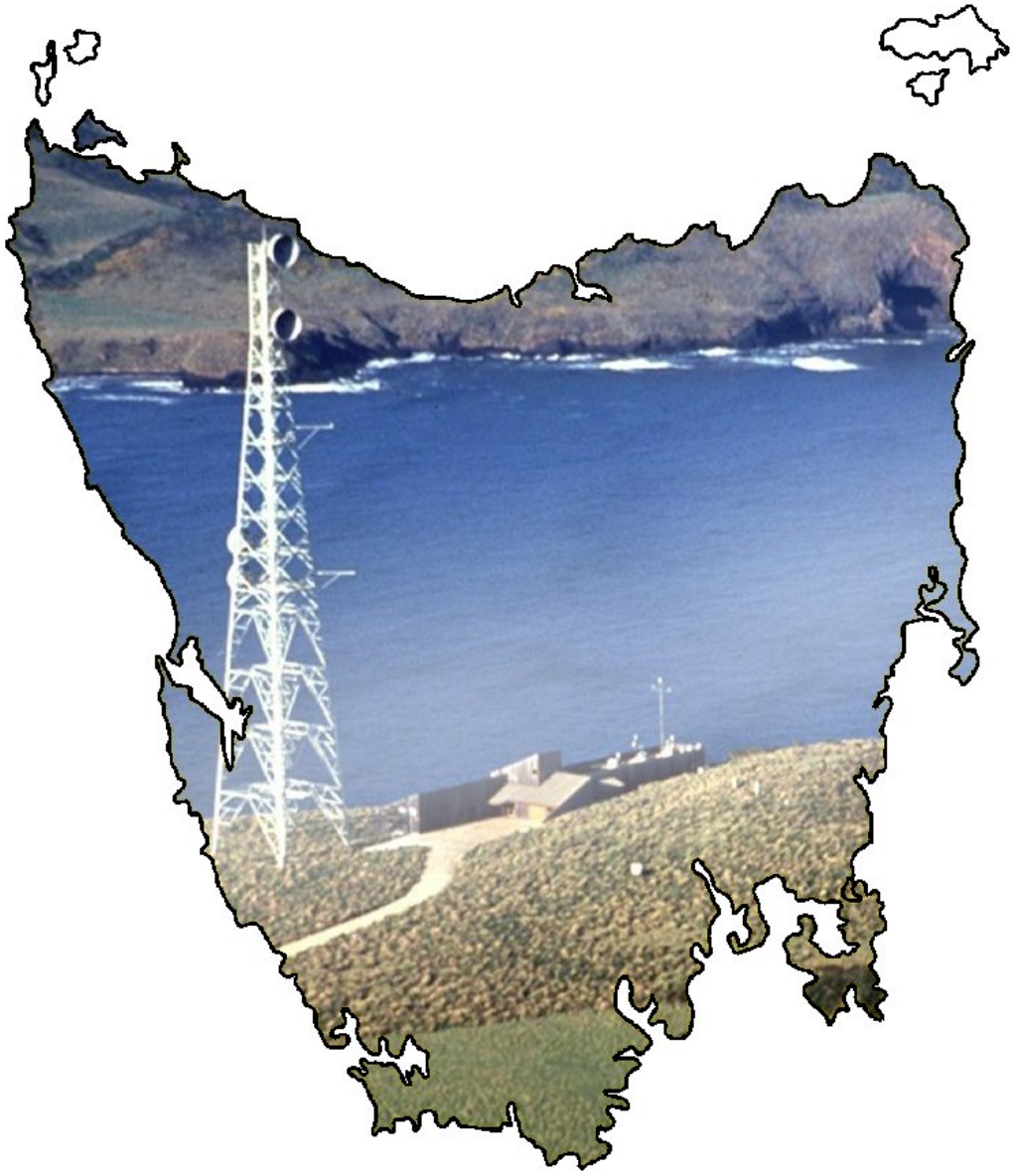
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Cape Grim Baseline Air Pollution Station Annual Science Meeting, 2004

ABSTRACTS



Edited by
Jill Cainey & Nada Derek

CSIRO Atmospheric Research, Aspendale, Victoria
14 – 15 October 2004

Cape Grim Baseline Air Pollution Station
Annual Science Meeting, 2004

Thursday, 14 October 2004		
Chair	**Jill Cainey**	
09:30	Convenors	General information on arrangements etc.
09:40	Paul Fraser	Welcome and opening of meeting
09:50	John Gras	Cape Grim particles 1977 - 2004
10:15	Melita Keywood	The secondary organic aerosol formation potential of Cape Grim air
10:40	**Morning Tea**	**Provided**
11:10	Rowena Moss	Baring Head trace gas measurements
11:35	Paul Steele	The seasonal cycle of atmospheric N_2O
12:00	Adam Hirsch	Inverse modeling estimates of the global nitrous oxide surface flux from 1998-2001
12:25	**Lunch**	**Own Arrangements**
13:30	Paul Krummel	Current status of the 2004 Antarctic ozone hole
13:55	Paul Fraser	Southern Hemisphere trends in total ozone and the chemical drivers of stratospheric ozone depletion – evidence of ozone recovery?
14:20	Stephen Wilson	O (^{1}D) Photolysis estimates for Cape Grim
14:45	Ian Galbally	Trends in near-surface ozone at Cape Grim and in the Southern Hemisphere troposphere
15:10	**Afternoon Tea**	**Provided**
15:40	Wlodek Zahorowski	Back trajectory analysis of low and high radon events in the Cape Grim baseline sector in 2001-2002
16:05	Vaughan Barras	An analysis of the stable isotope record for precipitation events over south-eastern Australia
16:30	Ian Galbally	The performance characteristics of the new surface ozone monitor at Cape Grim
16:55	Mick Meyer	Establishing a consistent time-series of greenhouse gas emission estimates from Savanna burning in Australia between 1989 and 2003
17:20	**Close of Papers**	
17:30	**Poster session**	**CSIRO-Atmospheric Research Canteen** **Wine and Cheese Evening**
19:30	**Meeting Dinner**	**Café Blah Blah, Cheltenham**

Cape Grim Baseline Air Pollution Station
Annual Science Meeting, 2004

Friday, 15 October 2004		
Chair	**Jill Cainey**	
09:00	Convenors / Hosts	General information on arrangements etc
09:10	David Etheridge	Carbon monoxide growth in the Southern Hemisphere over the past century
09:35	Colin Allison	Interannual variability of the global carbon cycle
10:00	Nicholas Deutscher	Inverse modelling of potential Australian FTIR measurements of carbon trace gases
10:25	**Morning Tea**	**Provided**
11:00	Rachel Law	Using hourly CO_2 data at Cape Grim to estimate sources for the Australian region
11:25	Christopher Pickett-Heaps	Use of the CSIRO Cubic Conformal ATM with multiple global CO_2 flux fields to model CO_2 vertical profiles contained in the Cape Grim Aerial Profile Archive
11:50	Cathy Trudinger	Long-term trends in the concentration and emissions of CF_4, SF_6, methyl bromide, methyl chloride, chloroform and dichloromethane
12:15	Michael Grose	Biogenic production of methyl halides by phytoplankton in Tasmanian coastal waters
12:40	Colin Allison	Firn and air archive PFC measurements on the Cape Grim GC-MS Medusa
13:05	**Close of Meeting**	

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Cape Grim Particles 1977 - 2004

J. L. Gras

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Abstract

The concentration of condensation nuclei have been determined at Cape Grim since 1977 and of cloud condensation nuclei since 1981. CN concentrations (D > 3 nm) determined with an automated Nolan-Pollak counter have shown a significant increasing trend over this period, and are present in notably greater concentrations during the latter half of the record. The trend for CCN concentrations on the other hand is not as strong, suggesting some change in the size distribution of the finer particle fraction. The record is also marked by quasi-periodic inter-annual variability, affording an opportunity to investigate connections with other aspects of the multiphase chemistry in the remote marine atmosphere.

The Secondary Organic Aerosol Formation Potential of Cape Grim Air

M. Keywood

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Abstract

Secondary organic aerosol (SOA) is produced when volatile organic compounds (VOC) oxidise to form products that have low enough vapour pressures to undergo partitioning from the gas to the particle phase. Oxidation may be initiated by hydroxyl or nitrate radicals or by ozone. Most data that are available on the chemical composition and concentrations of SOA compounds come from smog chamber experiments, where a known concentration of a known precursor VOC is oxidized under controlled conditions. Smog chamber experiments have determined the SOA formation potential of a number of individual VOCs, including many biogenic and anthropogenic compounds, under a range of conditions, such as oxidant-type, temperature and relative humidity [Odum *et al*., 1996, Griffin *et al*., 1999, Cocker *et al*., 2001a, Cocker *et al*., 2001b]. Importantly, they have determined that the total SOA formation potential of a mixture of VOCs is made up of the sum of the SOA formation potential of the individual VOCs (Odum *et al*., 1997). While there is still much experimental work needed before SOA formation is clearly understood, the work to date may give us an idea of how much SOA may form in a given environment. This presentation will apply the Odum two-product model for SOA yield to Cape Grim air (Odum *et al*., 1996), discussing the SOA forming potential of known precursors VOCs that are present in Cape Grim air, as well as those that may be present, but have not yet been identified. An experimental campaign aimed at investigating the SOA formation potential at Cape Grim will also be discussed.

Reference

Cocker, D. R., Clegg, S. L., Flagan, R. C., and Seinfeld, J. H. The effect of water on gas-particle partitioning of secondary organic aerosol. Part I: alpha-pinene/ozone system. *Atmos. Environ.,* 35(35), 6049-6072, 2001a.

Cocker, D. R., B. T. Mader, M. Kalberer, R. C. Flagan, and J. H. Seinfeld, The effect of water on gas-particle partitioning of secondary organic aerosol: II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems. *Atmos. Environ.,* 35(35), 6073-6085. 2001b.

Griffin, R. J., D. R. Cocker III, R. C. Flagan, and J. H. Seinfeld, Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, 3555-3567, 104, 1999.

Odum, J. R., T. P. W. Hoffmann, F. Bowman, D. Collins, R. C. Flagan, and J. H. Seinfeld, Gas/particle partitioning and secondary organic aerosol yields, *Environ. Sci. and Tech.*, 30, 2580-2585, 1996.

Odum, J. R., T. P. W. Jungkamp, R. J. Griffin, R. C. Flagan, and J. H. Seinfeld, The atmospheric aerosol-forming potential of whole gasoline vapor, *Science*, 1997.

Baring Head Trace Gas Measurements

R. Moss[e], G. Brailsford, T. Bromley, A. Gomez, D. Lowe, R. Martin, S. Nichol, and K. Riedel

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Abstract

The NIWA clean air station at Baring Head (41°S, 175°E) is situated on the south coast of Wellington harbour on top of an 80 m cliff. The exposed site experiences wind from two main directions, north and south. A clean air sector to the south of the site allows samples collections that are representative of air from the Southern Ocean region, back trajectories indicate the air has not been in contact with anthropogenic sources for 5 days or more.

Flask and cylinder samples are collected routinely for a variety of trace gas concentrations and isotope ratio analysis for carbon monoxide, methane and carbon dioxide. Continuous measurements of CO_2 have been made since 1972 and continuous measurements of O_2/N_2 were added to this in 1999 to further improve our understanding of carbon cycle processes. Data from Baring Head will be presented with an emphasis on carbon monoxide isotopes and the use of ^{14}CO as a tracer for OH.

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The Seasonal Cycle of Atmospheric N_2O

L. P. Steele[1], P. B. Krummel[1], P. J. Fraser[1], R. L. Langenfelds[1], L. W. Porter[2], S. B. Baly[2], and the international AGAGE team

[1]CSIRO Atmospheric Research, Aspendale, Victoria 3195, Australia
[2]Cape Grim Baseline Air Pollution Station, Australian Bureau of Meteorology, Smithton, Tasmania 7330, Australia

Abstract

The long-term increase in the abundance of atmospheric N_2O is well known, averaging 0.8 ppb per year (or 0.25% per year) over the past decade. The atmospheric lifetime of N_2O is ca. 120 years, and N_2O is removed from the atmosphere by photolysis and oxidation in the stratosphere. But the sources of N_2O are poorly quantified. One potential observational constraint on the sources of atmospheric N_2O is the phase and (small) amplitude of its seasonal cycle in the troposphere. The recent suggestion by Nevison *et al*. [2004] that exchange of air between the stratosphere and the troposphere does induce seasonality in the tropospheric mixing ratios of trace gases such as N_2O and some CFCs will be explored, using AGAGE data, flask data from GASLAB, and the vertical profiles of N_2O near Cape Grim.

Reference

Nevison, C.D., D. E. Kinnison, and R. F. Weiss, Stratospheric influences on the tropospheric seasonal cycles of nitrous oxide and chlorofluorocarbons, *Geophys. Res. Letts*., 2004 (in press).

Inverse Modeling Estimates of the Global Nitrous Oxide Surface Flux from 1998-2001

A. I. Hirsch[1,2], A. Michalak[3], L. M. Bruhwiler[2], W. Peters[1,2], J. B. Miller[1,2], E. J. Dlugokencky[2] and P. P. Tans[2]

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[2]Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, 80305 USA
[3]Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, Michigan, 48109 USA

Abstract

Measurements of nitrous oxide from 48 sites in the NOAA/CMDL Cooperative Air Sampling Network and the 3-dimensional chemical transport model TM3 were used in a Bayesian inverse modeling framework to estimate the magnitude and geographical distribution of the global surface flux of nitrous oxide from the beginning of 1998 through the end of 2001. For comparison with previous work, we estimated monthly surface fluxes for four 'semi-hemispherical' regions (90°S to 30°S, 30°S to EQ, EQ to 30°N, 30°N to 90°N). We also tested how well surface fluxes could be estimated with monthly time resolution for the 22 regions (11 land, 11 ocean) defined by the TransCom3 carbon dioxide inverse modeling project. These regions were aggregated further into 6 broad regions (Northern Land, Northern Ocean, Tropical Land, Tropical Ocean, Southern Land, and Southern Ocean) that were better constrained by the measurement network. Results are presented for monthly, annual, and multi-year averaged time-scales. Inferred fluxes are compared with the International Geosphere-Biosphere Programme (IGBP) Global Emissions Inventory Activity (GEIA) global gridded estimate of 1990 emissions, used here as an a priori emissions estimate. On a semi-hemispherical scale, the a posteriori fluxes show relatively less emission from northern and southern extra-tropical regions, and relatively greater emissions from the EQ-30N zone. Using aggregated TransCom3 regions, we see a lower flux from oceans in the southern hemisphere and greater emissions from tropical land and ocean regions. While we treated a priori emissions as not varying seasonally, the inferred fluxes show seasonal patterns in several regions, which will be described.

Current Status of the 2004 Antarctic Ozone Hole

P. B. Krummel[1], P. J. Fraser[1] and N. Derek[1]

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Abstract

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

Recently, NASA have released version 8 of their satellite borne TOMS (Total Ozone Mapping Spectrometer) global ozone dataset. In the presentation we will show the development and current status of the 2004 ozone hole based on this new version of the TOMS data. We have also reworked our ozone hole area and column minima calculations for all available version 8 TOMS data prior to 2004. These results will be presented and compared to the 2004 ozone hole size and depth.

Southern Hemisphere Trends In Total Ozone and the Chemical Drivers of Stratospheric Ozone Depletion – Evidence Of Ozone Recovery?

P. J. Fraser[1], P. B. Krummel[1], B. L. Dunse[1], N. Derek[1], D. M. Etheridge[1], L. W. Porter[2], R. McKenzie[3], G. Bodeker[3], A. Downey[4], M. Tully[4] and J. Easson[4]

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Abstract

Through *in situ* measurements at Cape Grim, and measurements on the Cape Grim air archive and on firn air samples from Law Dome, Antarctica, a unique, long-term picture (1940s – 2000s) has emerged of the growth, peaking and initial decline of ozone depleting substances (ODS) in the background atmosphere of the Southern Hemisphere. Continuous total ozone measurements using Dobson spectrophotometers have been made in Australia and New Zealand since the 1950s and satellite-borne TOMS total ozone observations have been available since the late 1970s. Their combined record at mid-latitudes shows evidence of long-term stratospheric ozone decline since the late 1970s, with ozone levels reaching a minimum in the late 1990s. Since then ozone levels have possibly increased – certainly further ozone decline has stopped. Is this the promised ozone recovery under the Montreal Protocol or do other factors such as solar activity and aerosol loading of the stratosphere have to be considered?

O (^{1}D) Photolysis Estimates for Cape Grim

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Abstract

The photolysis of ozone to produce excited oxygen atoms, (O ^{1}D), is one of the driving forces of atmospheric chemistry, especially of the clean atmosphere. Recent work [Creasey *et al.*, 2003] reports measurements of this photolysis rate made at Cape Grim over a period of one month in 1999. They show that the OH concentration is highly correlated with the O ^{1}D production, especially under clean air conditions.

This photolysis rate can be derived from the UVB measurements made at Cape Grim, although the required quantity is the actinic flux, whereas the measurements are of global and diffuse irradiance.

The derivation of the O ^{1}D production rate from the irradiance measurements, spanning 5 years will be outlined, and the results compared with previous data. A brief outline of how this may be extended back in time will also be presented.

Reference

Creasey, D. J., G. E. Evans, D. E. Heard, and J. D. Lee, Measurements of OH and HO_2 concentrations in the Southern Ocean marine boundary layer, *J. Geophys. Res.*, 108 (D15), 4475, 2003.

Trends in Near-Surface Ozone at Cape Grim and in the Southern Hemisphere Troposphere

I. E. Galbally, C. P. Meyer, and S. T. Bentley

CSIRO Atmospheric Research, Aspendale, Victoria 3195, Australia

Abstract

Ozone concentration measured in the surface air at Cape Grim Tasmania, 41°S, has increased by about 10% since the early 1980's. Similar increases have been observed at Cape Point South Africa, over the southern Atlantic Ocean and over Antarctica. Tropospheric ozone is a greenhouse gas, an ultra violet absorber, an essential precursor to the free radial chemistry (cleansing power) of the troposphere, and in high concentration can be harmful to health. Tropospheric ozone has a number of sources including: stratospheric ozone; production in the upper troposphere from lightning (NOx) and VOCs; production from urban and biomass burning pollutants, and production in the remote continental boundary layer due to biogenic sources of NOx and VOCs. Tropospheric ozone is removed by: photolysis and reaction with water vapour particularly in the marine boundary layer; titration with NO; catalytic destruction with halogens; decomposition reactions on soils, and decomposition reactions on aerosols. The possible causes of concentration changes include: stratospheric ozone changes; changed tropospheric ultra violet radiation; changed stratosphere/troposphere exchange, and increased NOx emissions from biomass burning. The likely causes of the observed southern hemisphere surface ozone increase will be discussed, including the effects of both changed sources and changed sinks, and likelihood of ongoing changes evaluated.

Back Trajectory Analysis of Low and High Radon Events in the Cape Grim Baseline Sector in 2001-2002

W. Zahorowski, S. Chambers and S. Werczynski

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Abstract

The introduction of a high sensitivity radon detector at Cape Grim late in 1998 enabled for the first time a systematic investigation of radon observations corresponding to least perturbed oceanic air.

A 2001-2002 subset of the now multiyear record of hourly radon concentrations has been used to investigate spatio-temporal structure of the oceanic footprint of the station. The analysis is based on 10-day back trajectories of air masses corresponding to radon concentrations higher (lower) than the 90th (10th) percentile value of the investigated radon distributions. The corresponding radon events are termed low and high. Based on the 3.8 day half-life of radon, and assuming a uniform supply of radon to the air mass, 10-day back trajectories should indicate the fetch regions responsible for about 85% of radon reaching the site.

The oceanic footprint is investigated on seasonal and synoptic time scales. Observations on the synoptic time are categorised by the time they occur within oceanic events (defined as any set of consecutive hourly observations coming from the baseline sector). Oceanic events have two distinctive features: (i) their frequency is quickly reduced as their duration increases (Figure 1a) and (ii) radon roncentrations recorded in the first 20-30 hours of an oceanic event are typically strongly perturbed from oceanic values; after the initial 20-30 hours radon concentrations seem to stabilise and be minimally perturbed (Figure 1b).

On synoptic time scales, footprints corresponding to low radon events show a considerable longitudinal, and a limited latitudinal, range. The latitudinal extent of footprints related to high radon events is bigger and, in general, their shape is more complicated. Low radon events correspond, without exception, to trajectories with no land contact. For high radon events, contact with land occurs for up to 10% of time. The degree of contact with land does not seem to be correlated with the time within oceanic event. The fraction of time air parcels spent within the marine boundary layer was also found to be similar for low and high radon events.

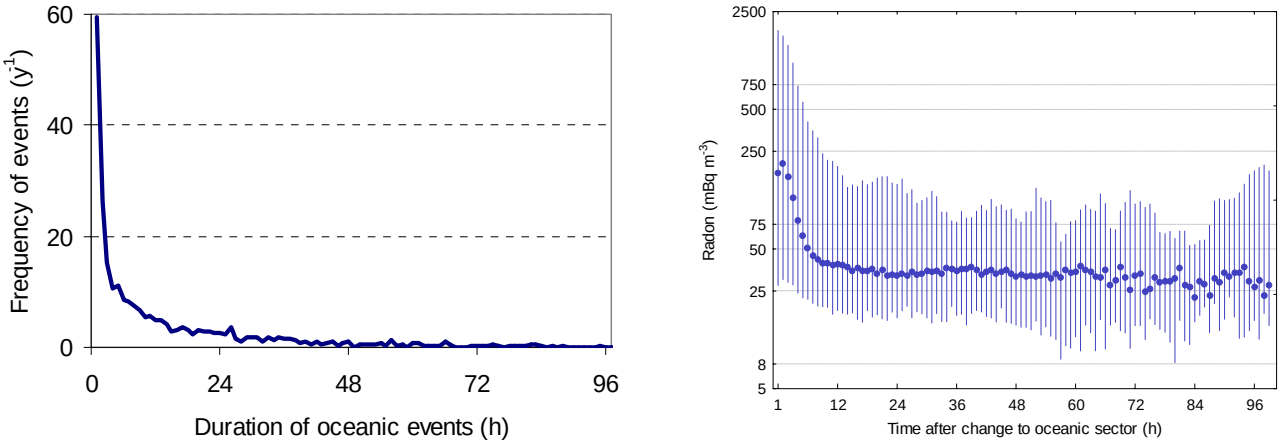


Figure 1. (a) Average frequency of oceanic event duration, and (b) distribution (median and the 10th and 90th percentiles) of hourly radon concentrations as a function of time after change to the baseline sector.

An Analysis of the Stable Isotope Record for Precipitation Events over South-eastern Australia

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Abstract

The relative abundances of the stable water isotopes ^{18}O and ^{2}H in precipitation are known to contain information about the condensation history of the parent air mass. Over the last ten years, rainfall has been sampled on a per-event basis at Cape Grim and Margate and analysed for ^{18}O (^{2}H currently unable to be analysed). From these records it is possible to characterise the synoptic setting and local circulation features for rain events categorised by their mass weighted isotopic depletion. In addition, preliminary backward trajectory analyses have indicated potential moisture source regions for precipitation falling across southeastern Australia. Whilst these methods have been useful for the Margate record, a number of interesting questions have been raised regarding the applicability of this approach to the Cape Grim data that contains significant seasonal biases. The precise nature of these biases are as yet unknown, however this in itself is an indication of a different climatic influence at the Cape Grim location.

Together with the monthly data supplied by the International Atomic Energy Agency (IAEA), these observational records have proven to be useful in the early stages of testing the local-scale performance of the isotopic scheme within the Melbourne University General Circulation Model (MUGCM). Results show it to be a good representation of isotopic variability on the scale of the study region.

A third aspect of this study is the establishment of the Melbourne University Network of Isotopes in Precipitation (MUNIP). This sampling network aims to measure the spatial and temporal isotopic variability of particular rain events as they cross over Port Phillip Bay. Results will investigate the use of isotopic abundance as a diagnostic of local cloud dynamics and of moisture source region. One such event (referred to as MUNIP 1.0) occurred on June 9, 2004. This first full network experiment measured a significant spatial variation of rainfall across the region. It also identified improvements to the observational procedure and site location for future MUNIP experiments.

The Performance Characteristics of the New Surface Ozone Monitor at Cape Grim

I. E. Galbally[1], C. P. Meyer[1], and I. A. Weeks[1] and Cape Grim Staff[2]

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[2]Cape Grim Baseline Air Pollution Station, Australian Bureau of Meteorology, Smithton, Tasmania 7330 Australia

Abstract

A new surface ozone monitor was installed at Cape Grim in May 2004, a Thermo Instruments Model 49C, locally described as TECO #3. This instrument complements the ongoing surface ozone measurements that have been conducted using a Thermo Instruments Model 49 surface ozone monitor, locally described as TECO #2 since 1985. The major difference, from the perspective of atmospheric monitoring, between these two surface ozone monitors is that TECO #3 has a limit of resolution of 0.1 ppbv whereas TECO #2 has a limit of resolution of 1 ppbv.

The recent record of ambient measurements and instrument checks will be presented and shows:

- The constancy of ambient ozone concentrations even at the resolution of 0.1 ppbv at Cape Grim under some conditions.
- New more precise definition of some phenomena of ozone variations in the ambient air with TECO #3
- Better information about the conduct of instrument checks

These and other features that can be explored with TECO #3 data will be discussed.

Establishing a Consistent Time-series of Greenhouse Gas Emission Estimates from Savanna Burning in Australia between 1989 and 2003

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Abstract

Trace gas emissions from biomass burning are known to be a major source of inter-annual variability in the global carbon cycle. More than 85% of emissions from fires in Australia occur in the savanna grasslands and woodlands of Northern Australia and the arid-zone grasslands of Central Australia. Before this study, the most reliable estimates of fire area are derived from satellite imagery, however these estimates are available only for 1997 to the present, with estimate prior to 1997 sourced from experts in state bushfire authorities. The merged time series indicated a substantial increasing trend in fire area between 1990 and 2001 which most experts viewed skeptically. In order to assess the reliability of this trend, the Australian Greenhouse Office commissioned a review of the methodology for calculating emissions from savanna burning including a new analysis of firescar areas in NT and WA using satellite imagery from 1989 to 1992.

The review found that:

- The fire scar areas for 1989 – 192 were close to those estimated previously
- That there was a 6 –fold increase in fire area in NT and WA between 1991 and 2001;
- Inter-annual variability in the savanna was approximately 50% while in central Australia the fire areas varied by more than 2 orders of magnitude within the 20-year record;
- Most of the variability could be explained by rainfall in the preceding two years; and
- A review of recent fuel load measurements, burning efficiencies and N:C ratios suggested that previous estimates of brning efficiencies and N:C ratios were robust, but that grassland fuel loads may have been overestimated.

The revised firescar history and fuel loads indicated that savanna fires may have been overestimated by approximately 20% when compared with the current National Greenhouse Gas Inventory.

Atmospheric Sulfur and its Role in Particle Formation, over the Southern Ocean, South of New Zealand

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Abstract

During the autumn of 2004 sulfur dioxide measurements were made as part of the SAGE cruise, which occurred in the Southern Ocean at 46°S and involved an attempt to fertilise the area of interest with iron sulfate, to promote a biological response.

The sulfur dioxide measurements were made as part of the atmospheric component of this experiment, which also included CN and ultra-fine CN number concentrations, atmospheric DMS concentrations and size-resolved aerosol chemistry.

The sulfur dioxide levels in unpolluted air were 17 ± 11 pptv, with a detection limit of 4 pptv. The measured levels agree well with levels obtained at two land based sites, Cape Grim, Australia and Baring Head, New Zealand and are typical of the Southern Ocean region.

Given the vigorous nature of the weather, particle numbers in unpolluted air were very low, matching the low levels of sulfur dioxide.

The CN data suggest that new particle formation was occurring during periods of high sunlight, but this was more likely linked to changes in air mass than local biological production and the role of sulfur was likely to be unimportant and it remains a challenge to identify the gaseous precursors that nucleate to form new particles.

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Seasonal Change in Radon Derived Fetch Region for Sado Island in 2002

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Abstract

Continuous hourly atmospheric radon concentration observations have been made at Sado Island since September 2001. This site is the northernmost in a network of ANSTO radon detectors established at selected ACE-Asia network sites. This poster reports on one complete year of observations (1-Jan-02 to 31-Dec-02), and uses radon in conjunction with back trajectory analysis, to characterise the seasonal variability in fetch regions for air masses subject to extremes of terrestrial influence. An analysis of back trajectories corresponding to ≥90th percentile radon concentration events at the island has shown a strong seasonal variability in fetch regions for air masses that are also responsible for bringing aerosols and trace gases into the Sea of Japan (Figure 1). The fetch regions comprise very different geographic areas that are likely to have distinctive pollution composition. The three fetch regions responsible for the majority of terrestrial influence on air masses arriving at Sado Island were: (i) southern Siberia (50-60°N) and northern China from November to February; (ii) eastern China and the Korean Peninsula in March, April and October; and (iii) central Japan in July and August. These results indicate that for much of the year, this region is subjected to trans-boundary pollution events. The mean annual radon concentration at the site was 2169 mBq m^{-3}. The seasonal cycle of radon had a low amplitude (2631 mBq m^{-3}) and two maxima: one in winter, the other in summer. The primary maximum was associated with air mass fetch from the Asian continent during the winter monsoon. The secondary maximum was associated with air mass fetch from central Japan during the summer monsoon. An analysis of trajectories corresponding to the ≥90th percentile radon concentrations in January indicated a latitudinal gradient in terrestrial radon flux in Asia decreasing with increasing latitude.

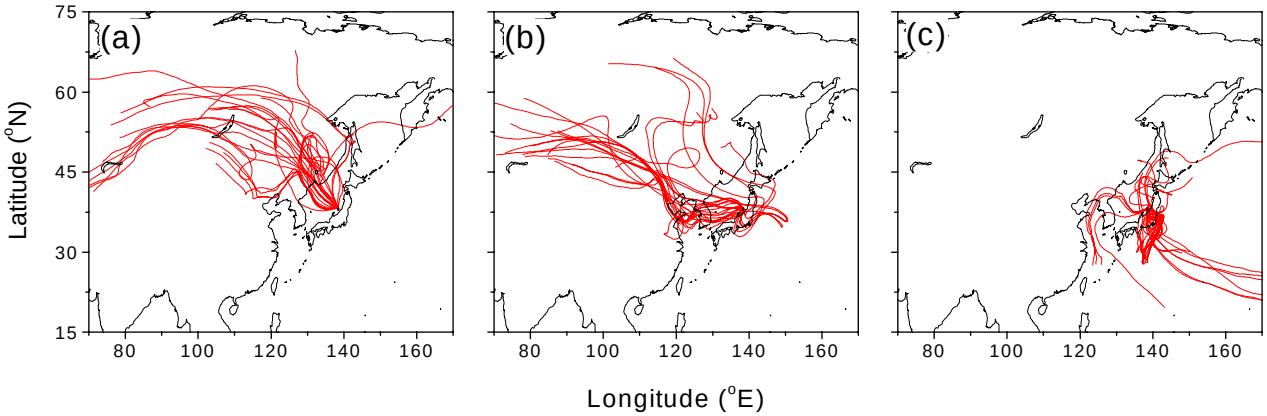


Figure 1. 7-day back trajectories from Sado Island corresponding to radon concentrations in excess of the monthly 90th percentile value in (a) January, (b) April and (c) August, 2002.

Investigation of Carbon Tetrafluoride Emissions by use of Atmospheric Measurements and Modelling

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Abstract

State-of-the-art GC-MS instrumentation for the measurement of atmospheric perfluorocarbons (PFCs) has been developed by Scripps Institution of Oceanography (USA), in conjunction with the University of Bristol (UK), CSIRO Atmospheric Research and the Bureau of Meteorology (Australia). This new technology, which can measure PFCs such as carbon tetrafluoride (CF_4) and perfluoroethane (C_2F_6) with significantly enhanced precision and accuracy compared to existing technologies, was installed at the Cape Grim Baseline Air Pollution Station in Tasmania in January 2004. PFCs, which are emitted to the atmosphere largely during the production of aluminium, are significant greenhouse gases and are therefore included in the Kyoto Protocol. Preliminary measurements of *in situ* CF_4 at Cape Grim will be presented. A series of model simulations have also been performed, with the aim of reproducing the emission and transport of CF_4 from three aluminium smelters in the south-east Australian region. Of particular interest is the transport of CF_4 from the smelters to Cape Grim in north-west Tasmania. Emissions from the three aluminium smelters; Portland and Point Henry (Victoria) and Bell Bay (Tasmania); have been simulated and preliminary results from model runs will be presented.

Trends in Emissions of Melbourne's non-CO_2 Greenhouse Gases: 1995 to 2003

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Abstract

An extensive suite of non-CO_2 greenhouse gases are measured at Cape Grim, Tasmania, as part of the Advanced Global Atmospheric Gases Experiment (AGAGE). The gases measured include:

(i) the non-CO_2 Kyoto Protocol gases – CH_4, N_2O, HFCs, PFCs and SF_6
(ii) the Montreal Protocol gases – CFCs, HCFCs, Halons, CCl_4 and CH_3CCl_3

Melbourne/Port Phillip region emissions have been estimated using a tracer-ratio technique for a number of these species since 1995. The tracer-ratio method compares measurements in air masses arriving at Cape Grim from Melbourne/Port Phillip of a tracer or reference species with known emissions (in this case carbon monoxide – CO) to measurements of species whose emissions are unknown.

The process of estimating emissions involves first identifying pollution episodes in the Cape Grim record that are attributed to air masses that passed over the Melbourne region before travelling across Bass Strait to Cape Grim. Pollution markers (CFC-12, CH_2Cl_2 and HFC-134a) are used to identify episodes caused by the Melbourne pollution. These 'pollution episodes' are extracted, and correlations between the trace species in the polluted air masses are derived. These correlations and an estimate of carbon monoxide emissions from Melbourne are used to deduce the mass of the Melbourne emissions.

The History and Status of the Cape Grim Air Archive

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Abstract

The Cape Grim Air Archive (CGAA) preserves a record of atmospheric composition now spanning more than a quarter of a century. Since 1978, air has been periodically collected under baseline conditions at Cape Grim and stored in high pressure cylinders, in anticipation of the need for future chemical analysis. This archive has proved to be a unique and invaluable resource, enabling reconstruction of atmospheric histories of a wide range of trace gases and some isotopomers. For many species, CGAA records precede the advent of direct atmospheric monitoring programs and provide the definitive history of atmospheric changes since 1978. For other species, CGAA records have been used to confirm or assess the quality of parallel, independent records. There is growing use of CGAA data for linking modern records to those obtained from air trapped in polar ice and firn, with specific need for CGAA data in constraining models of firn diffusion processes. This presentation will give a summary of the history of the archive, a selection of examples of reconstructed atmospheric records and an update on work in progress.

Law Dome Atmospheric Trace Gas Records Extended to 2000 years BP

C. MacFarling[1,2], D. Etheridge[1], T. van Ommen[3], P. Steele[1], R. Langenfelds[1] and C. Trudinger[1]

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Abstract

High precision multispecies trace gas measurements of Law Dome ice have been produced for the last 2000 years. The new records of CO_2 and CH_4 compare very well with the published Law Dome records of the last 1000 years. The new measurements are used to confirm the changes observed in these records, fill in gaps in the sampling and extend the record to 2000 BP with high sampling frequency and high temporal resolution. The new measurements confirm some variations in the published records, which are hard to explain with our current knowledge of the carbon cycle. The confirmation of the published CO_2 and CH_4 records indicates that the variations during the Little Ice Age period are indeed significant. As a consequence of the multispecies approach, measurements of N_2O and CO were also obtained for the past 2000 years.

An update of Cape Grim CO_2 Measurements, and a Comparison with CO_2 Data from a Regional Network of LoFlo CO_2 Analysers

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Abstract

In mid April 2004 a LoFlo Mark II version CO_2 analyser was installed at Cape Grim, replacing the LoFlo Mark I prototype which has operated there from May 2000. In July 2004 the BASGAM CO_2 analyser was turned off. Results are presented here for the comparison between BASGAM and LoFlo Mark II, as well as the current LoFlo CO_2 data series.

In addition to the recent Cape Grim LoFlo CO_2 data series, a comparison is presented here between results from Cape Grim and other LoFlo instruments operating regionally in Aspendale (Victoria) and Tumbarumba (NSW). This regional network is expanding with the recent LoFlo installation at the Danum Valley GAW station operated by the Malaysian Meteorological Service and the anticipated LoFlo installation at Macquarie Island in March 2005.

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Seasonally-Dependent Continental Footprint of a Proposed Global Atmosphere Watch Station at Gosan, Jeju Island

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Abstract

The Gosan site (Jeju Island, South Korea; 33.18°N, 126.09°E) was used as the ground station hub during the Intensive Operation Period of the Asian Aerosol Characterisation Experiment (ACE-Asia) in March-May 2001. The reasons for selecting Gosan included a long term meteorological record available for the site and its geographical location. Gosan is located on the eastern side of Jeju Island, 100 km south of the southern tip of the Korean peninsula, facing the Chinese coast over the Yellow sea. The site has recently been considered for upgrade and inclusion in the Global Atmosphere Watch network.

This poster shows the first systematic evaluation of the continental footprint of the station. The analysis is based on a three year record (2001-2003) of hourly radon (^{222}Rn) observations initiated and led by ANSTO in collaboration with Cheju National University. Seasonally-dependent continental footprints were delineated by analysing 10-day back trajectories of air masses corresponding to radon concentrations higher than the 90th percentile of the respective seasonal radon distributions. All resulting footprints are relatively well defined and have a strong seasonal dependence. By comparison, inter-annual variations in the footprints' shape and extent are not significant. k-means cluster analysis of trajectory patterns which define the continental footprints revealed that up to four clusters adequately depict the major air paths (Figure 1). The analysis was complemented by delineating areas (both over land and the sea) corresponding to the smallest terrestrial signal.

The findings are indispensable for post-analyses of continuous aerosol and trace gas observations made at the station, as well as for the planning of future campaign-type or long-term monitoring activities.

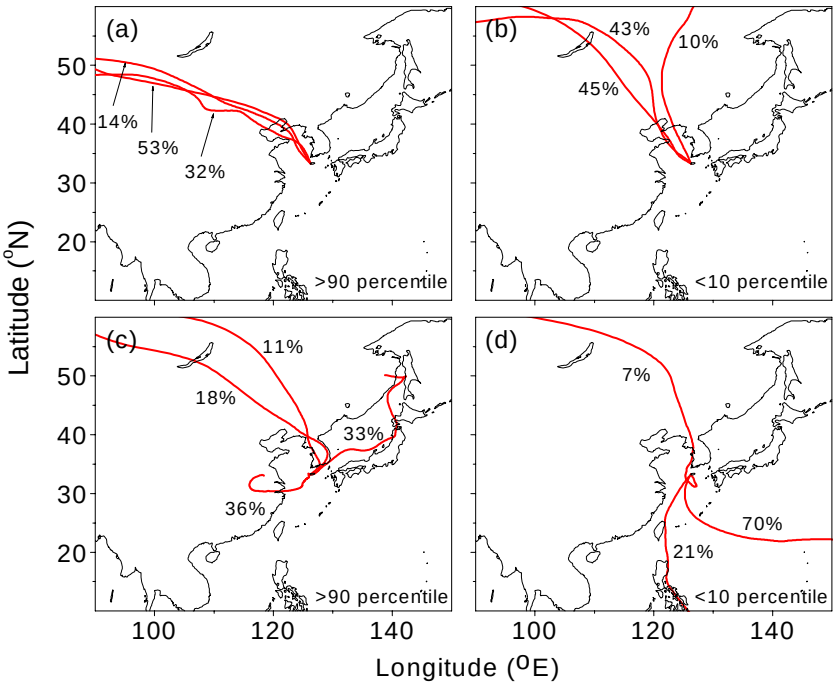


Figure 1. Main air transport paths for Gosan in winter (a, b) and summer (c, d). The paths are indicated by cluster-mean trajectories corresponding to high (>90th percentile) and low (<10th percentile) radon concentrations. The numbers adjacent to cluster trajectories indicate the percentage of all trajectories in the category represented by the respective cluster.

Carbon Monoxide Growth in the Southern Hemisphere over the Past Century

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Abstract

Measurements of air from Antarctic firn (the compressed snow layer) are merged with flask measurements from Cape Grim and other baseline stations to provide a record of CO in the Southern Hemisphere back to the early 1900s. Significant growth is found, most of which can be attributed to the in situ oxidation of methane, the concentration of which has also grown through this period. This paper will present the combined CO record and discuss the implications for the direct emissions of CO and its sinks.

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Interannual Variability of the Global Carbon Cycle

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Abstract

Cape Grim provides a key foundation for the CSIRO stable isotopes ($\delta^{13}C$ and $\delta^{18}O$) in CO_2 measurement program. The two independent stable isotope programs, the in situ program (CIA) and the flask sampling program (CGA), have allowed many analytical problems to be overcome and have been crucial to the development of a robust calibration procedure, CAR2003, for our stable isotope measurements.

The $\delta^{13}C$ records from the global flask network, obtained using the CAR2003 calibration procedure, are now being used with an improved time dependent inversion model, with increased spatial resolution, to estimate interannual variability of the global carbon cycle in the 1990s.

This talk will present the CAR global $\delta^{13}C$ records and preliminary results from running the inversion model.

Inverse Modelling of Potential Australian FTIR Measurements of Carbon Trace Gases

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Abstract

Carbon dioxide (CO_2) and methane (CH_4) are important greenhouse gases, and have both been contributing in increasing amounts towards positive radiative forcing. It is hence important to gain maximum possible understanding of the carbon cycle in the atmosphere, and the scale of carbon trace gas sources and sinks, not only globally but also on a more regional level. The launch of the Orbiting Carbon Observatory (OCO) satellite, scheduled for 2007, is designed to globally map CO_2. In order to investigate the usefulness of a variety of methods, including retrievals from satellite mapping, some preliminary inverse modelling, using a Bayesian synthesis technique is performed using pseudo data generated to represent possible future measurement regimes. This study will focus on the ability of in-situ measurements within Australia to reduce the uncertainties in Australian continental CO_2 fluxes. The specific measurements investigated include a Ghan railway transect between Adelaide and Darwin, and a number of continuous permanent sites. A basic global background network is assumed for all inverse modelling studies, which includes continuous CO_2 data from Cape Grim. The reduction in flux uncertainties from additional measurements is then examined.

Using Hourly CO_2 Data at Cape Grim to Estimate Sources for the Australian Region

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Abstract

Regional CO_2 sources can be estimated using a Bayesian synthesis inversion method. Over the last decade this method has been used to estimate monthly sources using monthly concentration data. Over recent years we have used synthetic data tests to assess whether continuous concentration data could be incorporated into the synthesis inversion and to what extent these data would improve the inversion estimates. The tests indicated that the sources would be significantly better constrained using continuous data but that the inversion set-up was critical in obtaining reliable results. Here we present preliminary results of inversions of hourly CO_2 concentration data at Cape Grim. For regions around Cape Grim, we will highlight how the hourly data change the source estimates obtained using monthly data and we will discuss whether those changes are credible.

Use of the CSIRO Cubic Conformal ATM with Multiple Global CO_2 Flux Fields to Model CO_2 Vertical Profiles Contained in the Cape Grim Aerial Profile Archive

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Abstract

The technique of modelling and validating the CO_2 vertical structure of the atmosphere represents a useful technique in validating CO_2 inversion models. The information gained may also contain implications on the calibration and validation of future CO_2 measurements from satellite instruments.

We have attempted to model the entire Cape Grim Aerial Profile archive spanning 11 years (1991 – 2000) using the CSIRO Cubic Conformal atmospheric transport model (CCC-ATM). Initially, pre-determined carbon fluxes were used to drive the CCC-ATM. However, because of unsatisfactory results, surface flux fields generated from the inversion of monthly averaged GLOBAL-VIEW CO_2 data were used within the CCC-ATM. A total of 77 GLOBAL-VIEW surface stations were included in the CO_2 inversion model. As well, 12 separate inversion models were run with randomly selected surface stations removed. Thus a total of 13 separate flux fields were generated and used within the CCC-ATM to model the Cape Grim aerial profiles.

A preliminary examination and explanation of the results of this modelling exercise is presented. Various model profiles over Cape Grim are extracted from the model data of the forward model run. A space/time averaged vertical profile (over a variable time window) and an instantaneous vertical profile are produced that coincide with the observed profile. An average RMS error of 0.5ppm between the respective model profiles and observed profile was obtained. Furthermore, half of the profiles exhibit trends within the residuals indicating errors in the modelled CO_2 profile gradient. Most of the model profiles contain a systematic offset that appears to be seasonally varying. There also appears to be significant 'scatter' amongst the observed profiles.

Long-term Trends in the Concentration and Emissions of CF_4, SF_6, Methyl Bromide, Methyl Chloride, Chloroform and Dichloromethane

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Abstract

A long-term record of CF_4 and SF_6 has been obtained by analysis of the Cape Grim air archive, and firn samples from 2 sites in Antarctica (DSSW20K and South Pole). We use a simple 2-box model of the atmosphere to infer emissions from the concentration records.

Atmospheric records of methyl bromide, methyl chloride, chloroform and dichloromethane dating back to before 1940 have been reconstructed from Law Dome firn air. We compare our reconstructions with previous reconstructions where they exist, and use a 2-box atmospheric model to investigate the budgets of these gases. Much of the variation in methyl chloride can be explained by biomass burning emissions that increase up to 1980 then are relatively stable apart from some high burning years such as 1997-98. Our reconstruction suggests that the anthropogenic source of chloroform is greater than previously thought, with human influence on the soil source a possible contributor here. Dichloromethane is consistent with industrial emissions estimates based on audited sales data, but suggests that the ocean source in less than previously thought.

Biogenic Production of Methyl Halides by Phytoplankton in Tasmanian Coastal Waters

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Abstract

Methyl halides (CH_3Br, CH_3I, CH_3Cl) produced in the ocean are important carriers of active forms of iodine, bromine and chlorine to the atmosphere. In the atmosphere, they play important roles in ozone destruction, and iodated species have been suggested as necessary initiators of new particle formation in the marine environment. This new particles can act as cloud condensation nuclei and hence have a role in climate modification. Biogenic production and emission by marine phytoplankton are among many natural and anthropogenic sources of methyl halide gases. However, the characteristics of this production are poorly understood. Here, we present ongoing work at the Cape Grim Baseline Air Pollution Station (CG-BAPS), and a field site at Couta Rocks, 50 km south of Cape Grim, investigating the relationship between phytoplankton ecology and methyl halide production. Preliminary results suggest that there is a significant relationship between nitrate limitation and methyl bromide production in coastal waters, and diatoms are just as likely as prymnesiophytes to be responsible for methyl halide production. Also, work at Couta Rocks indicates that the species composition of the local plankton communities has a critical role in controlling the levels of methyl halides in surface waters and in the air above these waters. Work is ongoing, and future directions are discussed.

Firn and Air Archive PFC Measurements on the Cape Grim GC-MS Medusa

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Abstract

In January 2004, a new GC-MS instrument (Medusa) was installed at Cape Grim as part of the AGAGE program (Advanced Global Atmospheric Gases Experiment). This new GC-MS [Prinn *et al*., 2001] uses a refrigerant-based cryogenic pre-concentration system that allows the measurement of perfluorocarbons (PFCs) in a 2 litre air sample. *In situ* measurements of CF_4 C_2F_6, and C_3F_8 in the ambient Cape Grim air commenced on January 20 (the first *in situ* measurements in the southern hemisphere) and one ambient air measurement is made every 2 hours.

The Medusa is also being used to analyse the Cape Grim air archive (1978-2004) and samples of air collected from Antarctic firn to extend the measurement record of PFCs back to the early 20th century and infer emissions for these species [Trudinger *et al*., 2004].

Measurements made so far on the air archive and the firn air are in excellent agreement and show that from the early 1980s to the mid-1990s CF_4 levels grew at about 1.1 ppt (part per 10^{12} molar) per year. From the mid-1990s to the early 2000s, the growth rate declined to about 0.8 ppt per year, and is currently about 0.6 ppt per year (based on *in situ* data).

This talk will give a description of the Medusa GC-MS system and present the results obtained so far from the measurements of the air archive and firn air.

Reference

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