sciences, University of Melbourne, Parkville, Victoria 3052

Abstract

For many years it has been recognised that there is interannual variability in the growth rate of CO_2 in the atmosphere which cannot be explained by variations of the fossil source component alone. Several authors have linked the variability to the ENSO phenomenon, showing correlations with a range of variables such as sea surface temperatures (SSTs), precipitation and circulation anomalies. However, the particular mechanism (or mechanisms) which results in the link between ENSO and the growth rate fluctuations has not been established to a substantial degree of confidence.

This paper presents a Principal Component Analysis of the atmospheric observations of CO_2 and of the sources generated from the observations using a mass balance inversion model coupled to a data assimilation technique. Results show that the atmospheric growth rate fluctuations occur globally, and due to the atmospheric mixing, the origin of the source anomalies cannot be located from the observations alone. By using a transport model we are able to represent the location of the source anomalies, which show considerable complexity. In an attempt to find a plausible mechanism to explain the observations global ocean surface wind speeds have been analysed. These show significant correlation with the source anomalies.

Recent Progress with the New Low-Flow CO_2 Analyser System

Grant Da Costa and Paul Steele

CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Abstract

A new infrared analyser system for measuring atmospheric carbon dioxide has been designed and built. While the heart of the system is a commercially available Li-Cor infrared analyser Model 6251, the majority of the system has been custom designed to increase performance and achieve the following goals:

- minimisation of the volume of calibration and reference gases used during normal operation
- improved precision and accuracy
- active control of the pressure, flow rate and temperature of gases passing through the sample and reference cells, to eliminate possible systematic biases in the analyser output
- recording of all operating parameters to allow thorough evaluation and monitoring of system performance
- remote operation from our Aspendale laboratory
- automated data processing.

Low gas consumption, remote operation and automated data processing should reduce the annual operating cost of the baseline atmospheric carbon dioxide monitoring program, making it much more sustainable in the long term.

The system is now complete apart from construction of the dryer box and the atmospheric air intake system. Remote operation is partly implemented. Initial experiments indicate that precision of the order of tens of parts per billion is achievable. Medium term experiments are currently being conducted to characterise system performance.

Most of the major obstacles remaining to be overcome relate to poor high pressure tank regulator materials performance, and include:

- loss of carbon dioxide from calibration cylinder air during its residence time in the cylinder regulator
- the potential for moisture trapped inside components such as cylinder regulators to affect results.

Another major challenge is to obtain a calibration suite capable of calibrating the analyser system to the level to which it can potentially measure.