Cape Grim Baseline Air Pollution Station
Annual Meeting, 1996
28-29 November 1996
Stanley, Tasmania

Cape Grim Baseline Air Pollution Station

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Program

Thursday, 28 November

Chair	*Roger Francey*	
08:50	Meeting opens	General information on arrangements etc.
09:00	Jill Cainey	Seasonal variation in the size-resolved aerosol chemistry at Cape Grim.
09:20	Hilton Swan	Measurement of atmospheric DMS at Macquarie Island during ACE-1
09:40	Mark Curran	The distribution of DMS and DMSP in Southern Ocean surface waters.
10:00	Georgina Sturrock	Measurements of DMS and CCN in the Southern Ocean region.
10:20	**Morning Tea**	
Chair	*Stewart Whittlestone*	
10:50	John Ivey	The Cape Grim Precipitation and High Volume Aerosol Chemistry programs: Reviews 1996.
11:45	Greg Ayers	The Cape Grim Sulfur program: Review 1996.
12:40	**Lunch**	
Chair	*Ian Galbally*	
13:40	John Miller	The WMO Global Atmosphere Watch system.
14:00	Jane Warne	Regional BAPMoN precipitation chemistry report.
14:20	Kevin Rosman	Progress in monitoring lead isotopes on aerosols.
14:40	John Gras	ACE-1: CCN concentrations from Cape Grim.
15:00	Neil Trivett	Some recent developments in the Canadian Baseline Program.
15:20	**Afternoon Tea**	
Chair	*Greg Ayers*	
15:50	Ian Galbally	Ozone, NOx and VOCs in near surface air at Cape Grim, Australia.
16:10	Mick Meyer	Performance and development of the surface ozone monitoring systems at Cape Grim, Tasmania and Bukit Koto Tabang, Sumatra.
16:30	Grant Da Costa	Preliminary performance of Cape Grim's new low flow rate CO_2 analyser system.
16:50	Nie Hong	A brief introduction to the China Global Atmosphere Watch Baseline Observatory and the Solar Radiation program.
17:10	Frances Phillips	Retrieval of atmospheric ozone from infrared and ultraviolet atmospheric transmission spectra.
17:30-17:50	Reinout Boers	A comparison of microwave radiometer and GPS retrievals of atmospheric water vapour path at Cape Grim, Tasmania.
	Dinner	**No formal arrangements this year. Note that the Stanley-on-the-Bay Restaurant will not be available.**

Friday, 29 November

Chair	*Paul Fraser*	
09:00	Ed Dlugokencky	Constraints on the CH_4 sink imposed by CMDL measurements.
09:30	Paul Steele	Spatial gradients of trace gases in the Southern Hemisphere.
09:50	David Etheridge	Before baseline stations: trace gas records from the polar air archive.
10:10	Tom Clarkson	Non-methane hydrocarbons in Southern Hemisphere marine air.
10:30	**Morning Tea**	
Chair	*John Ivey*	
11:00	Stewart Whittlestone and Wlodek Zahorowski	The Cape Grim Radon program: Review 1996.
11:55	Stephen Wilson	N_2O fluxes from south-eastern Australia.
12:15	Eva Kowalczyk	Comparison of DARLAM results with Cape Grim data.
12:35	**Lunch**	
Chair	*Reinout Boers*	
13:30	Richard Matear	Simulated oceanic uptake of anthropogenic CO_2 by a General Circulation Model.
13:50	Roger Francey	The long-term record of $\delta^{13}CO_2$ in the global atmosphere.
14:10	David Lowe	A new technique for the determination of $\delta^{13}C$ in atmospheric CO_2 in very small air samples.
14:30	Colin Allison	Stable isotopes of CO_2 in air collected at Cape Grim.
14:50	Ray Langenfelds	An 18-year O_2/N_2 record from the Cape Grim Air Archive.
15:10	Bernard Pak	Impact of biomass burning in the tropics on the vertical profiles of CO_2 concentration above Cape Grim.
15:30	**Afternoon Tea**	
Chair	*Chad Dick*	
16:00	Michael Esler	FTIR measurements of isotopic trace gas species.
16:20	David Griffith	High resolution FTIR analysis of oxygen isotopes in CO_2.
16:40	Bronwyn Dunse	An analysis of Melbourne pollution episodes observed at Cape Grim during 1995.
17:00	Georgina Sturrock	GC-MS analysis of the CFC replacement compounds.
17:20	Paul Fraser	Observations and modelling of halons in the Cape Grim air archive.
17:40	**Close of meeting**	**Informal dinner arrangements.**

Seasonal variation in the size-resolved aerosol chemistry at Cape Grim

Jill Cainey and Greg Ayers
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Martin Hooper
Monash University, School of Applied Science, Churchill, Victoria 3842

The aerosol chemistry at Cape Grim, Tasmania, was determined using a micro-orifice uniform deposition impactor (MOUDI), with eleven impaction stages covering 0.056 to 18 μm diameter, and ion chromatographic analyses. The inverted results provide significant insights into the relative importance of sea salt, sulfur and other compounds in the role of condensation nuclei formation. Sea salt components were found to dominate the super-micron size range, with non-sea-salt sulfate and ammonium predominating in the sub-micron size fractions. Gas phase species such as methanesulfonic acid showed a strong relationship with the surface area distribution. The same MOUDI impactor and system was also used to monitor the aerosol chemistry continuously over a period of thirty months, allowing an assessment of the seasonal variation in the size distributed chemistry, at Cape Grim. The results of this work indicate that sea salt becomes more significant in winter, while the generation of non-sea-salt sulfate and other species related to the oxidation of dimethylsulfide predominate in summer.

Measurement of atmospheric DMS at Macquarie Island during ACE-1

Hilton Swan
Australian Government Analytical Laboratories, Kingston, Tasmania 7050

The first real-time measurements of the atmospheric concentration of dimethylsulphide (DMSa) taken from Macquarie Island (MI) (54°30'S, 158°57'E) were conducted between 25/9/95-3/1/96 (n=404), as part of the International Global Atmospheric Chemistry Project, incorporating the ACE-1 field program. MI is in a uniquely represented geographical position of the Southern Ocean just north of the Antarctic Convergence and consequently experiences temperate and Antarctic derived airstreams. It was observed, during the sampling period, that the highest DMSa concentrations generally occurred in the more temperate moist air from the NW sector while the cooler and drier SW Antarctic derived air contained on average lower DMSa concentrations. A N to S gradation in this trend was apparent in the western wind sector.

DMSa levels showed a marked increase from early spring, peaking at 7.3 nmol/m3 on the 6th December 1995, followed by a steady decline. Over this sampling period an exponential relationship was observed between DMSa concentration and the amount of air moisture at the prevailing temperature, as determined from the wet bulb depression divided by the dry bulb air temperature.

The distribution of dimethylsulphide and dimethylsulphoniopropionate in Southern Ocean surface waters

Mark Curran
Antarctic CRC and Australian Antarctic Division, Hobart, Tasmania, 7001

Until recently, there were very little data on the distribution of dimethylsulphide (DMS) and dimethylsulphoniopropionate (DMSP) in Southern Ocean waters. During 1991-1995, six voyages to the Southern Ocean were undertaken on the ANARE vessel *Aurora Australis*, and one further voyage on the CSIRO vessel *Southern Surveyor*. Three of the *Aurora Australis* voyages formed part of the WOCE project and the Southern Surveyor cruise was part of the ACE-1 experiment. Measurements that were made include DMS and DMSP in seawater, DMS in air and DMSP in sea-ice.

Generally, as expected, higher levels of DMS and DMSP in seawater, and DMS in air, were found in late spring and early summer. Elevated levels of DMSP were found in association with frontal zones and at some Antarctic coastal sites. In summer, DMS levels in air were higher over the Antarctic convergence zone and south of the Antarctic divergence zone, compared with other latitudes. DMSP levels in sea ice cores agreed with other recently reported values; however there appeared to be a marked regional variation, similar to that of DMSP in coastal seawater.

The large spatial and temporal coverage of DMS levels in surface seawater of the Southern Ocean, and the resulting flux levels, enabled calculation of a more accurate annual DMS emission estimate than previously obtained. The annual emission of sulphur, as DMS, from the Southern Ocean was estimated to represent 28% of the currently accepted global estimate, from 20% of the total ocean area, highlighting this region as an important source of atmospheric sulphur.

Measurements of DMS and CCN in the Southern Ocean region

Georgina Sturrock
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195
and
CRC for Southern Hemisphere Meteorology, Monash University, Clayton, Victoria 3168

Dimethylsulfide (DMS) is the most abundant volatile sulfur gas produced biologically in the surface waters of the ocean, and is the only natural compound which contributes significantly to the tropospheric burden of non sea-salt sulfate. DMS is thought to be a major source of cloud condensation nuclei (CCN) in remote marine regions and gives rise to the proposal that the marine biosphere can influence or possibly control climate.

Measurements of DMS concentrations in the atmosphere and the ocean were carried out over the Chatham Rise, to the east of New Zealand, in the Southern Ocean. The oceanographic cruise took place during February 1995, a time of high productivity in the seasonal cycle for DMS in this locality. Results are reported from this study and factors governing the air-sea exchange of DMS are investigated.

Measurements of CCN made as part of the Aerosol Characterisation Experiment (ACE-1) on Macquarie Island (November-December 1995) are reported. The coherence between the DMS source and the CCN product is shown. The long term goal of this campaign is to provide information on CCN that can be incorporated into global and regional climate models.

The Cape Grim Precipitation and High Volume Aerosol Chemistry programs: Reviews 1996

John Ivey
Australian Government Analytical Laboratories, Kingston, Tasmania 7050

Collections of precipitation and bulk aerosols at Cape Grim for chemical analyses began on 1 December 1976. Many changes and additions have occurred as our understanding of what we could or couldn't do at a marine site such as Cape Grim. Analytical methodologies have improved and new species added to the list of those of interest. Improved sampling techniques allow the extraction of more useful data for the same effort and an archive allows retrospectivity in the light of new developments. In this review I will discuss chronologically, the developments over the last 20 years and the results obtained.

The Cape Grim Sulfur program: Review, 1996

Greg Ayers
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

This presentation will provide an overview of the rationale behind the Cape Grim sulfur Program, and a summary of this Program's development, progress and output over the decade from its inception in 1986 until mid 1996. A full bibliography of scientific papers produced by the Sulfur Program will be available and future directions of Sulfur Program research will be discussed.

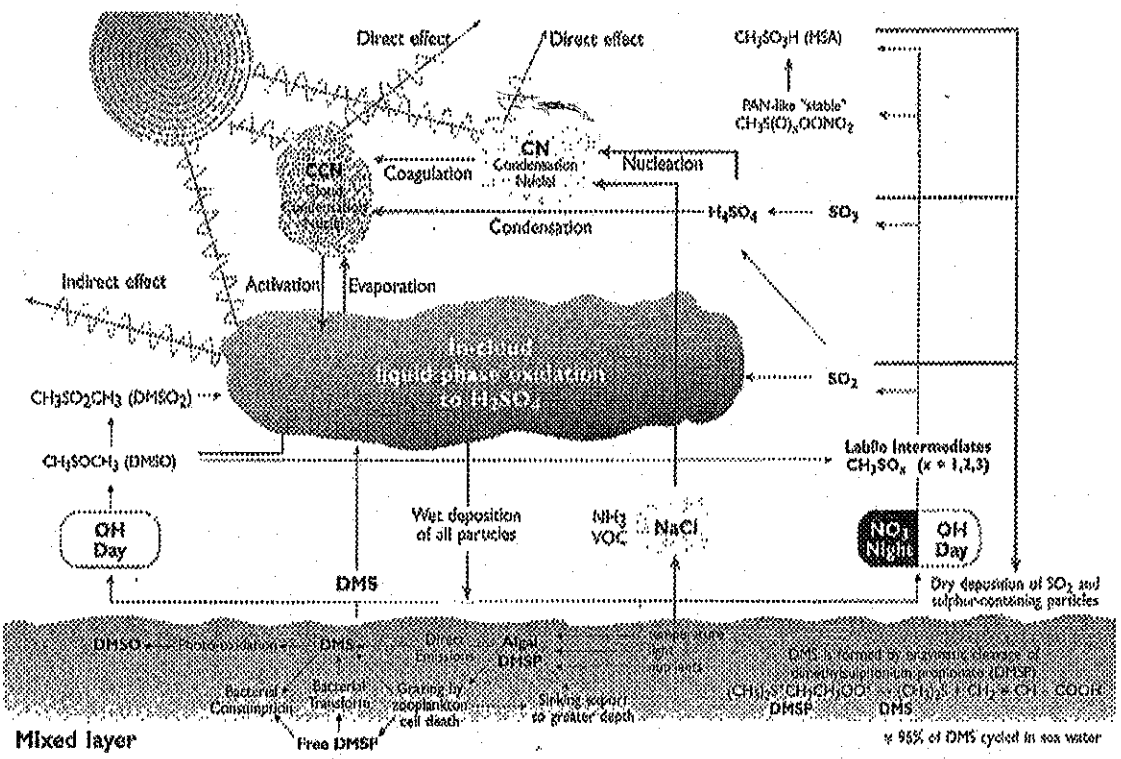


Figure 1. Contemporary view of some of the complexities of the marine atmospheric sulfur cycle (from Saltelli *et al., see http://rea.ei.jrc.it/~saltelli/DMS/*).

The WMO Global Atmosphere Watch system

John Miller
World Meteorological Organization, Geneva, Switzerland

Many urgent environmental problems confronting society, such as global warming, depletion of the stratospheric ozone layer, acid rain, etc. are connected with the man-made changes in the state and composition of the atmosphere and its interactions with other environmental media. Within the United Nations system the World Meteorological Organization (WMO) has a continuing responsibility for providing authoritative scientific information and advice on the state and behaviour of the Earth's atmosphere and climate using a number of its operational observation networks, one of which is the Global Atmosphere Watch (GAW).

The GAW system is designed to coordinate two related atmospheric chemistry environmental problems:

1. To understand the relationship between changing atmospheric composition and changes of global and regional climate
2. To describe the regional and long-range atmospheric transport and deposition of natural and man-made substances.

The GAW measurement programme includes ozone (total column, vertical profile and near the surface), greenhouse gases (CO_2, CFCs, CH_4, N_2O), solar radiation, UV-B, atmospheric turbidity, reactive gas species (SO_2, NOx, CO), chemical composition of rain and atmospheric particles, radionuclides and meteorological parameters. To ensure the required quality of data a number of measurement manuals have been and are being prepared and a data quality assurance/quality control plan for GAW has been recently developed.

To collect, process, analyse and distribute data obtained from the GAW stations, six World Data centres have been established by WMO: on ozone and UV-B (Toronto, Canada), greenhouse gases (Tokyo, Japan), precipitation chemistry (State University of New York, USA), turbidity (Asheville, USA), solar radiation (St. Petersburg, Russia) and on aerosols (Ispra, Italy). A new data centre is being considered for surface ozone to be established in Norway. The GAW data are regularly published and are available directly from the Centres upon request to all organisations, scientific institutions and individual scientists.

One of the most important new aspects of the GAW is the establishment of Quality Assurance Science Activity Centres (QA/SAC) to oversee the quality of the data produced under GAW. Three centres have been established in Germany, United States and Japan. Though their exact role is still being defined, it is expected that the centres will play a major role in training, quality control and establishing protocols for measurements. In coordination with the QA/SACs, system of World Calibration Centres have been designated for specific measurements.

The Australia contribution to the GAW programme has been a major one. The Cape Grim GAW Global Observatory now celebrating its twentieth year is a key measurement point in the southern hemisphere. Besides a full national programme of global and regional measurements, Australian scientists have assisted in establishing other GAW programmes in the region. This presentation will consist of two parts:

1. An overview of the GAW programme.
2. A discussion of Australian GAW activities especially in the early years of the programme's founding.

Progress in monitoring lead isotopes on aerosols

Kevin Rosman, and Warwick Chisholm
Curtin University of Technology, Bentley, W.A 6102

Chad Dick
Cape Grim Baseline Air Pollution Station, Smithton, Tasmania 7330

Lead is a common modern pollutant with isotopic characteristics that make it an ideal natural tracer. Although extremely small samples can be analysed, they are easily contaminated with anthropogenic lead. This has been a problem in the past but it has largely been overcome by an increased awareness of the problem, the construction of clean laboratories for sample processing, the availability of high purity chemical reagents and the development of clean handling techniques. The thermal ionisation mass spectrometer (TIMS) can measure samples as small as ~10 pg with high precision making it a sensitive tool for environmental studies.

A prerequisite to using lead isotopes to locate sources of pollution is a knowledge of the isotopic signature of each potential source. As the first stage in a program to identify the origin of aerosols, the isotopic signatures of global sources of the lead emission are being determined. A portable sampling kit has been assembled and units have been dispatched to major population centres throughout the world. This study will provide knowledge of the extent of the isotopic variations at the present time.

This paper will describe the 'Global Map' program and present some of the results obtained to date. Plans to sample aerosols from the Southern Ocean at Cape Grim are also underway and the progress made on this project will also be presented.

ACE-1: CCN concentrations from Cape Grim

John Gras
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

The first **IGAC Aerosol Characterization Experiment**, ACE-1, was carried out at Cape Grim and the surrounding Southern Ocean regions, in November - December 1995. This experiment, the first of a series, was set up to tackle the problem of improving the characterization of atmospheric particles in a range of representative regions. Such improvements are essential if the existing, unacceptably large, uncertainty in climate-forcing by aerosol is to be reduced.

The background to setting up the ACE experiments and a description of ACE-1, particularly the component at Cape Grim, will be discussed and some preliminary data presented.

Ozone, NOx and VOCs in near surface air at Cape Grim, Australia

Ian Galbally, Mick Meyer, Simon Bentley and Rose Ye
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Lucy Carpenter and Stuart Penkett
University of East Anglia, Norwich, UK

Paul Monks
University of Leicester, Leicester, UK

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

Key questions in this area of research are:

1. Can we explain the current distribution of ozone in the troposphere?
   and,
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 chemical kinetic calculations of the ozone compensation point at low NO concentrations as observed in SOAPEX I,
   and
2. The long-term trend in surface ozone at Cape Grim and its possible relationship to biomass burning in Africa. Specific observations to verify the biomass burning/ozone trend hypothesis will be proposed.

Performance and development of the surface ozone monitoring systems at Cape Grim, Tasmania and Bukit Koto Tabang, Sumatra

Mick Meyer, Ian Galbally and Russell Howden
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

The surface ozone monitoring system installed at Cape Grim in 1981 has yielded a continuous high quality time series to the present. The current system is the product of a decade of experience and improvements with UV absorption spectometers, combined with the development of a comprehensive protocol for data quality control and quality assurance. Weekly semi automatic calibrations and instrument status checks were implemented in 1991. In 1995, it was decided to fully exploit the control facilities provided by the Thermo Electron Ozone monitor and to develop a fully automatic control and logging system. A surface ozone monitoring system based on this new design was commissioned at the WMO GAW Station at Bukit Koto Tabang, Sumatra in September 1996, and a similar upgrade is planned for Cape Grim in 1997. This paper reports the instrument performance history of the Cape Grim surface ozone system since 1981 and presents the initial results from the new fully-automated design.

Preliminary performance of Cape Grim's new low flow rate CO_2 analyser system

Grant Da Costa and Paul Steele
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195.

The design of the new CO_2 analyser system will be briefly discussed. Features of the new system that are not available with the existing Cape Grim *in situ* analyser will be described, including ultra-low flow rates, self-calibration, flask measurement capability, natural air reference gas, cell reversal, configurability and field portability. The implications of these and other features for the future of the *in situ* CO_2 program will be explained. Finally, the sensitivity of the analyser system to various parameters such as temperature and pressure, and implications for current *in situ* systems, will be discussed.

A brief introduction to the China Global Atmospheric Watch Baseline Observatory and the solar radiation program

Nie Hong
China Global Atmospheric Watch Baseline Observatory,
Qinghai Province, Peoples' Republic of China

In September 1994 the founding of the China Global Atmospheric Watch Baseline Observatory (CGAWBO) was proclaimed and the observatory commenced routine observations. The CGAWBO observational laboratory is located on the top of Mt. Waliguan (36°N, 101°E, 3,816 m asl) in Qinghai Province. Mt. Waliguan is part of the Nanshan mountain system on the north-east sector of the Qinghai-Xizang plateau, with a relative height about 600 m above the plateau. It has the advantage of relative isolation from industrial and population centres. Its climate is typically plateau-continental. The daily variations in temperature are larger than seasonal variations. The climate is dry and windy, with high levels of sunshine.

By the end of 1995 there were 9 routine monitoring programs in operation. They are atmospheric greenhouse gas measurements (CH_4 and CO_2 by GC; CO_2 by NDIR), precipitation chemistry, solar radiation, optical depth and UV-B, ozone (surface, total column, vertical profile and SO_2), black carbon, monitoring of boundary layer meteorology and climate observations.

To provide an operational basis for the measurement programs in the observatory, a data acquisition system and a routine data processing procedure were established by Chinese and overseas experts. The data acquisition system comprises PCs, data logger, coaxial cable network and a central data micro-computer. Data processing is carried out on a daily and weekly schedule. The operators collect and check data from each measurement program on a daily basis and make quality control annotations on the daily data plots. Data backup is done once per week.

Some details of solar radiation are given to show the routine operational work in the station and the preliminary results. The program uses a pyrheliometer (NIP) and 3 pyranometers. Global, diffuse, infrared and direct radiation data will be acquired from these instruments. The NIP tracker is controlled by a Tander 120 unit. The data from these instruments are collected on a data logger located in the computer room and are transferred via an interface to the main computer. The data are converted into 3 minute format and stored. At the site the alignment of the NIP is reset daily and a daily plot of each pyranometer's data is made to check whether the optical alignment is correct.

Retrieval of atmospheric ozone from infrared and ultraviolet atmospheric transmission spectra

Frances Phillips
University of Wollongong, Wollongong, NSW 2522

The impact of atmospheric ozone on ground level ultraviolet levels is dependent on the vertical distribution of ozone. Information on the vertical distribution of atmospheric ozone is available from the measurement of the infrared, ultraviolet and visible transmission of the atmosphere. Such measurements are being made using three spectrometers interfaced to the same viewing optics at the University of Wollongong.

Infrared transmission spectra of the atmosphere potentially contains information of the vertical distribution of ozone. However, infrared spectroscopy is not very sensitive to the retrieval of tropospheric ozone due to the broader absorption lines resulting from the higher atmospheric pressures.

In comparison, atmospheric ozone retrieval from the ultraviolet transmission spectrum returns just total column ozone. Hence the retrieval of atmospheric ozone from the infrared and ultraviolet transmission of the atmosphere provides complementary information.

Infrared spectra have been collected on a regular basis, on clear sky days, since May 1996. Preliminary ozone retrievals have been carried out on the full data set of spectra, and show self consistent results.

Two small, diode array spectrometers have been used to collect ultraviolet and visible transmission spectra. The spectrometers have been operated on a limited number of clear sky days since June 1996. Initial ozone retrievals have been carried out using the ultraviolet spectra.

Because the spectrometers are viewing the same atmospheric column, these ozone retrievals are directly comparable.

A comparison of microwave radiometer and GPS retrievals of atmospheric water vapour path at Cape Grim, Tasmania

Reinout Boers and Denis O'Brien
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

Martin Hendy
Australian Surveying and Land Information Group, Canberra, ACT

As part of a program to monitor the atmospheric liquid water and water vapour path over climatologically important time scales, a dual-frequency microwave radiometer has been operated at the Cape Grim Baseline Air Pollution Station (CGBAPS) (40° 41'S, 144° 41'E) since November 1993. In August 1995, a Global Positioning System (GPS) was installed at CGBAPS. The main purpose of the installation of the GPS was to obtain a long-term co-located data set of water vapour, and to assess the validity of the GPS and microwave water vapour retrievals under a wide range of atmospheric conditions.

A sub-set of this data obtained during the Aerosol Chemistry Experiment (ACE) in November 1995, has been analysed. The microwave water vapour retrievals were calibrated using water vapour paths derived from radiosonde measurements obtained at six-hour intervals. The retrieval of water vapour from the GPS observations is completely independent from the retrievals from the microwave observations. The only necessary supplementary information is station pressure which could readily be obtained from the CGBAPS archives.

At Cape Grim, a mid-latitude Southern Hemisphere site, the water vapour path mostly varies between 0.5 and 4.0 cm. In late spring (November) these large fluctuations may occur in a matter of hours. They are due to the alternative influx of moisture of sub-tropical origin, and influx of cool, and relatively dry air of mid-latitude, and sub-arctic oceanic origin. Several days of GPS/microwave retrieval comparisons will be shown during the presentation. Most of the time, the agreement between the retrievals is better than 3 mm indicating that the GPS is capable of obtaining high accuracy water vapour paths under all weather conditions. It will be demonstrated that, at times of high liquid water path, a discrepancy of up to 10 mm between the GPS and microwave retrievals can occur. This discrepancy may be due to the inaccurate specification of microwave retrieval constants in the presence of deep clouds, or due to interference of clouds in the radio-transmission of GPS timing signals. The GPS- microwave comparison program is continuing and will eventually yield a co-located data set of 12 to 16 months duration. The data set could form the basis for the integration of GPS water vapour retrievals in the Bureau of Meteorology synoptic and climatological data sets.

Constraints on the CH_4 sink imposed by CMDL measurements

Ed Dlugokencky
NOAA-CMDL, Boulder, Colorado

Oxidation of atmospheric CH_4 by hydroxyl radical (OH) is the largest term in the global CH_4 budget. Though the average methane lifetime due to reaction with OH has been examined in many studies, interannual variations in [OH] and their effects on CH_4 growth rate are still poorly known. In this talk, two constraints on OH variations determined from analysis of the CMDL CH_4 measurements will be discussed. In the first, CH_4 observations from the high southern latitudes are examined for a long-term increase in the CH_4 seasonal cycle amplitude. Based on this analysis, it is unlikely that a positive trend in [OH] has been realised there. In the second, anomalies in CH_4 and CO growth rates during late-1991 and early-1992 in the tropics are consistent with a significant decrease in tropical tropospheric OH lasting up to 1 year after the eruption of Mt. Pinatubo.

Spatial gradients of trace gases in the Southern Hemisphere

Paul Steele, Ray Langenfelds, Marco Lucarelli, Lisa Cooper and Darren Spencer
CSIRO Division of Atmospheric Research, Aspendale, Victoria 3195

It has been known for many years that over much of the Southern Hemisphere the spatial gradients of several key trace gases at the surface are small compared to those observed elsewhere, particularly in the Northern Hemisphere. Our recent data from flask air samples collected at Cape Grim and a selection of other locations (fixed sites, ships and aircraft profiles) in the Southern Hemisphere help to place Cape Grim trace gas observations in a broad geographical context. The largest spatial gradients we have observed in the latitude range 40° S - 90° S are those in the Cape Grim vertical profiles. A selection of results will be shown, with some emphasis on methane. Some of the difficulties in making these measurements will be described, and the implications of the results discussed.

Before baseline stations: trace gas records from the polar air archive

David Etheridge, Roger Francey, Paul Steele, Ray Langenfelds, Colin Allison,
Cathy Trudinger and Vlad Levchenko
CSIRO, Division of Atmospheric Research, Aspendale, Victoria 3195

Manfred Maiss
University of Heidelberg, Heidelberg, Germany

Bill Sturges
University of East Anglia, Norwich, UK

Ice core records are well known for providing information on atmospheric composition and climate over the last 10^2 years to 10^5 years. A characteristic of most ice sheets is that the enclosed air at any one depth covers a wide range of ages (because bubble close-off occurs non-instantaneously and at depths of up to 120 metres). We have measured many atmospheric species and their isotopic ratios over more recent decades and with high time resolution, by using high accumulation-rate ice cores and firn air. These measurements allow validation of the longer term ice core measurements by comparison with contemporary baseline station records, and also extend the atmospheric records back in time with high precision. There is also the possibility to confirm some earlier, less well-calibrated direct atmospheric measurements.

The age resolution, age accuracy and isotopic modification of ice core and firn air samples remain limitations. However, measurements of tracers such as SF_6, HCFC-141b and $^{14}CO_2$, combined with modelling of the air diffusion and enclosure, are reducing uncertainties. Some examples will be given of where the ice core and firn air measurements supplement the atmospheric observations at baseline stations. They show that high CH_4 growth rates occurred in the 1960s and 1970s, before the more recent growth rate decreases observed in the direct atmospheric measurements, the Cape Grim air archive and the firn air record. The growth rate of CO_2 decreased to zero or less during the 1940s, shortly before the first reliable atmospheric CO_2 monitoring.

Non-methane hydrocarbons in Southern Hemisphere marine air

Tom Clarkson
NIWA, Wellington, New Zealand.

This is an update on work presented at this meeting in 1994. The seasonal variations of concentrations of the principal light NMHCs are now well established for clean air at the Baring Head and Scott Base sites. In addition, small numbers of samples have been analysed at other Pacific sites and on ship routes, as part of characterising the strong inter-hemispheric gradient in these concentrations. Some preliminary measurements of isotope ratios for ethane from clean and polluted sources show promise for future studies of NMHC sources.

Clarkson, T.S., R.J. Martin, J. Rudolph and B.W.L. Graham, Benzene and toluene in New Zealand air, *Atmospheric Environment, 30,* 569-577, 1996.

Clarkson, T.S., R.J. Martin and J. Rudolph, Ethane and propane in the southern marine troposphere, submitted to *Atmospheric Environment*, August 1996.

Rudolph, J., D.C. Lowe, R.J. Martin and T.S. Clarkson, A novel method for the compound specific determination of $d^{13}C$ in volatile compounds at ppt levels in ambient air, submitted to *Geophysical Research Letters*, October 1996.

The Cape Grim Radon program: Review 1996

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

The Radon program at Cape Grim was started in 1980. This review traces the development of the program from the first exploratory measurements to the present. It has been clear from the outset that radon is a better indicator of recent perturbation by contact with land than wind direction. The scope of the radon program has broadened beyond simple baseline selection to use of radon as a tracer for air transport from land. Additional species, the decay products of radon and thoron have been included in the program to extend characterisation of the air samples.

Suitable instrumentation has not been available commercially. Because of this, a large part of the program has been devoted to design and construction of detectors. Compared to the first instrument, the current state of the art radon detector is simple, reliable, accurate and cheap to run.

Given that the instrumentation currently planned is adequate for the foreseeable future, the focus of the program is moving towards providing high quality data promptly, and evaluating the radon source in order to place confidence limits on the radon input term for atmospheric transport models and tracer studies.

N_2O fluxes from south-eastern Australia

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

Chad Dick
Cape Grim Baseline Air Pollution Station, Smithton, Tasmania 7330

Paul Fraser
CSIRO, Division of Atmospheric Research, Aspendale, Victoria 3195

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

Nitrous oxide (N_2O) fluxes for south-eastern Australia have been estimated using a combination of the *in situ* N_2O and radon (Rn) measurements made at the Cape Grim Baseline Air Pollution Station. The average N_2O fluxes from Tasmania and from the south-eastern mainland of Australia over the nine years of record analysed (1985-1993) have been found to be 160 ± 25 kgN km^{-2} yr^{-1} and 130 ±15 kgN km^{-2} yr^{-1} respectively. These fluxes are larger than expected and a significant dependence of the flux on rainfall is observed, with greater fluxes in the spring (October-December) and during periods of positive Southern Oscillation Index.

Comparison of DARLAM results with Cape Grim data

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

The CSIRO DAR Limited Area Model is used to study a number of issues related to the emissions and transport of trace gases in the atmosphere. For example, through the use of the model, we can investigate the relationship between concentration measurements of trace gases at a selected site such as Cape Grim and emissions from sources in the Australian region. Such modelling studies can give us a broader picture of the trace gas cycle, including sources, sinks and chemistry.

In order to minimise the uncertainty in evaluation of the strength of sources and sinks, the model should transport the trace gases as accurately as possible. It is also desirable that the model should be able to accurately represent the meteorological variables, such as wind, temperature and humidity at the selected site. Here, the results of a 3 month simulation of these variables are compared with the Cape Grim observations.

Simulated oceanic uptake of anthropogenic CO_2 by a General Circulation Model

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This talk will give people an introduction to the progress in ocean carbon cycle modelling. It is relevant to understanding oceanic influences on the Cape Grim signal for CO_2, ^{13}C, O_2/N_2 and possibly other gases.

The long-term record of $\delta^{13}CO_2$ in the global atmosphere

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The Cape Grim record of $d^{13}C$ in baseline CO_2 commenced in 1977. Only data from 1982 have been published in the international literature. These published data exhibit interannual behaviour which is interpreted as reflecting the global atmosphere, but which is significantly different from previously published global records. In particular, the interannual behaviour over the two decades appears much smaller in the Cape Grim record (incidentally, requiring less demanding biogeochemical explanations).

In 1991, INSTAAR (Institute for Alpine and Arctic Research, University of Colorado) began $d^{13}C$ measurements on flask air from the most comprehensive global network, operated by NOAA/CMDL. Since 1991, intensive intercomparisons have been conducted between our GASLAB measurements and those of INSTAAR, on Cape Grim air [see *Allison et al.*, this conference]. However, until now, no means of verifying the data prior to 1990 has emerged. We present two new $d^{13}C$ determinations covering most of the last two decades. The first is from the Cape Grim Air Archive, the second uses air recovered from Antarctic firn. Both support the published Cape Grim record, however the support from the firn record is limited by poorly defined latitudinal gradients over the Southern Oceans, and by diffusive mixing of air from different years, and diffusive fractionation in the firn.

Recent GASLAB measurements of ship samples define a Southern Ocean latitudinal gradient [*Beggs*, 1996]; also measurements [*Levchenko et al.*, in press] and modelling [*Trudinger et al.*, in press] on air from Law Dome firn and ice accurately describe the modification of an atmospheric record in the firn and during ice bubble close-off. These studies have permitted us to link the Cape Grim record to an 800 year history of atmospheric $d^{13}C$ obtained from Law Dome ice. The status of this reconstruction will be given.

Stable isotopes of CO_2 in air collected at Cape Grim

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Two programs have reported the interannual behaviour in 'global' $\delta^{13}C$ of atmospheric CO_2 over the last 1-2 decades, however, the two programs disagree to greater then their quoted uncertainties. This disagreement leads to different biogeochemical implications for the global carbon budget. The disagreement most probably stems from systematic errors associated with the extraction of CO_2 from air and its subsequent isotopic analysis by mass spectrometer.

The Cape Grim programs to measure $\delta^{13}C$ in CO_2 involve several strategies providing a unique opportunity to explore possible systematic biases in the techniques used.

In this presentation we focus on a comparison between the Cape Grim *in situ* program, where CO_2 is extracted from air at Cape Grim and returned to Aspendale for analysis, and the various whole air flask collection programs, where flasks of air are collected at Cape Grim and returned to Aspendale, and other laboratories, for CO_2 extraction and isotopic analysis.

In particular, we document several unexpected discontinuities we have observed in the various records and, where possible, provide explanations. We also describe calibration strategies aimed at overcoming the problems.

An 18-year O_2/N_2 record from the Cape Grim Air Archive

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High precision measurements of variations in atmospheric oxygen (measured as the ratio of oxygen to nitrogen, O_2/N_2) provide a new avenue for improving our understanding of the global carbon cycle. O_2 is intimately linked to CO_2 through combustion of organic material and biological exchange processes but their air-sea exchange characteristics are markedly different. Consequently, knowledge of the long term O_2 trend will enable the partitioning of carbon uptake between the oceans and the terrestrial biosphere to be determined. Estimates of the O_2 trend have recently been published, using data obtained from contemporary global sampling programs (by SIO and URI, commencing in 1988 at La Jolla and later at other sites 1991 at Cape Grim), and from air retrieved from the South Pole firn (URI). The South Pole firn air provides data from 1977-1985 (but with large systematic corrections and age smearing). Here we present results from a new, independent and more direct record obtained from the Cape Grim Air Archive covering the period 1978-1996.

Impact of biomass burning in the tropics on the vertical profiles of CO_2 concentration above Cape Grim

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The Cape Grim Baseline Air Pollution Station in north-west Tasmania, Australia, is situated at the southern mid-latitudes. Its meteorology is dominated by the prevailing westerlies. From results of six day isobaric back trajectories, most of the high tropospheric air parcels above Cape Grim originate from the sub-tropics just off the coast of East Africa, some even come from places as far as the South American continent. There has always been a question on how biomass burning in the tropics, especially those in Brazil and the East African countries, affects the trace gas concentrations monitored at the station.

For many years, concentrations of radiatively important trace gases have been measured at the station. In recent times, this surface level record has been supplemented by monthly vertical profile sampling from aircraft flights directly over Cape Grim. The species measured in the vertical profile air samples are carbon dioxide, methane, carbon monoxide, hydrogen and nitrous oxide. In addition, the carbon and oxygen isotopic ratios of carbon dioxide are also analysed. Data from May 1992 to April 1995 have been treated, utilising the long-term trends in surface measurement, to yield the climatology of the vertical profiles [*Pak et al.*, 1996]. As the concentration of carbon dioxide, methane, carbon monoxide and hydrogen are coupled, some regular events (mostly attributed to long-range transport) are identified on top of the seasonal cycles. One of the findings is the especially high concentration of trace gases in mid and high troposphere during the austral winter. This could be interpreted as due to a combination of factors including (i) the seasonality of the magnitude of transport from northern hemisphere to southern mid-latitudes, and (ii) biomass burning in the tropics.

To investigate the causes of the phenomena, simulations using the Melbourne University Global Transport Model have been carried out for carbon dioxide gas. This model is forced with prescribed surface carbon dioxide sources and sinks with transport simulated by the use of wind-fields from the European Centre for Medium-Range Weather Forecasts data set. Here, we discuss the outcome of simulation using just one category of carbon dioxide sources and sinks - biomass burning. The geographical distributions of biomass burning are time-averaged for the 1980s and in the form of 5' x 5' resolution maps constructed by *Muller* [1992].

Muller, J.-F., Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases, *J. Geophys. Res.*, *97*, 3787-3804, 1992.

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 1992-95, in *Baseline Atmospheric Program (Australia) 1994-95*, edited by R.J. Francey, A.L. Dick and N. Derek, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia, 1996.

FTIR measurements of isotopic trace gas species

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A novel method of precise atmospheric trace gas analysis based on low resolution (1 cm^{-1}) FTIR spectroscopy has been developed. Some of these results for CO_2, CH_4, CO and N_2O mixing ratios have already been presented at this forum and elsewhere, and will be reviewed. More recently the method has been extended to encompass the analysis for different isotopomers of trace gas species, particularly $^{12}CO_2$ and $^{13}CO_2$, and hence their ratio $\delta^{13}C$.

We have made both modelling and experimental studies of isotopic analysis. The modelling approach uses the MALT program to calculate theoretical spectra, the HITRAN infrared database and chemometric algorithms. Synthetic spectra are calculated which closely simulate spectra of air or trace gas samples as if they had been measured on a real instrument; in other words, the computer becomes an experimental platform to examine the feasibility and expected precision of various instrumental measurements. Some aspects of experimental design can be optimised in the simulated environment. The parallel approach is experimental analysis itself. Our experience with $\delta^{13}C$ measurements is that the achieved precision is close to the optimal (simulated) precision. For δ^{13} CO_2, the demonstrated and optimal precisions are approximately 0.15 and 0.12 ‰ respectively for a 2 minute measurement of a 500 mL sample of dried whole air.

We also present the results of similar simulations of other isotope measurements in principle accessible by FTIR. With low resolution spectrometer as used for δ^{13} CO_2 analyses, other species considered include $\delta^{13}CO_2$, $\delta\Delta$ and δ18O in H_2O. High resolution FTIR is necessary to consider analysis of the first six ^{16}O, ^{17}O, ^{18}O and ^{12}C, ^{13}C isotopomers of CO_2; $\delta\Delta$ and $\delta^{13}C$ in CH_4; $\delta^{13}C$ and $\delta^{18}O$ in CO, and $\delta^{15}N$ and $\delta^{18}O$ in N_2O. Preliminary experimental measurements of oxygen isotopes in CO_2 with high resolution FTIR are presented in the following paper.

High resolution FTIR analysis of oxygen isotopes in CO_2

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High resolution FTIR spectroscopy unambiguously distinguishes the spectra of different isotopomers of gases. This provides a potentially important advantage over isotope-ratio mass spectrometery in determining isotope ratios for species of the same mass, such as ^{13}C and ^{17}O substituted CO_2, or symmetrically and unsymmetrically substituted ozone, eg. 18OOO and O18OO. However high resolution FTIR is not traditionally a high-precision analytical technique, and the question arises whether sufficient quantitative precision can be achieved to make geochemically-useful measurements of naturally-occuring isotope ratios. We have therefore extended the techniques we have developed for quantitative low resolution FTIR spectroscopy to determine $\delta^{13}C$ in CO_2 to high resolution spectra to make an assessment of the practicality of the technique.

A series of CO_2 samples with known, variable ^{17}O and ^{18}O ratios were prepared by equilibration with H_2O of known isotopic composition. These samples were analysed by high resolution FTIR using our newly-acquired Bomem DA8 FTIR spectrometer at 0.007 cm^{-1}. In this paper we will introduce the technique and present preliminary results of the analyses.

An analysis of Melbourne pollution episodes observed at Cape Grim during 1995

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Ken Masarie
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The AGAGE trace gas data set (consisting of ten trace species) from Cape Grim during 1995 has been 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. This approach indicates that emissions of CFC-113 from Melbourne have already reached negligible quantities.

GC-MS analysis of the CFC replacement compounds

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A fully automated GC-MS analytical system is described for the routine monitoring of trace levels of hydrohalocarbon compounds in the atmosphere, specifically the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs). Such a system is due to be installed at Cape Grim to monitor the accumulation of the CFC replacement compounds in order to assess and predict the atmospheric behaviour of these compounds. Results from the first instrument deployed at the atmospheric station at Mace Head in Ireland, in October 1994, are shown to illustrate the high performance achieved.

Observations and modelling of halons in the Cape Grim air archive

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Bromine is important in stratospheric ozone destruction, with 40% of ozone loss in the Antarctic and Arctic polar vortices and 10% of ozone loss at mid-latitudes involving reactive bromine species. The major sources of stratospheric bromine are the halons (40%, approximately equal contributions from $CBrF_3$ (H-1301), $CBrClF_2$ (H-1211) and $CBrF_2CBrF_2$ (H-2402)), methyl bromide (CH_3Br, 50%), methylene bromide (CH_2Br_2, 5-10%) and bromoform ($CHBr_3$, <5%). The halons are exclusively anthropogenic in origin, whereas CH_3Br is emitted by natural sources (70%: oceans, biomass burning) and anthropogenic processes (30%: fumigation, biomass burning, automobiles). CH_2Br_2 and $CHBr_3$ are probably largely natural in origin.

$CBrF_3$ and $CBrClF_2$ (≈1 ppt) were first detected in the atmosphere in the early 1980s, whereas $CBrF_2CBrF_2$ (≈1 ppt) and CBr_2F_2 (H-1202, <0.1 ppt) were first detected in the early 1990s. The atmospheric abundances of $CBrF_3$ and $CBrClF_2$ initially grew very rapidly (10-20% per year) during the 1980s, but the growth rates slowed in the 1990s, presumably in response to Montreal Protocol controls imposed on production.

All the halons were/are used as fire retarding chemicals ($CBrF_3$, fixed systems; $CBrClF_2$, portable systems), with $CBrF_2CBrF_2$ being used largely in the former Soviet Union and Eastern Europe and CBr_2F_2, which is produced as a by-product of $CBrClF_2$ manufacture, used in specialist military applications. These halons are removed from the atmosphere by UV photolysis in the stratosphere ($CBrF_3$, atmospheric lifetime 65 years), in the stratosphere and troposphere ($CBrClF_2$, 20 years; $CBrF_2CBrF_2$, <20 years) and in the troposphere (CBr_2F_2, 3 years).

Data are presented in this paper on the abundances and long-term growth rates for all four halons from GC-MS measurements on the Cape Grim, Tasmania, air archive (1978-1996). These are the first long-term trends for $CBrF_2CBrF_2$ and CBr_2F_2 that have been reported. The $CBrF_3$ and $CBrClF_2$ results are compared to other independent observations made at Cape Grim and to 2-D model calculations of Southern Hemispheric concentrations, derived from updated estimates of emissions and model generated photolytic sink processes. The observations of $CBrF_3$ and $CBrClF_2$ are compared to predictions based on the emissions expected to have occurred under the Montreal Protocol. The observational data on $CBrF_2CBrF_2$ and CBr_2F_2 are used to estimate time dependent emissions for these halons.

REGIONAL BAPMON PRECIPITATION CHEMISTRY REPORT

Jane Warne

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Abstract

Not available

SOME RECENT DEVELOPMENTS IN THE CANADIAN BASELINE PROGRAM

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Abstract

Not available

A NEW TECHNIQUE FOR THE DETERMINATION OF $\delta^{13}C$ IN ATMOSPHERIC CO_2 IN VERY SMALL AIR SAMPLES

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Abstract

Not available