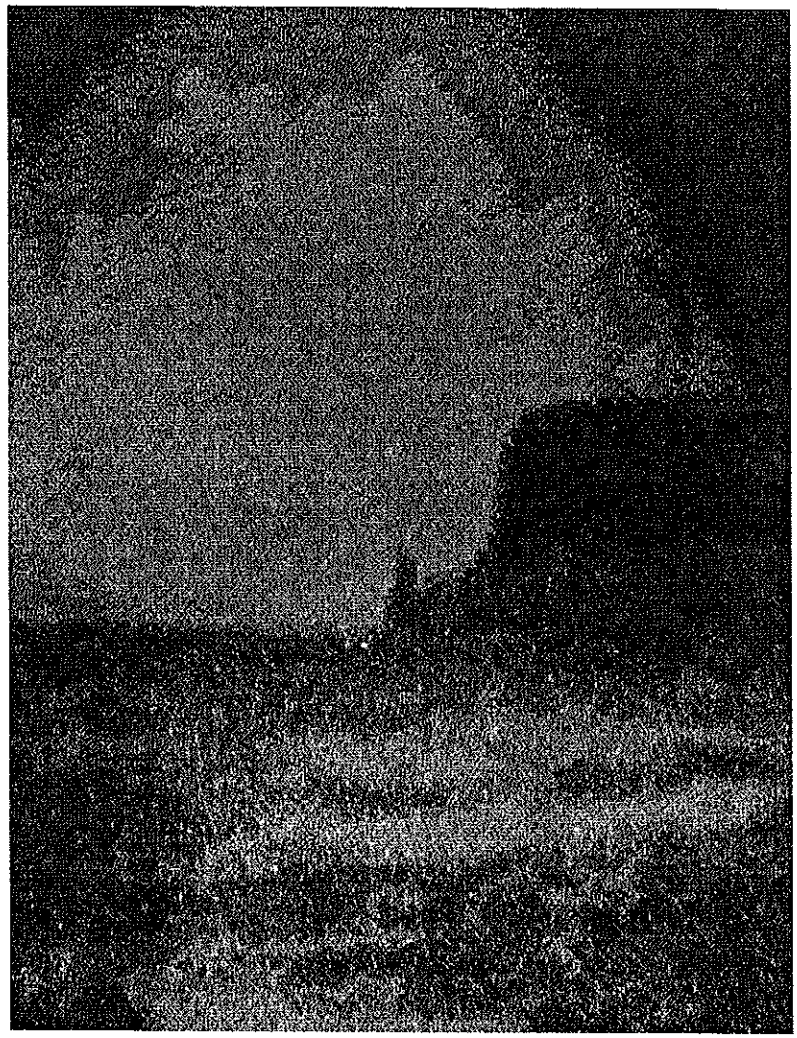
Cape Grim Baseline Air Pollution Station
Annual Scientific Meeting



9-10 November, 1998

Monash University, Clayton, Victoria

Bureau of Meteorology

Edited by Neil Tindale & Nada Derek

CSIRO

Cape Grim Baseline Air Pollution Station
Annual Meeting, 1998

Monday, 9 November

Chair	***Neil Tindale***	
09:00	Convenors / Hosts	General information on arrangements etc.
09:10	Neil Tindale	Update on Cape Grim happenings and plans
09:35	Fred Turatti	Measurement of Atmospheric Methane Isotopes by High Resolution FTIR
10:00	Roger Francey	Refining the Global Carbon Budget – the Next Step
10:25	**Morning Tea**	
11:00	Georgina Sturrock	*In situ* Measurement of CFC Replacement Chemicals at Cape Grim, Tasmania: The AGAGE GC-MS Program
11:25	Michelle Cox	Characterisation of AGAGE GC-MS Halomethane Pollution Episodes at Cape Grim
11:50	Stuart Whittlestone	Plateout of the Ultra-Fine Component of Radon Daughters to the Ocean
12:15	Paul Krummel	Quality Control in Trace Gas Measurement Programs at Cape Grim
12:40	**Lunch**	
13:35	Rebecca Webb	The Potential Impact of Light Hydrocarbons on the Remote Marine Boundary Layer
14:00	Bernard Pak	Biomass Burning Contribution to the Cape Grim Overflight Data Set
14:25	Bronwyn Dunse	An Analysis of Melbourne Pollution Episodes Observed at Cape Grim from 1994-1998
14:50	Ian Galbally	Tropospheric Ozone Science: Studies at Cape Grim
15:10	Mick Meyer	Characteristics of Ozone in Background Air in Wet Sumatra, Indonesia
15:30	**Afternoon Tea**	
15:50	Stephen Wilson	*In situ* Assessment of UV-B Spectrometer Performance
16:15	Stuart Young	Initial Results of Minilidar Measurements at CGBAPS
16:40	Ray Langenfelds	Calibration of the CSIRO Carbon Monoxide (CO) and Hydrogen (H_2) Records
17:30	**Close of meeting**	
18:30	**Dinner**	**'Cactus Lounge'**

Tuesday, 10 November

Chair	***Roger Francey***	***Firn air samples***
09:05	David Etheridge	Firn Air Record of Atmospheric Composition Now Extends Back More Than 50 years.
09:30	Vlad Levchenko	The $^{14}CO_2$ Bomb Pulse – A Unique Dating Tool for Firn Air Samples.
09:55	Paul Fraser	Halocarbon and Sulfur Hexafluoride Measurements on Antarctic Firn Air
10:20	**Morning Tea**	
Chair	***Neil Tindale***	
10:50-12:40	**Panel Presentations & Open Discussion**	**The Cape Grim Station: Plans for the Future?**
12:45	**Lunch**	
Chair	***Paul Fraser***	
13:45	Daniel Cohan	Peroxides and Methyl Iodide in the Tropical Troposphere
14:10	Ross Martin	Nitrous Oxide Measurements in the New Zealand Region
14:40	Jane Warne	An Overview of Precipitation Chemistry Measurement at Darwin
15:05	Jim Butler	Progress in Understanding the Global Cycle of Atmospheric Methyl Bromide
15:35	**Afternoon Tea**	
Chair		
16:00	Eva Kowalczyk	Recent DARLAM Simulations for Cape Grim
16:25	John McGregor	Trace Gas Transport Using the Conformal-Cubic Model
16:50	Grant Da Costa/Paul Steele	Cape Grim's New CO_2 Analyser System – One Foot in the Door
17:45	**Close of meeting**	

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Measurement of Atmospheric Methane Isotopes by High Resolution Fourier Transform Infra-Red (FTIR) Spectroscopy

Fred Turatti, David Griffith and Stephen Wilson

Department of Chemistry, University of Wollongong, NSW 2522

Paul Steele

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

The isotopic ratios $^{13}C/^{12}C$ and D/H in methane (CH_4) can be used to constrain uncertainty in CH_4 emissions, as each CH_4 generating process fractionates the isotopes of CH_4 by different amounts. Measurement of these isotopic signatures by Fourier Transform Infra-Red (FTIR) spectroscopy offers complementary information to the established technique, isotope ratio mass spectroscopy, namely the ability to simultaneously distinguish molecules of the same nominal mass, for example CH_3D and $^{13}CH_4$.

This talk will present progress made towards the development of the FTIR technique. Development of the instrument and gas cell, methods of preconcentrating CH_4 from atmospheric samples, and chemometric analysis of FTIR CH_4 isotopic spectra will be discussed.

Refining the Global Carbon Budget – the Next Step

Roger Francey, Paul Steele, Colin Allison, Peter Rayner and Ian Enting
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Abstract

The Kyoto Protocol represents a new and urgent challenge for the global atmospheric composition community – the provision of reliable, quantitative estimates of regional (large-scale) net carbon emissions. The potential advantages are regional estimates, which are inherently globally consistent, and a methodology which can monitor emissions near-continuously at relatively low cost. Bayesian synthesis inversion modelling, using global observations of CO_2, $\delta^{13}C$, O_2/N_2 (etc.) and an atmospheric transport model, is a preferred framework, since it permits inclusion of all available independent information on carbon exchange as constraints. The synthesis also has the potential to realistically track uncertainties in all components.

Of the various inputs to the synthesis process, it is now clear that systematic measurement error of atmospheric composition (particularly between laboratories) is a limiting factor. A new international calibration scheme is proposed which directly addresses the intercalibration problem.

In situ Measurement of CFC Replacement Chemicals at Cape Grim, Tasmania: The AGAGE GC-MS Program

Georgina Sturrock and Paul Fraser

CSIRO Atmospheric Research, Aspendale, Victoria 3195
CRC Southern Hemisphere Meteorology, Monash University, Clayton, Victoria 3168

Abstract

In October 1997, a fully automated gas chromatograph-mass spectrometer (GC-MS) was installed at Cape Grim as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) program for the first quasi-continuous measurements of the principal chlorofluorocarbon (CFC) replacement chemicals, along with a number of other important trace halocarbons. The additional species include several minor CFCs and chlorinated solvents, the major halons, and the methyl halides, which are of natural and anthropogenic origin. This is the first such *in situ* measurement program established in the southern hemisphere.

The aim is to produce near real-time data on the background trends of these species, thus ensuring that any unexpected increase in their levels will be detected early, thus providing an 'early warning' of a possible repetition of the CFC pollution saga. In addition, the data from pollution events will be used to estimate emissions of CFC replacements, both globally and from SE Australia, thus contributing to the national inventory of hydrochlorofluorocarbons (HCFCS) and hydrofluorocarbons (HFCs) required under the Montreal and Kyoto Protocols respectively. Some of the results arising from the first year of operation at Cape Grim are reported here.

Characterisation of AGAGE GC-MS Halomethane Pollution Episodes at Cape Grim

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CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

The halomethanes that are being studied in this project are methyl chloride (CH_3Cl), methyl bromide (CH_3Br), dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$). These halomethanes are measured *in situ* at the Cape Grim Baseline Air Pollution Station (CGBAPS) by gas chromatography-mass spectrometry (GC-MS) techniques. There are 6 measurements and 6 calibrations per day and high quality data have been collected since March 1998. Chlorine and bromine are catalysts for ozone destruction in the stratosphere. The halomethanes account for approximately 20% of the chlorine and 50% of the bromine found in the stratosphere. In general, the sources and sinks of these halomethanes are not very well understood and one of the major aims for this project is to reduce the uncertainties associated with their regional sources in south-eastern Australia. The results, so far, of a study of low level (~183 m) back-trajectories and their relationship to pollution episodes in the GC-MS record at Cape Grim will be presented. The back-trajectories are produced using the Division of Atmospheric Research Limited Area Model (DARLAM) at 75 km resolution. Possible source regions for the halomethanes will be discussed based on current general knowledge about their sources, information on local and regional anthropogenic emissions and the results of the trajectory study so far.

Plateout of the Ultra-Fine Component of Radon Daughters to the Ocean

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Stephen Schery

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Abstract

The decay products of radon, 'radon daughters', are formed as ions which quickly attract a few molecules from the atmosphere to form ultra-fine particles with sizes of the order of 1 nanometre. The daughters may decay, become attached to the ambient aerosol or be lost by plateout to the ocean. Plateout leads to an equilibrium factor, (F= daughter concentration/ equilibrium concentration) of less than 1. Attachment results in an unattached fraction (U=concentration in ultra-fine mode/total daughter concentration) less than 1. Measurements of F and U contribute to the understanding of dry deposition of reactive species. Since the source of the daughters, radon gas, is largely uniform in the boundary layer, a model of the atmosphere should be able to calculate the plateout of the ultra fine mode and generate both F and U. On a technical level, knowledge of F is important because if it is known, radon concentration can be deduced from measurements of radon daughters. It is necessary to know the unattached fraction because it is difficult to design an inlet which transmits the ultra-fine fraction to the collection filter.

With the commissioning of a very high sensitivity radon detector at Cape Grim in 1995, it became possible to carry out high accuracy measurements of F and U under a range of conditions including deep baseline. Under baseline conditions, U ranged from 0.27 to 0.72, and F from 0.13 to .47. The values of U are higher than values usually obtained over land. This is because the very high CN concentrations usually present result in a very high attachment rate. Good agreement with F and U values calculated by a simple box model were obtained when reasonable estimates of plateout rates were assumed. The implication for experiments measuring radon daughters is that the inlet must be able to transmit particles of about 1 nm diameter since these particles may constitute up to half the total radon daughter concentration.

Quality Control in Trace Gas Measurement Programs at Cape Grim

Paul Krummel, Paul Steele, Paul Fraser, Ray Langenfelds, Darren Spencer and Lisa Cooper

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Laurie Porter

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Ray Weiss, Peter Salameh and Chris Harth

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Abstract

The science, technology (and art) of making atmospheric trace gas measurements have evolved in important ways since they began at Cape Grim up to 20 years ago. This evolution has been driven by such factors as improved instrumentation, and the interfacing of instruments to powerful and relatively low cost computers. These computers can then, by operating appropriate software, control the operation of the instrument, monitor and record a wide variety of data, and process data in real-time. The scientific demands on the trace gas data have also increased significantly, requiring increasingly rigorous assessments of all aspects of the measurement process. In particular, the requirements on being able to reliably combine trace gas data from different laboratories (and different countries) for meaningful modeling or interpretive studies are becoming steadily more stringent.

Some of the quality control procedures will be described. Of these, some are already routine, while others are still under development.

The Advanced Global Atmospheric Gases Experiment (AGAGE) gas chromatograph system has been in operation at Cape Grim for just over 5 years, and it will be used to help illustrate some of these quality control procedures. On this system, ambient air for trace gas analysis is drawn alternately from the 10 and 70-meter air intakes. Data from these different air intake lines will be compared, illustrating the desirability of having more than one intake line.

Flask samples of air are collected at Cape Grim and measured in the Global Atmospheric Sampling Laboratory (GASLAB) at Aspendale, for a variety of trace gases, some of which overlap with those measured by the AGAGE system. Comparisons of flask data and *in situ* data are another way of assessing the quality of the measurements, and several examples will be shown.

The Potential Impact of Light Hydrocarbons on the Remote Marine Boundary Layer

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Greg Ayers

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Barry O'Grady

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

Chad Dick

Institute of Antarctic and Southern Ocean Studies, University of Tasmania, Hobart, Tasmania 7001

Tom Clarkson

NIWA, Wellington, New Zealand

Abstract

The seasonal cycle of some light hydrocarbons has been modelled satisfactorily given a flat source term and the limitations of a zero-dimensional box model. The effect of these hydrocarbons on species such as the hydroxyl radical, ozone, peroxides and formaldehyde is discussed along with their potential impact on the photochemistry of the remote marine boundary layer. The parameters used to constrain the model will also be described in detail.

Biomass Burning Contribution to the Cape Grim Overflight Data Set

Bernard Pak and Ian Simmonds

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Roger Francey

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Abstract

The multiple species Cape Grim Overflight data from April 1992 to February 1997 are analysed. Interesting features observed in the average seasonal cycles have already been presented in previous meetings. When comparing the observed carbon dioxide seasonal cycles and seasonally-averaged vertical profiles with model simulated results, discrepancies are found. Subsequent investigations have shown that the overflight data could be affected by photochemical reactions, oceanic influence, interhemispheric transport and biomass burning plumes. Here, we show how flasks with strong biomass burning influence are singled out. The identity is confirmed with emission ratios, isotopic signatures and back-trajectories. Thus, by identifying this subset of data, the biomass burning contribution to the data set can be estimated.

An Analysis of Melbourne Pollution Episodes Observed at Cape Grim from 1994-1998

Bronwyn Dunse

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CSIRO Atmospheric Research, Aspendale, Victoria 3195

Paul Steele and Paul Fraser

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Stephen Wilson

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

Abstract

The Advanced Global Atmospheric Gases Experiment (AGAGE) 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 Melbourne. Key features of the methodology will be described. The observed correlations between the trace species during the episodes, and an independent estimate of annual emissions of carbon monoxide from the Melbourne region are used to estimate emissions of other species.

Future work will involve running the CSIRO conformal-cubic model (the C-C model), with the aim of investigating the emission and transport of trace gases in the atmosphere. This model has the ability to 'stretch' the grid in parts of the model domain. This feature can provide the high spatial resolution required over the Melbourne region, to produce a more realistic simulation of the specific locations of emissions.

A tracer experiment will be performed within the next few months. This will involve release of a gas (yet to be determined) from Melbourne, with the aim of measuring it at Cape Grim on the new gas chromatograph-mass spectrometer (GC-MS).

Tropospheric Ozone Science: Studies at Cape Grim

Ian Galbally, Mick Meyer, and Simon Bentley
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Abstract

Key questions in this area of research are:

1. Can we explain the current distribution of ozone in the troposphere?
2. Can we explain and predict with confidence the past and future trends in ozone in the troposphere?

We address these questions through:

1. an examination of observations and photochemical calculations of the diurnal variation of ozone at low NO concentrations as observed in baseline conditions over the last 16 years at Cape Grim; and

2. analysis of the long-term trend in surface ozone at Cape Grim, Macquarie Island and Little America, Antarctica spanning the last 40 years.

Specifically we find that there appears to be a significant contribution to the diurnal destruction of ozone that is not included in current model photochemical schemes, and that as opposed to the northern hemisphere, the southern hemisphere appears to have near constant surface ozone concentrations over the last 30 to 40 years.

Characteristics of Ozone in Background Air in West Sumatra, Indonesia

Mick Meyer and Ian Galbally

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Eddy Kelana

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Hery Harjanto

Meteorological and Geophysical Agency, Kemayoran, Jakarta, Indonesia

Abstract

The reactive greenhouse gases such as ozone and their precursors remain a major source of uncertainty in the understanding of global warming processes. While most major cities now have extensive programs for monitoring and predicting photochemical ozone production from urban pollution, there are relatively few stations around the world where the chemistry of the background troposphere is monitored. This is particularly true for the tropics. Consequently the Global Atmospheric Watch Program of the World Meteorological Organisation has facilitated the construction of several new laboratories for monitoring background air in the low latitudes. An ozone monitoring system was installed in the station in central Sumatra, Indonesia in 1996. This paper reports the results of the first year's continuous ozone measurements and interprets the ozone concentration time series in comparison with a tropical oceanic monitoring station. The influence of large scale regional pollution events, such as the 1997 fires in Java and Sumatra are discussed.

In situ Assessment of UV-B Spectrometer Performance

Stephen Wilson

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Bruce Forgan

Observations and Engineering, Bureau of Meteorology, Melbourne, Victoria 3000

Richard McKenzie

NIWA, Lauder, New Zealand

Abstract

The calibration of UV-B spectral radiometers poses particular problems, especially when looking for the relatively small changes expected due to changes in the ozone column. A properly calibrated instrument must have a well-calibrated and characterised wavelength scale, instrumental band-pass, angular response and sensitivity at each measurement wavelength. While some of these can be checked readily through examination of the spectra, others are much more difficult to assess *in situ*.

We have completed a measurement campaign involving two spectral radiometers and a well-characterised sunphotometer at Lauder, New Zealand. Results from this campaign will be presented which compares the results obtained by using the sunphotometer as a reference and those obtained using a more standard calibration method.

Initial Results of Minilidar Measurements at CGBAPS

Stuart Young, Graeme Patterson and Reinout Boers
CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

Following limited-term deployments of the CSIRO Multiwavelength Lidar at Cape Grim Baseline Air Pollution Station (CGBAPS) during the Southern Ocean Cloud Experiment (SOCEX1) in June and July 1993, and the Minilidar during SOCEX2 in January and February 1995, during which valuable information was obtained on the range of atmospheric conditions experienced at Cape Grim, the Minilidar was finally deployed permanently at CGBAPS in June 1998. This full-time deployment was made possible by the development of hardware and software that allow the Minilidar to operate autonomously, both in the optimisation of the system recording parameters and in the management of data.

The presentation will briefly describe aspects of the system and the aims of the experimental program.

Examples of data acquired since installation will be shown. These will include time-height images of clouds and precipitation during the passage of cold fronts, and the variability in the height and backscatter intensity in the boundary layer.

Calibration of the CSIRO Carbon Monoxide (CO) and Hydrogen (H_2) Records

Ray Langenfelds, Paul Steele, Lisa Cooper and Darren Spencer

CSIRO Atmospheric Research, Aspendale, Victoria 3195

Michael Esler and David Griffith

Department of Chemistry, University of Wollongong, NSW 2522

Paul Novelli and Ken Masarie

NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado, USA

Abstract

Although carbon monoxide (CO) and hydrogen (H_2) are not significant greenhouse gases, they do indirectly affect the radiative forcing of the atmosphere. Both are emitted by combustion processes (CO is subsequently oxidised to CO_2) and both are involved in atmospheric OH chemistry, thus influencing and/or serving as tracers of the dominant sink of atmospheric methane (CH_4).

Existing measurement records of CO show serious discrepancies. For example, independent estimates of the long-term trend in the Southern Hemisphere fail to agree on even the sign of the trend. A striking example of inter-laboratory differences is provided by the 'flask air sharing' inter-comparison of CSIRO and NOAA-CMDL. Over the 6-year period of comparison, the difference in long-term calibration of the two programs equates to 10% of atmospheric CO levels. This is despite analytical precision and calibration stability of better than 2% claimed by each laboratory independently. Disagreement in H_2 records is also larger than expected.

The CSIRO measurement programs employ a gas chromatographic (GC) technique with reduction gas detection (HgO is reduced to Hg vapour which is detected by UV absorption). Our experience shows that many pitfalls await the unsuspecting operator. Calibration strategies must address potential for systematic errors from shape and stability of instrument response, analytical artefacts, stability of calibration standards and gas-handling procedures.

A selection of CSIRO's calibration standards were provided to University of Wollongong in 1994 and again in 1998 for analysis by Fourier Transform Infra-Red (FTIR) spectroscopy. Comparison of FTIR and GC measurements presents a new avenue for resolving remaining uncertainties in CSIRO's CO calibration scheme.

Firn Air Record of Atmospheric Composition now Extends Back More Than 50 Years

David Etheridge[1], Andrew Smith[2], Paul Steele[1,4], Ray Langenfelds[1], Roger Francey[1,4], Colin Allison[1], Vladimir Levchenko[1,2,3], Paul Fraser[1,4], Georgina Sturrock[1,4], Cathy Trudinger[1,4], Lisa Cooper[1], Darren Spencer[1], Alan Elcheikh[3] and Ingeborg Levin[5]

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[2]*Australian Nuclear Science and Technology Organisation, Physics Division, Menai, NSW 2234*
[3]*Australian Antarctic Division and Antarctic CRC, Hobart, Tasmania 7001*
[4]*CRC Southern Hemisphere Meteorology, Monash University, Clayton, Victoria 3168*
[5]*University of Heidelberg, Heidelberg, Germany*

Abstract

Air samples from the Antarctic firn layer were collected during a field program in 1997/98. Three very different sites on Law Dome were sampled, representing a wide range of snow accumulation rates and thus, air age and resolution. The oldest firn air profile extends back to about 1940. The advantages of firn air over air extracted from ice cores include larger air volumes and less influence of the extraction technique on the air composition, both of which enable a greater number of trace gases and their isotopes to be measured. Preliminary results include CO_2, $\delta^{13}CO_2$, $\Delta^{14}CO_2$, CH_4, H_2, CO, N_2O, SF_6, and several halocarbons.

The $^{14}CO_2$ Bomb Pulse - a Unique Dating Tool for Firn Air Samples

Vladimir Levchenko[1,2,3], David Etheridge[1], Andrew Smith[2], David Lowe[4], Paul Steele[1,5], Ray Langenfelds[1], Roger Francey[1,5], Cathy Trudinger[1,5], David Fink[2] and Quan Hua[2]

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[3]*Australian Antarctic Division and Antarctic CRC, Hobart, Tasmania 7001*
[4]*NIWA, Wellington, New Zealand*
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Abstract

Measurements of $\Delta^{14}CO_2$ were carried out on the air samples from the Antarctic firn layer, collected during a field program in 1997/98. Radiocarbon content of the atmosphere due to the perturbation from the nuclear tests exhibited a sharp pulse in the 1950s with a subsequent decline to present day. Comparison of the $\Delta^{14}CO_2$ signal recorded in the firn air with the measured atmospheric pulse allows precise dating of the firn air samples, and fine tuning of models of diffusion and enclosure of air in ice. Also, some limits on the *in situ* radiocarbon input to the firn and ice air can be established, thus providing invaluable information on the possible interference by natural impurities in the ice.

Halocarbon and Sulfur Hexafluoride Measurements on Antarctic Firn Air

Paul Fraser, Georgina Sturrock, Michelle Cox and David Etheridge

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

Jochen Harnisch

Max Planck Institute for Aeronomy (MPAE), Katlenburg-Lindau, Germany

Ingeborg Levin

University of Heidelberg, Heidelberg, Germany

Abstract

Antarctic firn air samples (1944-94), collected on Law Dome in 1997/98, have been analysed on the Cape Grim GC-MS and GC-ECD/FID/MRD instruments. The following halocarbon species have been detected in the firn air: CFCs-11 (CCl_3F), -12 (CCl_2F_2), -113 (CCl_2FCClF_2), -114 ($CClF_2CClF_2$), -115 ($CClF_2CF_3$), halons-1211 ($CBrClF_2$), -1301 ($CBrF_3$), HCFCs-22 ($CHClF_2$), -123 ($CHCl_2CF_3$), -124 ($CHClFCF_3$), -141b (CH_3CCl_2F), -142b (CH_3CClF_2), HFCs-125 (CHF_2CF_3), -134a (CH_2FCF_3), -152a (CH_3CHF_2), carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), methyl chloride (CH_3Cl) and methyl bromide (CH_3Br). In addition, sulfur hexafluoride (SF_6) has been measured on sub-samples of the firn air at the University of Heidelberg (UoH) and SF_6 and carbon tetrafluoride (CF_4) at Max Planck Institute for Aeronomy (MPAE). Where possible the data will be compared to independent measurements made on the Cape Grim air archive at Cape Grim Baseline Air Pollution Station (CGBAPS), Scripps Institute of Oceanography (SIO), National Oceanic & Atmospheric Administration-Climate Monitoring & Diagnostics Laboratory (NOAA-CMDL) and the University of East Anglia (UEA).

Peroxides and Methyl Iodide in the Tropical Troposphere

Daniel Cohan

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and
Department of Earth and Planetary Sciences, Harvard University, Cambridge USA

Abstract

Peroxides (H_2O_2, CH_3OOH) and methyl iodide (CH_3I) were investigated in tropical troposphere during the NASA PEM (Pacific Exploratory Mission) Tropics (A) mission over the South Pacific in September-October 1996. The PEM Tropics (A) data show that methyl iodide is an excellent tracer of marine convection and photolysis of the convected peroxides is a major source of HOx in the convective outflow.

Nitrous Oxide Measurements in the New Zealand Region

Ross Martin
NIWA, Wellington, New Zealand

Abstract

Nitrous oxide (N_2O) is a potent greenhouse gas with predominantly agricultural sources. Emissions of the gas and its distribution are of scientific and political interest in New Zealand because of the possible implications for climate change and the ramifications of the Kyoto protocol.

In 1996 a high precision gas-chromatograph-electron capture detection (GC-ECD) system for the analysis of flask samples collected at Baring Head was set up at NIWA's laboratories in Wellington. The operating principles of this system and its performance will be discussed. Since the introduction of the system, the analysis program has been expanded to include samples collected at Scott Base, Antarctica and shipboard samples collected aboard container ships sailing between New Zealand and the West Coast of the USA. Trends and latitudinal gradients observed in the data will be discussed and compared with other data sets.

An Overview of Precipitation Chemistry Measurement at Darwin

Jane Warne

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Abstract

The Bureau of Meteorology has trailed and operated a precipitation chemistry Baseline Air Pollution Monitoring Network (BAPMoN) (Background) since the wet season of 1991-2. There are now four good wet seasons of data for the site which show some very interesting trends in the deposition. This talk will outline the general quality of the data and compare it to the other two BAPMoN stations at Coffs Harbour and Wagga Wagga and the baseline site at Cape Grim. It will also briefly discuss the impact of monsoon weather patterns on the chemistry of the rain water collected.

Progress in Understanding the Global Cycle of Atmospheric Methyl Bromide

James Butler

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Abstract

Methyl bromide (CH_3Br) is present in the atmosphere at only a fraction of the levels of chlorofluorocarbons (CFC's), yet its contribution to ozone depletion is considerable because it contains bromine. Atom for atom, free bromine in the stratosphere is about 50 times more effective at removing ozone under today's conditions than chlorine alone. Methyl bromide differs from CFC's and other man-made, regulated, ozone-depleting gases in that its sources are not entirely anthropogenic and its sinks derive from reactions not only in the atmosphere, but also in the oceans and on land. Thus, estimating the contribution of industrially produced methyl bromide to the depletion of stratospheric ozone and calculating the atmospheric lifetime of methyl bromide are less straightforward procedures than they are for the other regulated halocarbons.

Considerable research has been done by investigators at NOAA-CMDL and other institutions to understand the budget of atmospheric methyl bromide. CMDL scientists have amassed data not only on recent atmospheric levels of methyl bromide, but also on its global oceanic flux and it atmospheric history through sampling of polar firn air. Our most recent effort has involved the multi-institutional investigation of air-sea exchange, *in situ* biological production, and chemical and biological removal of methyl bromide, all while monitoring its saturation state in the surface ocean (GASEX-98, *NOAA Ship Ronald H. Brown*). Removal of atmospheric methyl bromide by the ocean, (which is now believed to be a net sink) proceeds with a probable lifetime of less than 2 y. This, combined with findings of a soil sink and a re-evaluation of the amount of tropospheric OH, has lowered the estimated total atmospheric lifetime from 2.0 years in 1992 to 0.7 years today.

The biggest problem in our current understanding of this atmospheric gas is that of an unbalanced budget. Although the atmospheric mixing ratio has remained reasonably constant through the 1990's, known sources today add up to 122 Gg y^{-1}, whereas sinks add up to 205 Gg y^{-1}. Determination of the anthropogenic contribution to methyl bromide in the atmosphere is made particularly difficult in light of this apparent discrepancy, which cannot be explained by underestimated, agro-industrial emissions, nor can it be resolved easily by considering all uncertainties together. The evidence either points to an unidentified source or sources that amount to almost half of the entire atmospheric budget, or requires a significant re-evaluation of how these atmospheric sinks work, not only for methyl bromide, but for other atmospheric gases as well.

Recent DARLAM Simulations for Cape Grim

Eva Kowalczyk and John McGregor
CSIRO Atmospheric Research, Aspendale, Victoria 3195

Abstract

When performing multi-month simulations of trace gas transport to Cape Grim using DARLAM, our main emphasis is on validating the gas concentrations and understanding the processes. We have thus considered it desirable to ensure the meteorological fields approximately follow the observed sequence of synoptic events. For this purpose we have been re-initialising DARLAM daily with the analysed meteorological fields. An alternative approach is to 'nudge' the modelled fields towards the sequence of analyses. Some relevant experiments will be described, using various nudging options. The second part of the talk will describe further experiments with Melbourne industrial sources of carbon dioxide (CO_2). Simulations will be presented for high concentration CO_2 events of industrial origin, and compared with observed CFC-12 (CCl_2F_2) events at Cape Grim.

Trace Gas Transport using the Conformal-Cubic Model

John McGregor and Eva Kowalczyk

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Abstract

Transport of trace gases has recently been incorporated into the CSIRO conformal-cubic model. This is a global grid-point primitive equations model with semi-Lagrangian numerics and attractive stretching options. The talk will show preliminary simulations of transport of carbon dioxide (CO_2) and radon, for both stretched and non-stretched grids. For these simulations the stretched grid has a resolution of about 75 km over Australia. Comparisons will be presented for simulations from DARLAM run at a similar resolution, and for the concentrations of radon and CO_2 observed at Cape Grim during a selected period.

Cape Grim's New CO_2 Analyser System – One Foot in the Door

Grant Da Costa and Paul Steele

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Abstract

With the high-pressure cylinder regulator problems presented at last year's meeting solved, and a trial installation of the full system at Aspendale underway soon, things are looking good for delivery of the new system to Cape Grim in the first half of 1999.

Some surprisingly good results have recently emerged. Precision achieved when measuring a test baseline atmosphere is 7 parts per billion, or 0.002%. Instrument span remains constant for at least a week at a time, allowing large reductions in the consumption of span calibration gas. Under the proposed new operational strategy of one span check per day, the lifetime of span tanks can be increased from the current 3 months to 91 years. Alternatively, the existing 35 litre tanks could be reduced to 1 litre tanks and still have a lifetime of 2.6 years.

Full live remote control of the system is now operational, within our Aspendale site. The ultimate goal of remote operation from Aspendale to Cape Grim has not yet been tested but there is every reason to believe it will be achieved.

Software is being developed to automatically handle the analyser system data stream, once it comes on line. Processing and release of hourly means is but a few mouse clicks away. Reprocessing if necessary can occur almost instantly, and runs seamlessly across discontinuities such as reference tank and calibration scale changes.

Inability to calibrate the system to the precision to which it can measure remains a limitation. This is being addressed through a joint venture with Laurie Besley of CSIRO's National Measurement Laboratory. The project involves the development of new techniques for the preparation of gravimetric standards. The aim is to produce a calibration set (seven standards) with an internal consistency of 10 parts per billion CO_2.

The final part of the talk will concentrate on the impact that the technology and methods developed for this project is likely to have on the future of atmospheric CO_2 measurements.