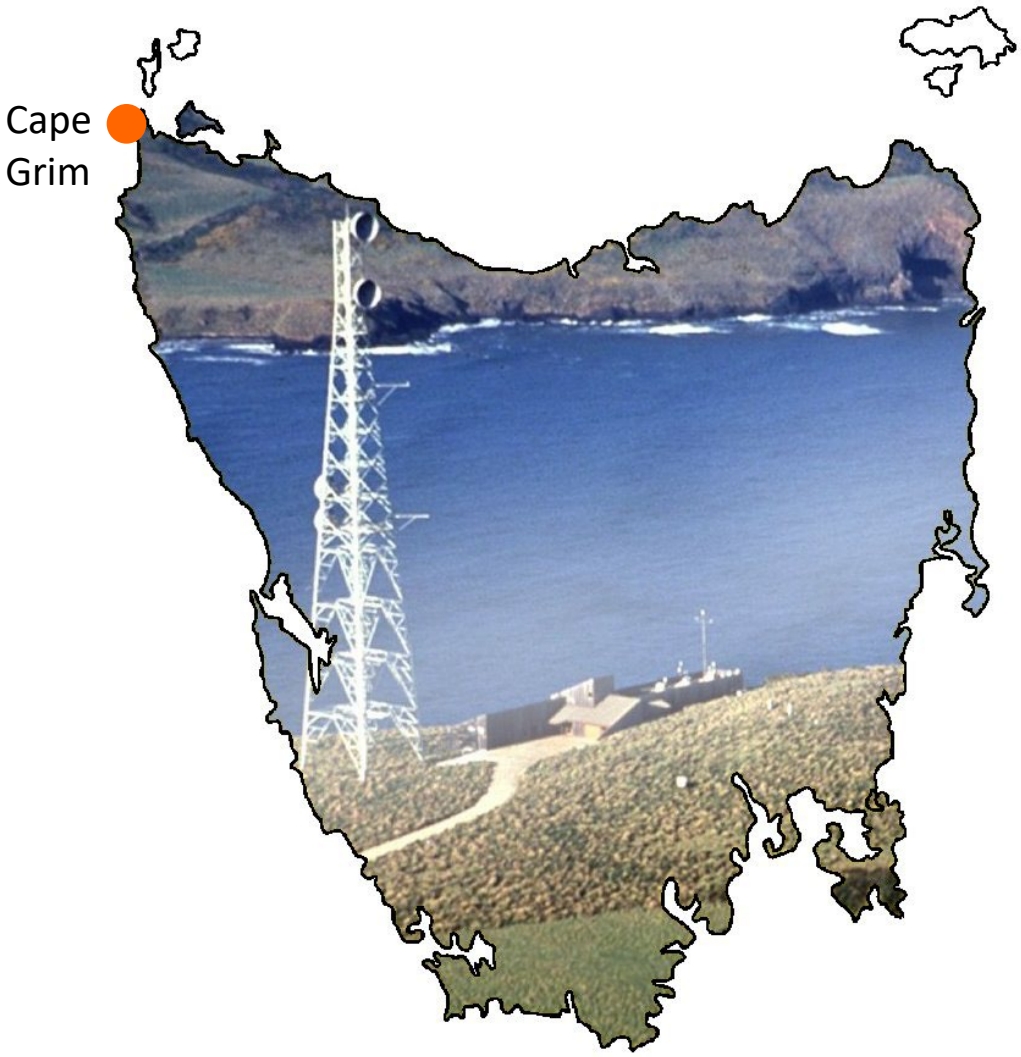
Cape Grim Baseline Air Pollution Station Annual Science Meeting, 2003

ABSTRACTS



Edited by
Jill Cainey & Nada Derek

CSIRO Atmospheric Research, Aspendale, Victoria
23-24 October 2003

Cape Grim Baseline Air Pollution Station
Annual Science Meeting, 2003

Thursday, 23 October		
Chair	***Jill Cainey***	
09:00	Convenors	General information on arrangements etc.
09:10	Host – Greg Ayers	Welcome and opening of meeting
09:20	Wlodek Zahorowski	Seasonal changes in the radon-222 defined fetch regions at four ground stations in the ACE-Asia study domain: a comparison with Cape Grim
09:45	Ray Langenfelds	A climatology of tropospheric O_2/N_2 vertical profiles above Cape Grim
10:10	Bronwyn Dunse	Melbourne emissions of synthetic gases involved in the Montreal and Kyoto Protocols
10:35	**Morning Tea**	
10:55	Henk Jansen	The CIO/RuG Air Sampling Program
11:20	Andrew Klekociuk	Ozonesonde and lidar measurements of stratospheric conditions above Davis, Antarctica during 2003
11:45	Laurie Porter	Sulfur hexafluoride: long-term trends and regional emissions
12:10	Colin Allison	Calibration of stable isotope measurements of atmospheric carbon dioxide in the CSIRO Atmospheric Research Global Atmospheric Sampling Laboratory – the HC453-2003 and CAR-2003 assignments on the V-PDB (CO_2) scale
12:35	**Lunch**	
13:30	Andrew McMinn	What controls the production of methyl halides by phytoplankton; three years of data from Cape Grim
13:55	Paul Fraser	Methyl bromide: long-term trends and regional emissions
14:20	James Elkins	Trace gas emissions estimated from observations using aircraft, balloon, tower, and railway platforms
14:45	Paul Krummel	AGAGE observations at Mt St Leonard, Victoria
15:10	**Afternoon Tea**	
15:40	Vanessa Haverd	Retrieval of isotopomer-specific ozone vertical profiles from solar infrared spectra recorded at Lauder, New Zealand
16:05	Rachel Law	Designing a LOFLO CO_2 network for estimating Australian CO_2 emissions
16:30	Roger Francey	LoFlo Mark2 CO_2 Analyser update
16:55	Paul Steele	CO_2 emissions from the Melbourne region
17:20	**Close of Papers**	
17:30	**Poster, Wine and Cheese Evening**	**CSIRO-Atmospheric Research Canteen**
19:00	**Meeting Dinner**	**Lobster Cave, North Concourse, Beaumaris**

Cape Grim Baseline Air Pollution Station
Annual Science Meeting, 2003

Friday, 24 October		
Chair	***Jill Cainey***	
09:00	Convenors / Hosts	
09:10	Ian Enting	Statistical modelling of episodic concentration data
09:35	Steve Siems	The sensitivity of simulations of air pollution events at Cape Grim to the modeled meteorology
10:00	Matt Tully	Progress in the detection and correction of anomalies in Cape Grim wind data
10:25	**Morning Tea**	
11:00	David Etheridge	Carbon-13 evidence of natural and anthropogenic changes to the global methane budget in the past 1000 years
11:25	Stephen Wilson	UV measurements at Cape Grim BAPS, 1992-2003
11:50	Clare Paton-Walsh	Aerosol optical depth used to estimate trace gas emissions from biomass burning
12:15	Mark Curran	Ice core evidence for Antarctic sea ice decline since the 1950s
12:40	**Lunch**	
13:30	John Gras	Dioxins and dioxin-like compounds at Cape Grim
13:55	Salah Jimi	Nanoparticles at Cape Grim, Tasmania
14:20	Vin Morgan	Stable isotope ratios in rain from Cape Grim, Margate and Macquarie Island; a first look
14:45	Mark Curran	Why do we observe negative non-sea-salt sulphate values in Antarctic ice core and aerosol records?
15:10	**Afternoon Tea**	
15:30		Wind Workshop
17:00	**Close of meeting**	

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Seasonal changes in the radon-222 defined fetch regions at four ground stations in the ACE-Asia study domain: a comparison with Cape Grim

W. Zahorowski[1], S. Chambers[1], T. Wang[2], C.-H. Kang[3], K. Matsumoto[4] and M. Uematsu[4]

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Abstract

Wind direction was generally found to be a poor indicator of air mass origin at the four ground stations of the ACE-Asia campaign at which atmospheric radon concentration measurements were made (Hok Tsui, China; Gosan, South Korea; Sado Island, Japan; Mauna Loa, Hawaii). Consequently, fetch regions of air masses subjected to the greatest and least terrestrial influence were determined at these sites by 10-day back trajectory analysis. This choice of trajectory duration ensured that fetch regions responsible for more than 80% of the observed radon were represented under normal conditions. The definition of thresholds for high and low concentration radon events was complicated by a pronounced seasonal variation in the background radon concentration not observed at Cape Grim. Event selection criteria were thus defined based on the 10th and 90th percentile radon concentrations of the distribution of hourly observations, after the seasonally dependent background had been removed. During the half of the year that continental outflow conditions prevailed, fetch regions for air masses with the highest radon concentrations were quite consistent. For the east Asian sites, these air masses originated in southern Siberia or Mongolia and passed over north eastern China (Figure 1a, b). Air masses with the lowest radon concentration at this time originated from northern Siberia or regions above the Arctic Circle, and, as a rule, were not of oceanic origin. The corresponding fetch regions for high concentration radon events at Mauna Loa was central China, quite distinct from that of the east Asian sites (Figure 1d). During conditions of onshore monsoonal flow, air masses with the highest radon concentration had no consistent fetch regions, whereas those with the lowest radon concentrations originated mainly from the Pacific (Figure 1c).

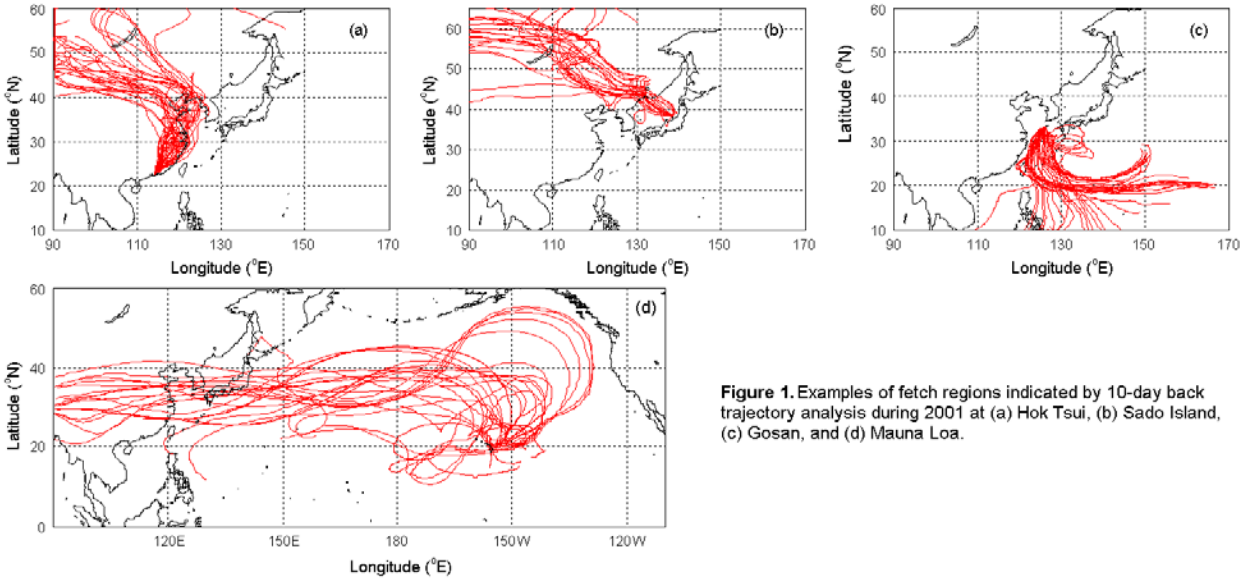


Figure 1. Examples of fetch regions indicated by 10-day back trajectory analysis during 2001 at (a) Hok Tsui, (b) Sado Island, (c) Gosan, and (d) Mauna Loa.

A climatology of tropospheric O_2/N_2 vertical profiles above Cape Grim

R. L. Langenfelds, R. Law, P. Rayner, R. Francey and P. Steele

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Abstract

Since 1995, a subset of flask air samples collected from CSIRO's aircraft-based sampling program over Bass Strait and Cape Grim were routinely analysed for O_2/N_2 ratio. Five years of data from 1995-1999 have been collated to produce a climatology of the seasonal variation in O_2/N_2 vertical profiles from the surface to 6-8 km altitude. Observations of O_2/N_2 and other related species (CO_2, $\delta^{13}C$) were compared with output from an atmospheric transport model using independent prior estimates of global surface fluxes from exchange with oceans, land biota and fossil fuel use. These results are used to explore the sensitivity of vertical profiles to various surface exchange and transport processes. The variations in O_2/N_2 are dominated by just two processes, air-sea exchange and vertical mixing in the Southern Hemisphere troposphere, and can thus be used to constrain vertical mixing schemes in atmospheric transport models.

Melbourne emissions of synthetic gases involved in the Montreal and Kyoto Protocols

B. L. Dunse[1], P. J. Fraser[1], L. P. Steele[1], P. B. Krummel[1] and L. W. Porter[2]

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

Abstract

In this study we have analysed trace gas measurements made during 1998 - 2002 on the AGAGE GC-MS instrument at Cape Grim. Melbourne emissions have been estimated using a tracer-ratio technique for:

(a) the Montreal Protocol gases – CFC-114, CFC-115, HCFC-22, HCFC-124, HCFC-141b, HCFC-142b, H-1211, H-1301 and methyl bromide (CH_3Br)

(b) the Kyoto Protocol gases – HFC-125, HFC-134a and HFC-152a

(c) dichloromethane (CH_2Cl_2) – a solvent whose emissions have been estimated independently in the Melbourne inventory

The tracer-ratio method compares measurements in air masses arriving at Cape Grim from Melbourne of a tracer or reference species with known emissions (in this case carbon monoxide – CO) to measurements of species whose emissions are unknown. Melbourne emissions for these species are then derived from these comparisons. The process of estimating emissions involves first identifying pollution episodes in the Cape Grim record that were 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) were used to identify episodes caused by Melbourne pollution. These 'pollution episodes' were extracted, and correlations between the trace species in the polluted air masses were derived. These correlations and an estimate of carbon monoxide emissions from Melbourne were used to deduce the mass of Melbourne emissions. Where possible, comparisons of these estimates have been made with estimates from established inventory techniques.

The CIO/RuG Air Sampling Program

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Centrum voor Isotopen Onderzoek, Rijksuniversiteit Groningen, Netherlands

Abstract

The Centre for Isotope Research (CIO) at the State University of Groningen maintains a program of measuring CO_2, CO and CH_4 concentrations, and isotope ratios in these species, from air samples collected at a number of continental European stations. Our main sampling location is Lutjewad (53°23' N, 6°22' E), located on the north coast of the Netherlands, about 30 km north of the CIO laboratory in Groningen. Other sampling locations are in France, Germany, Hungary and Siberia.

For this program we have developed a remote controlled automated air sampling system that allows us to collect air, at ambient pressure, under specific conditions. The conditions include time, meteorological conditions and operator intervention (remote control).

Our sampling system contains 20 sample bottles, each of 2.5 litres, which are constantly flushed for two hours before sample collection. If an 'event' occurs, the automatic sampling is stopped and the collected samples are returned to the CIO laboratory for analyses. If no event occurs the sample is replaced the next day.

Because of the humid conditions, water must be removed from the air stream before entering the sample containers. To do this we use a double cooler system; one part of the system refrigerates the water out from the sampling line while the other part is regenerated. After 24 hours the cooling systems are reversed enabling the cooling systems to run for months without operator intervention.

In this talk we will describe the automated sampling system and present some results from past 'events'.

Ozonesonde and lidar measurements of stratospheric conditions above Davis, Antarctica during 2003

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Abstract

A new program of stratospheric ozone studies has been established at Australia's Davis station in Antarctica (69ºS, 78ºE) by the Australian Antarctic Division (AAD) and the Bureau of Meteorology (BoM). This effort has included Australia's first in-situ measurements of stratospheric ozone from Antarctica, and is part of the larger investigation of the polar middle atmosphere being undertaken by the AAD.

The aims of the Davis ozone study are;

- To investigate the influence of atmospheric wave processes on the structure of Polar Stratospheric Clouds (PSCs) and chemical ozone depletion.
- To provide local ozone data for the derivation of Rayleigh temperature profiles from the Davis lidar, and to provide in-situ temperature measurements in the upper stratosphere for comparison with lidar observations.
- To contribute to international ozone depletion studies through participation in the European Union program 'Qualitative Understanding of Ozone Losses by Bipolar Investigations' (QUOBI), and provision of data to the World Ozone and Ultraviolet Radiation Data Center.

Conditions in the Antarctic stratosphere during the 2003 winter were notable for below-average mean temperatures across the polar cap, and the development of a large and stable polar vortex. These factors allowed the extensive and persistent coverage of the lower stratosphere by PSCs. The atmospheric chemical processing produced by the clouds, together with the extent and stability of the vortex, provided conditions favourable for the development of a large ozone hole in early spring. The hole grew unusually rapidly during August, and attained a near-record maximum extent in September.

In this presentation, an overview of stratospheric conditions over Antarctica during 2003 assessed from global atmospheric data will be provided. This will be followed by first results from the Davis ozone measurements, including observations of the development of the ozone hole and the interaction of atmospheric gravity waves with PSCs.

Sulfur hexafluoride: long-term trends and regional emissions

L. W. Porter[1], S. B. Baly[1], P. J. Fraser[2], P. B. Krummel[2], C. M. Trudinger[2], B. L. Dunse[2], L. P. Steele[2], N. Derek[2], R. L. Langenfelds[2], D. M. Etheridge[2], I. Levin[3], D. E. Oram[4], J. H.Butler[5] and M. Vollmer[61]*Cape Grim Baseline Air Pollution Station, Commonwealth Bureau of Meteorology, Smithton, Tasmania 7330, Australia*
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Abstract

Sulfur hexafluoride (SF_6) has been measured at Cape Grim since March 2001 by gas chromatography with electron capture detection (GC-ECD), as an auxiliary project to the Advanced Global Atmospheric Gases Experiment (AGAGE) program. This report summarises the methodology employed and compares the *in situ* observations of SF_6 to measurements on flask air samples collected by a number of international laboratories. A long-term SF_6 record has been obtained by analyses of both the Cape Grim air archive, and firn air samples from Antarctica. Sulfur hexafluoride pollution episodes have been observed at Cape Grim in air masses that have previously passed over or near Melbourne (the Port Phillip region). These data have been used to calculate regional SF_6 emissions using inter-species correlation techniques.

Calibration of stable isotope measurements of atmospheric carbon dioxide in the CSIRO Atmospheric Research Global Atmospheric Sampling Laboratory – the HC453-2003 and CAR-2003 assignments on the V-PDB (CO_2) scale

C. E. Allison and R. J. Francey

CSIRO Atmospheric Research, Aspendale, Victoria 3195, Australia

Abstract

In 1978, CSIRO Atmospheric Research (CAR) began measuring the stable isotope composition of CO_2 in air at the Cape Grim Baseline Air Pollution Station (41ºS, 141ºE). This program involves cryogenic *in situ* extraction of CO_2 from the Cape Grim air. Prior to 1991 the collected CO_2 samples were measured at CAR using a VG602D dual inlet isotope-ratio mass spectrometer (IRMS), and from 1991, using a Finnigan MAT-252 IRMS. The HC453-2003 'scale' describes the re-assignment on the V-PDB (CO_2) Scale of isotope values in the pure CO_2 used as a reference to calibrate the measurements

Since 1991 CAR has used the same Finnigan MAT-252, equipped with a 'MT Box C' cryogenic extraction accessory, to carry out CO_2 stable isotope ratio measurements on chemically dried air collected in glass flasks from a global network of 'clean air' sites (including Cape Grim). The CAR-2003 'scale' describes the re-assignment on the V-PDB (CO_2) Scale of stable isotope values to the CO_2 in a suite of ambient air standards in high-pressure cylinders used as a reference to calibrate the measurements from this program.

The CAR Global Atmospheric Sampling LABoratory (GASLAB) has also initiated a number of sample and standard inter-comparison exercises with international institutions. These comparisons document unresolved systematic bias that hinders or degrades the merging of data from different global sampling networks.

Comparisons between the two CAR Cape Grim programs, with quite different collection, sample storage, analysis and calibration strategies, provides an unusual opportunity to identify sources of systematic bias, implement correction strategies and test for their effectiveness. The 2003 scale re-assignments come from the consistent application of independently derived algorithms that describe the several sources of bias recognised in the data, in particular, a cross contamination effect that has been inadequately addressed in previous data releases. The resulting good agreement between the two Cape Grim records, supported by additional information, is presented as confirmation that the significant sources of bias in the CAR programs are now correctly accounted for.

Differences from previously published selected data from these programs that arise from these new 'scale' assignments are relatively minor.

What controls the production of methyl halides by phytoplankton; three years of data from Cape Grim

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Abstract

The global production of methyl bromide and methyl iodide is known to be dominated by marine phytoplankton. Some phytoplankton groups, such as the Prymnesiophytes (ie *Phaeocystis* spp., *Emiliana huxleyi*) are thought to be more closely associated with this production than groups such as diatoms and dinoflagellates. We have been investigating the phytoplankton ecology and related methyl halide production since 2000.

The composition of the phytoplankton off Couta Rocks in 2001/2 was very different from that in 2000/1. In 2000/1 the species compostion was dominated by diatoms with smaller contributions from dinoflagellates and small flagellates, mostly *Phaeocystis* spp. In 2001/2 and 2002/3 the species composition was overwhelmingly dominated by colonies of *Phaeocystis*. Prymnesiophyte taxa, including *Phaeocystis* and coccolithophoroids such as *Emilliana huxleyi*, have been widely reported to be associated with high methyl halide production and so their occurrence with high levels of methyl halides in 2001/2 was much less suprising than the high methyl halide concentrations associated with diatom blooms in 2000/1.

In 2000/1 there was a correlation between the N:P ratio and methyl halide concentration. However, regression correlations between methyl halide concentrations and major oceanographic and ecological variables in 2001/2 are consistently poor. There are good, although unsuprising, correlations between integrated cell numbers and chlorphyll *a* (Fig 1a) and between the different nutrient concentrations (Fig 2d). If the season is broken up, there is a good correlation between methyl bromide and the N:P ratio for most of the season (21/11/01 to 8/3/02) but this breaks down in late March. With methyl iodide, there is an inverse relationship with N:P between all dates except 18/01/02; at all other dates when N:P rises, methyl halide falls and vice versa.

In 2003 we began to systematically use pulse amplitude modulation (PAM) fluorometry to measure the photosynthetic health of the phytoplankton community. This has proved to be a valuable tool for measuring ecological stress and is likely to assist in the interpretation of methyl halide production.

Methyl bromide: long-term trends and regional emissions

P. J. Fraser[1], B. L. Dunse[1], C. M. Trudinger[1], M. L. Cox[2], G. A. Sturrock[3], P. B. Krummel[1], D. M. Etheridge[1], L. W. Porter[4], N. Derek[1], B. R. Miller[5] and C. McCulloch[1]

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Abstract

Methyl bromide and hydrochlorofluorocarbons (HFCs) are the remaining ozone depleting substances for which consumption policy options continue to evolve under the Montreal Protocol. Because it has large natural sources and significant anthropogenic consumption outside the Protocol domain, possible reductions in the future atmospheric levels of methyl bromide are uncertain. Nevertheless methyl bromide continues to attract interest from policy makers because, unlike the chlorofluorocarbons (CFCs), it has a short atmospheric lifetime and initiatives to reduce consumption have immediate impacts on atmospheric content.

Cape Grim *in situ* data (1993-2003), measurements on the Cape Grim air archive (1978-2003) and on Antarctic firn air (1935-2000) are combined to produce the most comprehensive record of methyl bromide in the Southern Hemisphere background atmosphere. Significant growth in methyl bromide has occurred over the past 50 years and the past levels of methyl bromide may indicate the extent of future changes for this species.

The Cape Grim record also contains information on the location of regional emissions of methyl bromide. Source regions are identified and flux chamber experiments are used to quantify some of these emissions.

Trace gas emissions estimated from observations using aircraft, balloon, tower, and railway platforms

J. W. Elkins

National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado 80305, USA

Abstract

Our measurements of climatically important trace gases at baseline observatories like those from Cape Grim have been recently supplemented by observations from aircraft, balloon, tower, and railway platforms. The goal of these observations is to gain insight on the regional emissions of trace gases. Using tracer-tracer correlations and estimates of trace gases with known emissions, like radon, carbon monoxide, and tetrachloroethene, it is possible to estimate emissions on a regional and perhaps national scale. The method can be tested by comparing known emissions for either fossil fuel emissions or respiration estimates from forest for carbon dioxide. An *in situ* gas chromatograph was recently flown across North America twice once every two weeks in the early summer of 2003. A second Siberian experiment is planned on the Trans-Siberian Railway in February 2003. A new five channel gas chromatograph has been completed that will allow shorter-lived compounds (PAN, hydrocarbons, chlorofluorocarbon replacements) to be measured in the future. The talk will describe recent emission estimates in Europe, the United States, and Russia and potential implications for stratospheric ozone depletion, climate forcing, and air quality.

AGAGE observations at Mt St Leonard, Victoria

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Abstract

Regional pollution episodes observed in AGAGE data at Cape Grim have been used to estimate annual emissions (1994-2002) of greenhouse and ozone depleting trace gases into the Melbourne (Port Phillip) air shed. The technique employed is interspecies correlation and the calibrating species used is carbon monoxide, which has well-documented (EPAV) Port Phillip emissions.

Because the sources of these gases are typically not co-located with those of carbon monoxide, averages are necessary over many pollution episodes to obtain a representative estimate of emissions from the Port Phillip region. The inhomogeneity of the Melbourne source region is, in part, compensated by the intra-air shed and intra-plume mixing that occurs during the time the air mass spends over Melbourne and *en route* to Cape Grim (0.5 - 3 days).

The technique, as applied to the Cape Grim data, assumes that an air mass entering the Melbourne air shed, typically from the north to north east, *en route* to Cape Grim, does so with baseline levels of carbon monoxide and the other correlated species of interest (for example methane, nitrous oxide, CFCs, HFCs etc.). While this assumption might be expected to be robust for those species predominantly emitted in urban environments (CFCs, HFCs etc.), potential problems arise with those species that have both urban and rural sources and/or sinks such as methane, nitrous oxide and, most-importantly, the calibrating species carbon monoxide.

In order to test this assumption, a regular air-sampling program has commenced at Mt St Leonards (1100 m, 37.57°S, 145.53°E, 65 km north east of Melbourne CBD), at the head of the Yarra Valley. The site has a secure 30 m Telstra tower/Melbourne Water fire tower and a 10m public-access observation tower. Public vehicular access to the site is restricted by a locked gate, 2 km north of the towers. Initial sampling has commenced on the observation tower and the samples have been analysed at Cape Grim on the AGAGE instruments. These initial Mt St Leonard data will be assessed and compared to corresponding Cape Grim data under baseline conditions.

Retrieval of Isotopomer-Specific Ozone Vertical Profiles from Solar Infrared Spectra Recorded at Lauder, New Zealand

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Abstract

The isotopic composition of atmospheric ozone column over Lauder has been studied by high resolution ground-based solar Fourier Transform Infrared Spectrometry, with retrievals being performed by the Optimal Estimation Method. Firstly, vertical profiles for the main isotopomer ($^{16}O^{16}O^{16}O$) were retrieved in the 1001.3-1004.3 cm^{-1} interval and validated against independent microwave radiometer measurements, balloon sonde data and Dobson spectrophotometer data. Profiles of the minor isotopomers ($^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$) were then retrieved in separate spectral intervals with three vertically independent partial columns being achieved. For these retrievals, the profile of $^{16}O^{16}O^{16}O$ was constrained to the previously retrieved profile, which was also used as the a-priori profile for the target species. Results are compared to previous ground-based, balloon-based and satellite measurements of isotopic enrichments in atmospheric ozone and found to have smaller uncertainties. The results should therefore provide useful data for validating proposed mechanisms for the anomalous mass-independent isotopic enrichments in atmospheric ozone.

Designing a LOFLO CO_2 network for estimating Australian CO_2 emissions

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Abstract

Given the large costs involved in setting up a CO_2 monitoring network, it is helpful to explore whether CO_2 inversion techniques can be used to provide any guidance about where measurement sites are located. The Bayesian synthesis inversion method estimates surface CO_2 fluxes and their uncertainties from CO_2 atmospheric concentrations and associated data uncertainties. A network can be assessed by the magnitudes of the source uncertainties obtained, with better networks giving smaller uncertainties. Here we estimate sources for 12 Australian regions from model-generated CO_2 concentrations. The atmospheric transport model is forced with fossil, biosphere and ocean emissions. The biosphere emissions are from the CSIRO Biosphere model and contain diurnal and synoptic variability. We will show how the inversion is able to recover the known mean monthly emissions as well as the mean diurnal amplitude of emissions, when a dense network of concentration data is used. We will then present results from a number of network design tests in which we assume that continuous CO_2 measurements are available from Cape Grim and we want to determine the impact of adding new continuous CO_2 measurement sites at other Australian locations.

LoFlo Mark2 CO_2 Analyser update

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Abstract

Ten LoFlo Mark2 instruments are now constructed or under construction. Of particular relevance to the GAW community is the system for the new GAW site at Danum Valley, North Borneo, operated by the Malaysian Meteorological Service. In order to better characterise continental CO_2 values, vertical-profiling modes of operation (from 3-intake heights) are being developed for the Malaysian system. In the 'BWG' LoFlo2 for operation in continental Australia, it is planned to provide both concentrations and CO_2 fluxes. Modelling studies show the effectiveness of adding these two LoFlo systems to the existing global network.

Three suites of 7 high-pressure cylinders, dedicated to individual LoFlo2 units have been calibrated at the WMO CO_2 Central Laboratory at CMDL/NOAA. The LoFlo2 precision is superior to that of the CCL assignment so that independent assessment and refinement of the CCL calibration is possible for the first time. Comparisons involving 2 of the CAL suites and 2 LoFlo2 units will be presented.

The unique precision of the LoFlo has also been exploited in additional diagnostic tests, including testing the influence of Dekabond intake tubing on CO_2 values, and explorations of lower reference gas flows (and extended operational lifetimes of working standards).

In the process a reasonably complete record of Aspendale CO_2 has emerged, with sufficient near-baseline episodes for a useful comparison to the Cape Grim LoFlo1, as well as LoFlo2A which, when not at sea, has been deployed from the roof of CSIRO Marine Research in Hobart.

CO_2 emissions from the Melbourne region

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Abstract

It is well documented that many trace gases exhibit elevated mixing ratios at Cape Grim during those periods when winds quickly transport air from the Melbourne region to Cape Grim [Dunse *et al*., 2001; Dunse, 2002; Dunse *et al*., 2003].

A trace gas which has not been so far included in such analyses of these Cape Grim 'pollution episodes' is CO_2, although these non-baseline CO_2 data have been used to aid the estimation of regional terrestrial carbon fluxes for the Australian continent [Wang and McGregor, 2003].

This talk will present some preliminary findings from analysis of CO_2 pollution episodes at Cape Grim, some during times when atmospheric CO_2 measurements were also made at Aspendale. It will also examine CO_2 spatial gradients between Cape Grim, Aspendale, and Hobart. The longer-term objective of this work is to develop capabilities to monitor for change in regional CO_2 fluxes from a variety of sources.

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Statistical modelling of episodic concentration data

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Abstract

Virtually all forms of analysis of trace gas data can be regarded as some form of extracting a `signal' from a noisy data record. A statistical model of both the signal and noise is necessary, both for designing the signal extraction procedure, and for determining the uncertainties on the estimated signal. When cast in this form, it can be seen that many data-analysis techniques are making the implicit (or even explicit) assumption of normally-distributed noise, possibly with a simple autocorrelation structure.

While the assumption of normally-distributed errors has proved adequate for global-scale inversions of baseline CO2 data, when the full record from locations such as Cape Grim is considered, it is clear that better statistical models will be needed. This presentation describes an initial step towards developing such models. To a large extent, the concepts are based on the formalism of the Kalman filter. This has the desirable characteristics of (a) being readily adaptable to mixed stochastic/deterministic models (b) applicable to non-stationary data (c) able to handle multi-variate data. All these characteristics are retained in the generalisation.

The procedure tracks two independent representations of an trace gas `state' representing `baseline' and `polluted' conditions. Each of these states can have the full generality associated with state space modelling of trace gas behaviour, as for example in AGAGE studies. Data are assimilated into these state representations on the basis of a Bayesian likelihood for the data being `baseline' or 'polluted'. Potential applications (in an approximate order of increasing sophistication) are (a) data separation, in a statistical sense, between baseline and non-baseline conditions; (b) the use of multi-tracer analysis to refine baseline selection; (c) data assimilation into transport models, incorporating a statistical representation of model uncertainty. Various examples are presented.

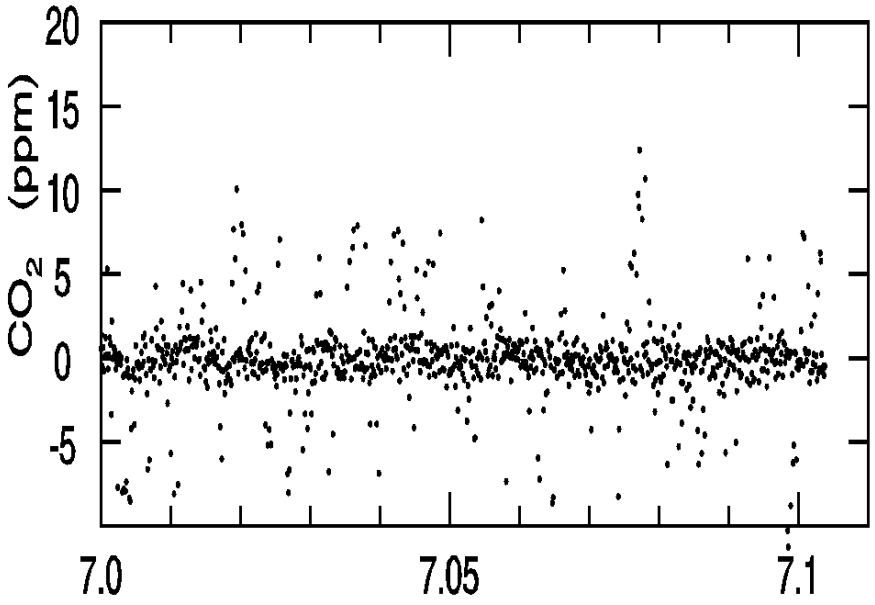


Figure 1. *Data simulated by the statistical model proposed for episodic data.*

The sensitivity of simulations of air pollution events at Cape Grim to the modeled meteorology

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Abstract

Observations from the Cape Grim Baseline Air Pollution Station (CGBAPS) have recently become popular in testing regional air pollution models. Commonly, emissions of carbon monoxide (CO) from the greater Melbourne region are used as the source for the numerical models. The models simulate the evolution of the CO, which allows for a comparison of simulated concentrations to the observed concentrations. A long-term goal of this work would be to couple a model with the observations to make an estimate of the strength of various regional sources. Cox *et al*. (2003) attempted to do this with the CGBAPS observations of dichloromethane observations and the Air Pollution Model (TAPM), and suggested that the estimated source was roughly a factor of two too low.

For individual case studies, the accuracy of the simulated concentration obviously depends heavily on the strength of the simulation of the underlying meteorology. As pollution events often take 10-15 hours to travel from Melbourne to Cape Grim it is not uncommon for relatively small errors in the meteorology to lead to absolute errors in the simulated concentrations arriving at Cape Grim, i.e. an observed pollution event might simply miss Cape Grim in the simulation or vice versa. Over long periods of time, however, one might anticipate that these errors would average out in some sense and that a simulated cumulative concentration would be similar to that which is observed. This work examines the sensitivity of yearlong cumulative TAPM simulations to the underlying meteorology as defined by the boundary conditions. A more primitive choice of boundary conditions leads not only to a weaker immediate simulation of the meteorology, but also a systematic error in the cumulative concentration distribution over the course of a year.

Progress in the detection and correction of anomalies in Cape Grim wind data

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Abstract

While wind speed and direction data are widely used by the Cape Grim community, it has been known for some time that there are a number of difficulties with the dataset, in particular distortions due to the placement of the sensors and the local topography.

We will describe progress made towards producing a more reliable dataset, with a target having been set of producing data accurate to within 5 degrees and 2 m/s. Various methods of assessing the data have been employed including the careful comparison of data from different sensors, in conjunction with an accurate determination of the geometry of local obstructions. We will describe progress made towards understanding the effects of obstructions and developing quality control procedures for re-processing past data.

Some interesting features of circular statistics will also be touched upon.

Carbon-13 evidence of natural and anthropogenic changes to the global methane budget in the past 1000 years

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Abstract

The causes of the 150% increase in the concentration of atmospheric methane since 1700 AD are investigated using $\delta^{13}CH_4$ in air from Antarctic ice cores, firn and the Cape Grim air archive. A new GC-IRMS technique was developed to analyse the very small air samples with high precision. $\delta^{13}CH_4$ increased over the past century, consistent with the emission of isotopically enriched methane from anthropogenic activity. Significant $\delta^{13}CH_4$ variations are observed during pre-industrial time, in particular a large and unexpected decrease in $\delta^{13}CH_4$ from 1500AD to about 1700AD. These changes imply that the pre-industrial methane budget was not in balance, despite the small, observed changes in methane concentration. Likely causes of these $\delta^{13}CH_4$ changes include variable emissions in enriched sources such as biomass burning.

UV measurements at Cape Grim BAPS, 1992 – 2003

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Abstract

In 1992 a spectral radiometer (SRAD) began operating at Cape Grim with the aim of quantifying the forces driving UV (and particularly UV-B) at this 'clean air' site. This was augmented with a broadband 'UV-B' detector in 1993. The location, in terms of both the environmental conditions and scientific goals, placed significant constraints on the measurements.

An overview and assessment of the original measurement strategy (in particular calibration) and equipment will be presented, along with a summary of the data collected to date. In the light of this experience, an outline of the replacement for SRAD will be given.

Aerosol optical depth used to estimate trace gas emissions from biomass burning

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Abstract

Significant correlations between aerosol optical depth (AOD) and column amounts of carbon monoxide, hydrogen cyanide, formaldehyde and ammonia have been observed in bushfire smoke plumes over SE Australia during the 2001/2002 and 2002/2003 fire seasons. Over 1500 solar Fourier transform infrared spectra were collected directly through the smoke plumes over Wollongong with coincident sun-photometer measurements of radiance. Total columns amounts of the gases were calculated from the FTIR spectra, whilst radiance measurements were used to calculate AOD at the time.

There are several important applications of the AOD-to-gas correlation. The estimation of global emissions from biomass burning currently has very large associated uncertainties. The use of visible radiances measured by satellites, and hence AOD, could significantly reduce these uncertainties by giving a direct estimate of global emissions of gases from biomass burning through application of the AOD-to-gas correlation. On a more local level, satellite-derived aerosol optical depth maps could be inverted to infer approximate concentration levels of smoke-related pollutants at the ground and in the lower troposphere.

Ice core evidence for Antarctic sea ice decline since the 1950s

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Abstract

The instrumental record of Antarctic sea ice in recent decades does not reveal a clear signature of warming despite observational evidence from coastal Antarctica. Here we report a significant correlation ($p<0.002$) between methanesulphonic acid (MSA) concentrations from a Law Dome ice core, and 22-years of satellite-derived sea ice extent (SIE) for the 80-140°E sector. Applying this instrumental calibration to longer-term MSA data (AD 1841-1995) suggests that there has been a 20% decline in SIE since ~1950. The decline is not uniform, showing large cyclical variations with periods of approximately 11 years that confuse trend-detection over the relatively short satellite era.

Dioxins and dioxin-like compounds at Cape Grim

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Abstract

Nanoparticles at Cape Grim, Tasmania

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Keywords: Nanoparticle, MBL, Free Troposphere, Frontal Passage, ACE 1

Abstract

Factors influencing the concentration of nanoparticles were investigated during 1999 - 2000. Diurnal variations were examined for three broad air mass origins, namely Tasmania, continental Australia and clean maritime. Substantial differences are found in the diurnal patterns between the three sectors, with a broad daytime enhancement in the Tasmanian sector, attributed to urban/industrial activities. Low nanoparticle concentration was observed in the early morning (0000 - 0600) and night (1800 - 2300) in this sector. In summer, the major peaks are observed earlier while in winter they are delayed, with the peaks for the moderately warm seasons lying between the two extremes. In general, major continental nanoparticle peaks were observed at about mid-day, and extended to late afternoon and evening. This wide range delay is expected because continental sources are vast and arrival times of air masses at Cape Grim are also expected to vary. Continental diurnal cycles are more complicated with no clear evidence for seasonality. In the 'baseline' sector, seasonal variations are clearly evident with periods of marked elevation in nanoparticle concentration during summer, autumn and spring. Winter shows the lowest nanoparticle concentration with almost no diurnal patterns. Seasonal variability in the 'baseline' sector is likely to be influenced by the amount of precursor material available during the different seasons.

The behaviour of nanoparticle concentrations following frontal passages during the two years period was also investigated. The findings show that periods with enhanced concentration occur throughout the year and that nanoparticle enhancement events are strongest in summer (~ 480 cm^{-3}) and weakest in winter (~ 152 cm^{-3}). Enhancements in spring (~ 325 cm^{-3}) and autumn (~ 183 cm^{-3}) are intermediate between these extremes, consistent with the seasonal cycle in particle number at Cape Grim and suggesting the importance of photochemical processes. Typically, nanoparticle concentrations peaked about 10 to 15 hours after frontal passage and the events lasted for about 6 to 13 hours. These results are consistent with nanoparticle observations from ACE 1 although in most cases the enhancements following individual frontal passage at Cape Grim were of greater magnitude than those observed during ACE 1.

Meteorological data were used to examine possible relationships between the strength of frontal passages and properties of the nanoparticle enhancement events, but all correlations were found to be weak. Enhanced nanoparticle concentrations, however, occur with drier air during post-frontal subsidence, and wind speeds are also elevated during these events, suggesting stronger mixing between the free troposphere and the boundary layer. Whilst the preceding frontal passages initiate the conditions necessary for nanoparticle production events, these observations show that fronts are not the main controlling factor for their magnitude.

Stable isotope ratios in rain from Cape Grim, Margate and Macquarie Island; a first look

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Abstract

Stable isotope ratios of oxygen ($\delta^{18}O$) have been measured in rain from Cape Grim and Margate in Tasmania and from Macquarie Island in the Southern Ocean. Measurements are generally on a single days precipitation.

The data for Cape Grim and Margate shows a noisy seasonal cycle. The amplitude of the annual cycle is approximately 4 ‰ however the scatter is large ~ 5-6 ‰. Summer maximum values average ~-1 ‰ i.e. not much depleted from ocean water. The seasonal cycle is different at Cape Grim and Margate. Summer $\delta^{18}O$ values are similar while in winter Cape Grim $\delta^{18}O$ values are higher than Margate. Macquarie Island annual average $\delta^{18}O$ is -4.8, the same as Margate however Macquarie shows a negligible seasonal variation.

Why do we observe negative non-sea-salt sulphate values in Antarctic ice core and aerosol records?

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Abstract

Sulphate is an important constituent of ice core climate records, having a number of sources including seawater sea salt, volcanoes and biological activity. In order to remove the sea salt contribution, it is common to subtract a portion based on the ratio of sodium:sulphate in bulk seawater. This is generally reported as non-sea-salt sulphate (nss-sulphate). This is adequate for multi-annual samples, however, at seasonal resolution, negative values of nss-sulphate are often the rule in winter rather than the exception.

Negative values have been found in aerosol studies and corrections have been made to the winter aerosol data to take this into account. However, it is not always possible to clearly distinguish winter and summer ice core data due to the lack of sub-seasonal horizons or dates. At Law Dome, we have looked at the distribution of nss-sulphate with sodium, which shows an increasing tendency towards negative values with higher sodium levels. This distribution appears to have a hard lower negative limit. Using only the lower 5th percentile of data, a slope of 0.035 was found for the line of best fit. Fine tuning using a multi-correlation analysis of nss-sulphate with methanesulphonic acid, nitrate and sodium found that using a correction of 0.0325 gave a maximum correlation with MSA and nitrate, and a minimum with sodium. This correction of can be applied to the entire nss-sulphate data, since the correction is highest for winter (high sodium) and lowest for summer (low sodium). The exact numeric value of this correction will vary from site to site, however at Law Dome this indicates an average of 28% of sulphate is depleted from sea salt aerosols.

What is causing this depletion? Recently, it has been reported that depletion of sulphate occurs at the source of the aerosol and is solely due to frost flower formation on sea ice and precipitation of sodium sulphate (Rankin et al., 2002). They also claim that the exclusive source of sea salt aerosols is the sea ice and not the open ocean surface as previously accepted. Negative values of nss-sulphate have been found at Cape Grim, indicating that processes other than frost flower formation can produce this depletion. Investigations are continuing at the high altitude Law Dome ice core site to establish the source of negative winter nss-sulphate values and the dominant source of sea salts. Results from ice cores recently taken from an iceberg, close to the suspected source of the sea salt aerosol, may enlighten this debate.

Seasonal and latitudinal dependence of background radon-222 at three ground stations in East Asia

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Abstract

Atmospheric radon concentration was measured at three ground stations in south-east Asia (Hok Tsui, China; Gosan, South Korea; Sado Island, Japan), as part of the Asian Aerosol Characterisation Experiment. The radon concentration at each site represents a combination of a high frequency signal, from synoptically driven changes in fetch region, and a low frequency signal associated with large-scale (monsoonal) weather effects on the background concentration (Figure 1). This poster characterises both the seasonal and latitudinal variation in background radon concentrations at each site, based on the first complete year of observations. The annual range of weekly 10th percentile radon concentrations at these sites was 4-18 times greater than that observed at Cape Grim in 2001 (480 mBq m^{-3}). At Hok Tsui and Gosan, background radon concentrations representative of marine baseline values (<100 mBq m^{-3}) were only observed in summer. Whilst similarly low radon concentrations were observed at Sado Island, this usually occurred in late spring and early autumn. By contrast, at Cape Grim, radon concentrations can drop to baseline values within 6 hours of a shift to the baseline sector irrespective of season. Apart from the observed seasonal cycle of background radon concentration in East Asia, there was also a pronounced change with latitude. The range of weekly 10th percentile radon concentrations decreased northwards, 8810, 2920 and 1610 mBq m^{-3} at Hok Tsui (22.2°N), Gosan (33.3°N) and Sado Island (38.2°N), respectively. The observed behaviour of background radon concentration at these sites was primarily attributed to the influence of the Asian monsoon, and relative proximity to the continental Asian source. The seasonal variability in fetch regions of background radon events was characterised by 10-day back trajectory analyses. When onshore flow dominated, air masses with the lowest radon concentrations had fetch regions in the Pacific Ocean between 20-30°N, although occasionally they originated from the Bering Sea area. When continental outflow conditions dominated, the air masses with the lowest radon concentrations had fetch regions in Siberia (~60°N) and northern China. Much of the ground in these regions would be frozen at that time of year with resulting reduction of the radon flux.

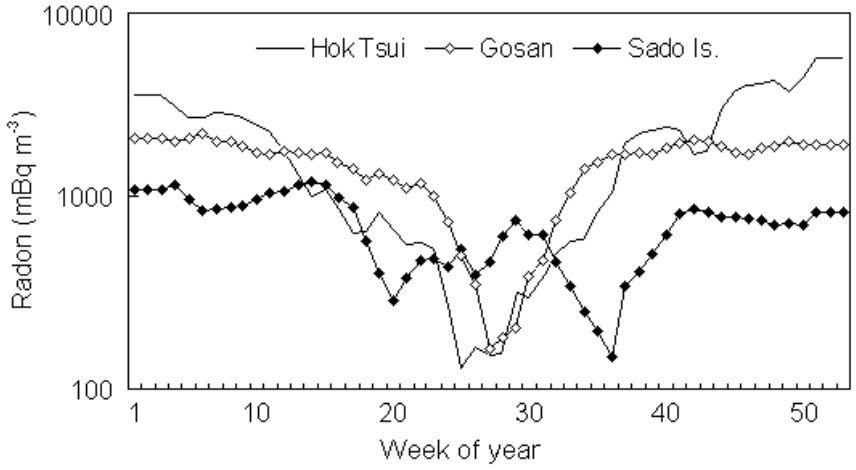


Figure 1. *Weekly 10th percentile radon concentrations at three ground stations in East Asia smoothed via a 5-week runningmean.*

Radon-222 observations at the Mauna Loa Observatory: latitudinal and seasonal variations of the Asian continental signature in the free troposphere

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Abstract

Natural and anthropogenic pollution from sources within Asia have a large impact on the Pacific Basin. There are two main paths for Asian continental outflow to the Pacific: low-level outflow within the marine boundary layer, and upper-level flow within the tropospheric jet-stream. At 3,400m above sea level, the Mauna Loa Observatory is ideally situated to study the tropospheric outflow events from Asia. Nocturnal measurements are required in order to sample tropospheric air free from local influences caused by anabatic winds. The nocturnal sampling window for this study (22:00 – 07:00) was defined based on analysis of the composite diurnal radon concentration. The fetch regions for high concentration radon events at Mauna Loa in 2001, determined by 10-day back trajectory analysis, were throughout central China, primarily within the latitude band 20-40°N. Trajectories were used to categorise air masses based on the latitude band within which they crossed the Asian coastline (eg. 20-30°N or 30-40°N). The radon concentration of air masses originating from the Asian continent (corrected for time over the ocean), were then collated by season and latitude and their distributions shown in Figure 1a. Figure 1b shows an example of 30-40°N latitude band trajectories in spring 2001. For both latitude bands, spring (winter) was the time of greatest (least) terrestrial influence on tropospheric air masses at Mauna Loa. Furthermore, there was a latitudinal gradient (increasing to the north), in the radon concentration of Asian air masses. The observed latitudinal gradient in radon concentration opposes the latitudinal gradient in the radon source function that is commonly assumed to exist. This apparent contradiction could be explained by a concurrent latitudinal gradient in the frequency or strength of events (fronts and deep convection) that inject boundary layer air to the free troposphere over central China.

Acknowledgments: The authors wish to thank Mr Paul Fukumura-Sawada of the Mauna Loa Observatory for his help in running the radon program at the station.

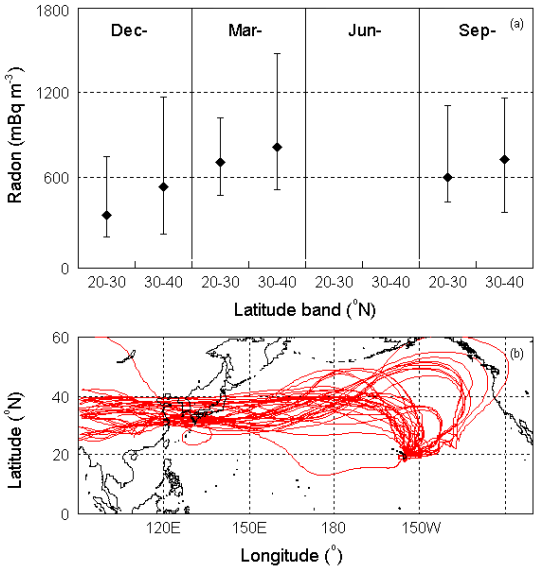


Figure 1. *(a) 10th, 50th and 90th percentile radon concentrations of Asian continental air masses by fetch latitude and season, and (b) example of 30-40°N latitude band trajectories in spring 2001. There were insufficient data from the Asian continent between June and August to derive statistics.*

Global Atmosphere Watch Activities of the South African Weather Service

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Abstract

Long-term measurements of important atmospheric parameters have been conducted in South Africa for more than two decades now.

The main monitoring and research activities comprise the Cape Point Global Atmosphere Watch (GAW) Station, the Baseline Surface Radiation Network (BSRN) site at De Aar, and two column ozone monitoring stations forming part of the Global Ozone Observing System (GO_3OS).

Measurements at Cape Point date back to the late 1970s, when the CSIR started measurements of CO together with the German Max Planck Institute in Mainz. Over the years the measuring programme has been enlarged and consolidated, with close co-operation involving the Fraunhofer Institute IFU (now IMK-IFU of the Research Center Karlsruhe). Major milestones in the Cape Point activities were the integration into the WMO's GAW network and the transition of the station management from the CSIR to the South African Weather Service (SAWS) in 1997. The present measuring programme includes CO_2, CH_4, N_2O, CO, surface O_3, five halocarbons, ^{222}Rn, total gaseous mercury, solar radiation and standard meteorological parameters.

While the build-up of halocarbons in the atmosphere has slowed down or even declined after the successful implementation of the Montreal Protocol, the greenhouse gases CO_2, CH_4 and N_2O have maintained their upward trend as a result of anthropogenic activities worldwide. Supplementary measurements of ^{222}Rn, a tracer for air mass origin, were started in 1999, with technical support from ANSTO (Australia).

The first total column ozone measurements (Dobson #89) were made at Pretoria during the late 1960s until early 1970s, which unfortunately, were only resumed again in 1989. During 1995 a second Dobson spectrophotometer (#132) was acquired and a measurement programme started at Springbok.

Ozonesondes were launched at Irene on a weekly basis from 1990-1993. This also included participation in the SAFARI-92, -94, -2000 and THESEO field campaigns. From 1999 onwards this work became part of the NASA Southern Hemisphere ADditional OZonesonde (SHADOZ) program.

In 1999, efforts from the BSRN programme and WMO resulted in the establishment of the new BSRN station at De Aar in the southern Karoo. The solar radiation parameters measured on site comprise short wave, global (direct and diffuse) as well as down-welling long wave radiation and UVB measurements.

Since 1992 the SAWS has also established a national UVB-Solar Light Model 501 network, currently comprising six stations around the country.

Comparison of first surface ozone measurements from Sanae IV, Antarctica with adjacent Neumayer Station

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Abstract

Surface ozone measurements in Arctic and Antarctic regions are of particular interest, because of the prevalence of special phenomena (reported in the literature), such as those involving reactions with brominated compounds.

Since January 2002, O_3 measurements have been conducted at the South African Antarctic base, SANAE IV (71°40' S, 2°50' W) using a TEI 49 analyser. The SA base (continental) is situated on a mountainous site (851m a. s. l.), 170 km inland from the coast and 300 km SE from the German base, Neumayer (70°39' S, 8°15' W). That coastal station maintains a comprehensive O_3 measuring programme as part of the WMO Global Atmosphere Watch (GAW) network.

In general, the monthly means of surface O_3 measured at the two sites are in excellent agreement (92% correlation). There are, however, some noteworthy differences in the fine structure, which is being addressed.

Like Neumayer, the SANAE IV O_3 data (18 months) display a seasonal cycle with a winter (July) maximum (32 ppb) and a summer (January) minimum (14 ppb), characteristic for Southern Hemispheric sites, e.g. Cape Point at SH mid latitudes.

For the months August till October ozone depletion events have been observed at both stations, however, with a higher frequency and intensity at the coastal, Neumayer site. This could possibly be attributed to the release of reactive bromine compounds from sea-salt aerosols originating from the sea-ice covered ocean. Such processes could hence explain the correspondingly lower impact observed at SANAE IV, located further inland.

Chemical composition of the PM10 aerosol at Cape Grim: contribution of carbonaceous matter

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Abstract

From August 2002 to September 2003 weekly samples of PM10 aerosol were collected at Cape Grim under baseline conditions on ultra-clean quartz fibre filters and analysed for mass, soluble ion composition, organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC). The results were used to perform a more detailed chemical mass apportionment of the aerosol than has been achieved previously. As expected, the aerosol was found to be dominated by sea-salt components, accounting for 54 ± 9% of PM10 on average. OC accounted for only 1.6 ± 1.1% of the PM10 mass, whilst EC was most often below the detection limit of 0.01 μg m^{-3}. The bulk of the remaining aerosol mass is likely to be associated with dust derived from the cliff face. WSOC was found to account for 40 ± 14% of OC, suggesting that a large portion of the organic aerosol fraction is hydrophobic in nature. The origin of much of the OC is likely to be the sea-surface micro-layer, which has been shown to be enriched in many naturally-produced organic surfactants, such as humic and fulvic acids, fatty acids, phenols, polysaccharides and proteins, as well as marine bacteria and some species of micro-algae. The evaporation of seawater droplets - ejected into the air by wind and wave action - would be expected to lead to the production of primary marine aerosol enriched in these organics relative to the amounts found in bulk seawater. In accordance with this, the ratio of OC to Na in the PM10 samples was found to be significantly higher than that of bulk seawater (ca. 10^{-1} vs. 10^{-5}). Although the absolute amounts of organic matter in the Cape Grim aerosol are very low, this material may be confined largely to the surface of the aerosol and, hence, influence the overall properties of the aerosol to a greater degree than anticipated on the basis of its mass contribution. These properties could include the light extinction efficiency, chemical reactivity, hygroscopicity and cloud droplet nucleating potential of the aerosol particles.

Atmospheric sulfur hexafluoride still on the increase

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Abstract

Sulfur hexafluoride (SF_6) has been increasing in the atmosphere at ~5% (~0.2 pmol mol^{-1}) per year over the past seven years. Although it is present at only 5 pmol mol^{-1}, its growth rate is significant because of its long lifetime (~700-3200 y) and its high global warming potential (GWP). Calculated for 20-500 year horizons, the GWP for SF_6 is 15,000 to 32,000 times that of CO_2, making it one of the strongest greenhouse gases known. Its GWP is much higher than that of any other gas evaluated in recent global assessments, including chlorofluorocarbons, hydrocarbons, and fully fluorinated species. Also because it is essentially inert in nature, SF_6 has been a useful tracer for tropospheric, stratospheric, oceanic, and groundwater studies. It derives mainly from its use in insulating high voltage electrical equipment, such as transformers and circuit breakers.

NOAA/CMDL has been monitoring SF_6 in the atmosphere since 1995. Currently, these measurements include analysis of weekly flask samples from 13 sites across the globe, as well as hourly in situ measurements from the four NOAA/CMDL baseline observatories. We also have begun to include SF_6 measurements of flasks collected weekly as part of the carbon cycle network, which represents over 50 sites globally. Finally, we have analyzed archived air from Niwot Ridge, Colorado, dating back to 1987, and we have analyzed air in firn (unconsolidated snow) from polar sites in the northern and southern hemispheres. Measurements are all calibrated to a common scale of standards prepared gravimetrically in our laboratory in Boulder, CO. This collection of measurements demonstrates that SF_6 in the atmosphere results entirely from human activities of the past century and provides a robust documentation of its global and regional distributions and trends.

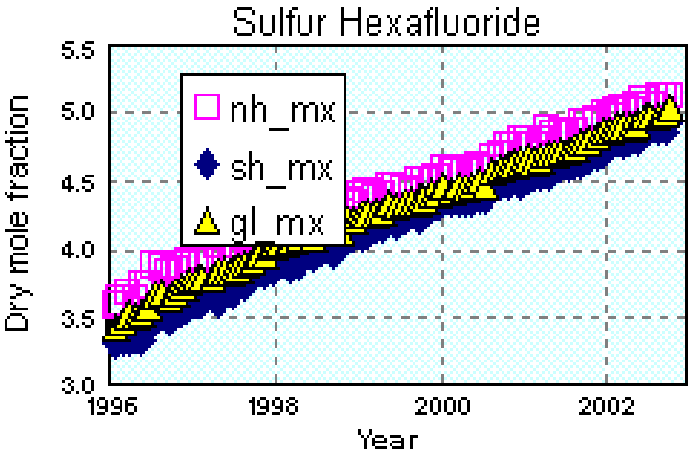


Figure 1. *Hemispheric and Global Distributions of Sulfur Hexafluoride over the past 7 years. These data are condensed from from flask measurements at 8 background stations, including the CMDL Observatories.*

Trends of halocarbons and implications for total chlorine

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Abstract

Since the early to middle 1990s, the growth rates of all major chlorofluorocarbons (CFCs) have been declining, with the exception of CFC-12 (CCl_2F_2). These chlorine-containing compounds have a variety of uses that take advantage of their inertness and low toxicity. However, their inertness has allowed these gases to survive in the atmosphere for decades, thus allowing them to be transported into the stratosphere where they play a major role in ozone destruction.

Developed countries responded to the Montreal Protocol by reducing and ultimately eliminating production of CFCs and other halogenated gases and solvents. By 1994, total atmospheric chlorine peaked and is now decreasing. Early and rapid decreases in total chlorine were a result of the swift decline of methyl chloroform (CH_3CCl_3). However, in recent years methyl chloroform's decline has slowed to its present-day global growth rate of –4.7 parts per trillion (ppt) per year. The largest CFC contributor to total chlorine, CFC-12, and the only CFC that was still increasing in the 21st century, dropped below zero growth at the end of 2002. It remains to be seen whether this negative growth will continue in 2003. As methyl chloroform's contribution to total chlorine diminishes, CFCs will be increasingly important to the steady decline of atmospheric chlorine.

The CMDL Halocarbons and other Atmospheric Trace Species (HATS) in situ programs have been monitoring the concentrations and growth rates of CFC-11 (CCl_3F), CFC-113 (CCl_2FCClF_2), CFC-12, CH_3CCl_3, carbon tetrachloride (CCl_4), and sulfur hexafluoride (SF_6) since 1987. In particular, the Chromatograph for Atmospheric Trace Species (CATS) has been making continuous hourly air measurements at the NOAA baseline sites. An update on current trends of these gases is presented.

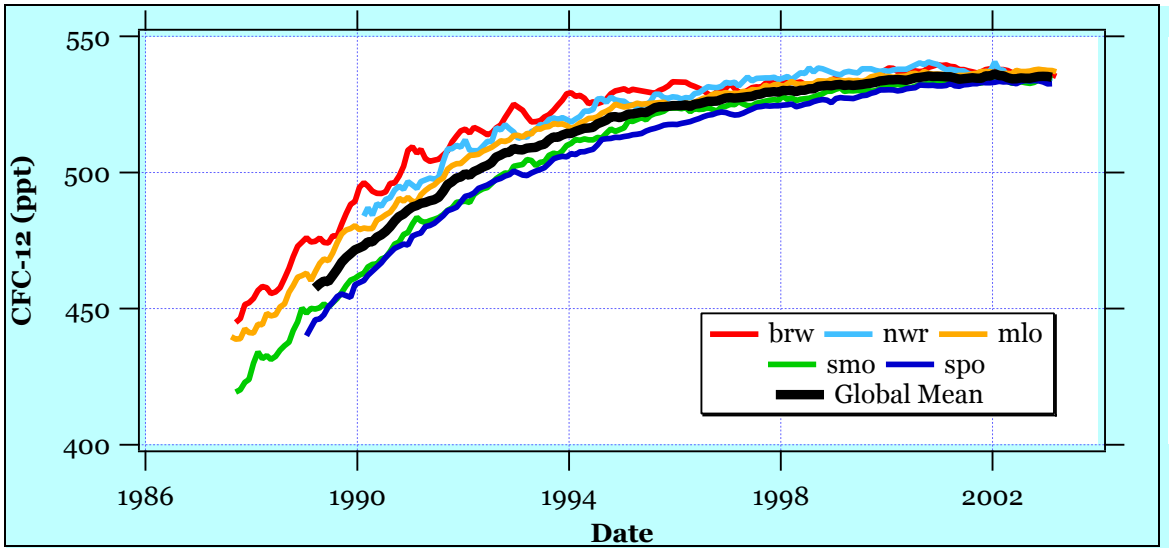


***Figure**: The* in situ *program in the CMDL/HATS group has been measuring CFC-12 since 1987. A global mean atmospheric concentration of 535 ppt, CFC-12 (CCl_2F_2) is the largest single contributor to total chlorine.*

Validating Satellite-Derived Snow Temperatures on the Antarctic Plateau

Validating satellite-derived snow temperatures on the Antarctic Plateau

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In May 2002 NASA launched Aqua, a polar-orbiting satellite equipped with an Atmospheric Infrared Sounder (AIRS) designed to measure surface and atmospheric temperatures, and humidity. AIRS will monitor these variables on a global scale, but must first be validated using "groundtruth" data collected at a number of representative locations. One location, on the Antarctic Plateau, was chosen because intervening atmospheric effects are minimal there; water vapor and aerosol content are extremely low, and the surface is flat and uniform. Dome Concordia (3280 m, 75ºS), a station operated under the Italian and French Antarctic programs, was selected as an ideal site because it offered excellent logistical support for the first campaign (January 2003).

The experiment involved making precise surface temperature measurements using the University of Idaho Polar Atmospheric Emitted Radiance Interferometer (PAERI) in conjunction with a mobile observatory deployed by CMDL. The AIRS Mobile Observing System (AMOS) platform consists of a suite of radiometers mounted on a sled that was pulled behind a snowmobile (Figure 1, left). Transects were run around triangular tracks several kilometers in length at times coincident with overpasses of Aqua and the operation of the tower-mounted PAERI. At a 1-second sampling rate, AMOS is able to map the detailed thermal and reflective properties of the snow surface on a spatial scale that approximates the AIRS field of view. After cross-calibrating the AMOS infrared thermometer and the PAERI, integrations of the transect data produce accurate estimates of pixel-scale surface temperatures for validation purposes.

Preliminary results demonstrate the validity of this approach. Examples of data are presented. One fascinating result is illustrated in the Figure 1 (right), which shows how snow temperatures vary, in this instance >2°C, over distances of <10 m. This is due to heating/cooling effects that result when the sun differentially illuminates snow features called sastrugi. Uncertainties in AIRS retrievals that may result because of those effects will be further investigated during the 2003-2004 campaign at Dome C.

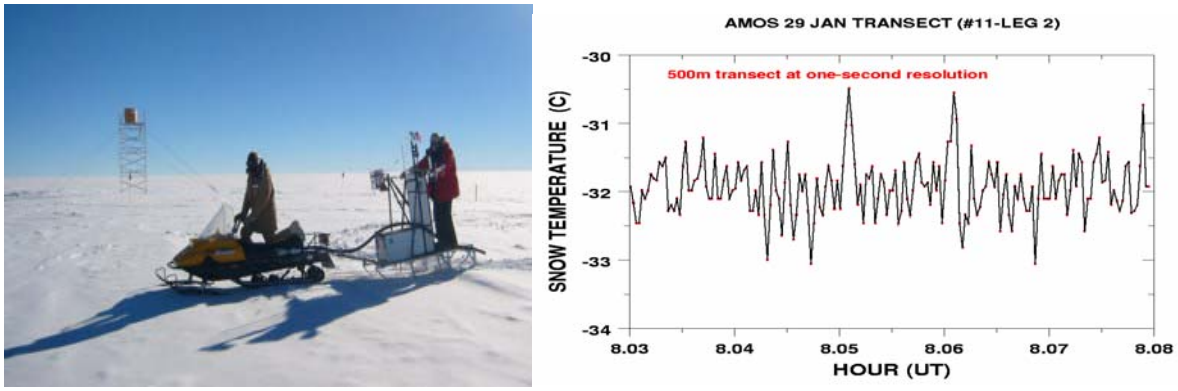


Figure 1. *Left*: *AMOS being towed around a track by snowmobile at times coincident with Aqua overpasses. The PAERI is mounted on the tower behind. Right: Time series of 1-s resolved snow temperatures along 500 m of the track run by AMOS on January 29, 2003.*

Aerosol model development using trajectory clustering

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Abstract

The uncertainties associated with assumptions of generic aerosol properties in radiative transfer codes are unknown, which means that these uncertainties are frequently invoked when models and measurements do not agree. In general, the radiative calculations require specification of the aerosol optical depth $\delta(\lambda)$, single-scattering albedo $\varpi_o(\lambda)$, and asymmetry parameter $g(\lambda)$, all as functions of wavelength λ and altitude. Here we use existing aerosol data from the ARM SGP and NSA sites to begin development of a set of 'models' that describe the radiative properties of different types of aerosols at these sites

Aerosol properties at SGP and NSA show considerable variability on multiple time scales (Delene and Ogren, 2001). Our hypothesis is that this variability is not random, but rather is connected with changes in the types of particles prevailing at any given time. We anticipate that airmass origin will be the dominant meteorological parameter influencing the aerosol type. Here, we segregate surface aerosol properties at SGP and NSA as a function of airmass back trajectory to provide a first cut at identifying aerosol types prevalent at these two sites.

Significant differences are evident in some but not all aerosol optical properties for the trajectory clusters at the two sites. Aerosol loading, as indicated by extinction coefficient, varies by a factor of two among trajectory clusters. The variation in extinction is consistent with airmass source regions. Aerosol chemistry measurements at SGP and NSA allow further characterization both among all trajectory clusters and between similar loaded trajectory clusters. Surprisingly, despite different source regions and trajectory paths, the aerosol ϖ_o does not appear to depend strongly on trajectory for either site. This preliminary analysis illustrates the utility of including airmass trajectory in the statistical evaluation of aerosol types, but also demonstrates that airmass trajectory alone may not be adequate for choosing an aerosol type.

Reference

Delene D.J., and J.A. Ogren, 2002: Variability of aerosol optical properties at four North American surface monitoring sites. *J. Atmos. Sci*., 59, 1135-1150.

Asian dust signatures at Barrow: observed and simulated

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Abstract

Atmospheric aerosols affect the Earth's radiation budget both directly through interactions with solar and terrestrial radiation and indirectly as cloud condensation and ice nuclei. Because polar atmospheres are generally very clean, small increases in aerosol concentrations can perturb radiative fluxes significantly. During spring 2002, dust storms from the deserts of China and Mongolia were tracked over the Arctic, suggesting that such remote regions are not immune to the dispersion of Asian dust. Corroborating evidence for transport of dust to the Arctic is provided by increased aerosol optical depths and lidar measurements at Barrow, Alaska in conjunction with trajectory analyses and dust transport. Here, a variety of measurements and model results are employed to characterize the radiative properties associated with a dust layer for a particular occurrence during the first half of April 2002.

Surface measurements of aerosol optical properties during this time period show several periods when the aerosol Ångström exponent dips below 1.0, suggesting the presence of enhanced amounts of large aerosol particles. (For comparison, the 25 year median value of the Ångström exponent at Barrow is ~1.8 during April.) Increased aerosol optical depths, lidar measurements, trajectory analyses and dust transport models provide corroborating evidence that these are dust events emanating from Asia.

Using Barrow spectral aerosol optical depth measurements the size distribution of the dust layer was inferred; Mie scattering theory was used to determine the optical properties of the dust and these were then used to initialize a radiative transfer algorithm (MODTRAN4). A set of MODTRAN-based capabilities have recently been developed to address energy deposition within the lower atmosphere and are used to generate flux profiles of heating and cooling in both the solar and thermal spectral regimes. From this combination of measurements and MODTRAN outputs, an energy budget for the dust event has been produced, providing estimates of the direct radiative forcing associated with Asian dust intrusions. Analytic calculations of the surface forcing as a function of aerosol optical depth (AOD) are compared with empirical results obtained using a suite of radiometers at Barrow.

LACE and PANTHER GC-ECD and GC-MSD airborne instruments

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Abstract

We show photos of the LACE and PANTHER airborne gas chromatograph instruments which have taken data from the upper troposphere to as high as 32 km in the tropics, the mid-latitudes, and the northern vortex. Representative data is shown which has been used to estimate the following transport and chemistry: 1- Ascent and entrainment rates in the tropical stratosphere, 2- Strat-trop exchange in the lowermost stratosphere, 3- Vortex dynamics including descent, mixing, and isolation from the mid-latitudes, 4- Stratospheric mean age in the mid-latitude and tropics, 5- The SF_6 atmospheric lifetime, 6- Stratospheric 'maximum path height' distributions, and 7- The partitioning and distribution stratospheric Cl and Br.

Measured SF_6 loss and its influence on age of air calculations

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Abstract

In situ measurements from the Lightweight Airborne Chromatograph Experiment (LACE) inside the northern vortex taken during the SOLVE campaign show air with very low mixing ratios of SF_6. Elevated CO and H_2 mixing ratios indicate that this air had originated primarily in the mesosphere, where SF_6 is believed to undergo photochemical destruction. Age of air estimates using SF_6 measured in the vortex are several years older near 32 km altitude than age of air estimates using CO_2. This age difference combined with the mesospheric source of the vortex air indicates loss of SF_6 had occurred in the sampled vortex air. Based on the observed loss of SF_6 and a simple model of the vortex in each hemisphere an estimate is made of the effect the loss has on age of air estimates using SF_6 in the rest of the stratosphere. The effect is shown to be small but measurable due to the relatively small amount of mass of the air which contains depleted SF_6 compared to the mass of the entire stratosphere. The observed loss is also used to calculate the atmospheric lifetime of SF_6.

Emissions of ozone-depleting substances in the trans-Siberian railway corridor during summer 2001

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Abstract

The atmospheric loading of ozone-depleting halogens is currently in decline because of large reductions in the global production and emissions of ozone-depleting substances (ODSs) during the 1990s. The bulk of production abatement occurred prior to January 1, 1996, the Montreal Protocol-requisite deadline for chlorofluorocarbon (CFC) manufacture in developed countries. Despite these reductions, considerable emissions of many ODSs continue today and will likely persist for several decades in transitional nations, and in Article 5 (developing) countries where production is allowed until 2010-2015. Estimates of the magnitudes of these current and impending emissions are central to projections of the stratospheric ozone layer recovery during this century.

The Russian Federation, a non-Article 5 country and producer of approximately 10% of the world's CFCs and halons during 1989-1995, continued to manufacture these chemicals until the end of 2000 with allowances from the Protocol as a transitional nation. Russian ODS emission estimates for years prior to 1986 are based on pure conjecture because manufacturing companies never disclosed production figures. Since 1986, Russia has reported ozone-depletion potential (ODP)-weighted, aggregated production figures in accordance with the Protocol, but these are not audited for accuracy and require speculative apportionment into production estimates for individual compounds. Consequently, even production-based estimates of more recent Russian ODS emissions carry large uncertainties.

During summer 2001, we made thousands of measurements of 6 different ODSs along 17,000 km of the Russian trans-Siberian railway with the intention of estimating the magnitudes of their emissions in the rail corridor. This work was part of the seventh Trans-Siberian Observations Into the Chemistry of the Atmosphere (TROICA-7) expedition, a collaboration between Russian, German, and American scientists. Our measurements reveal strong emissions of CFC-12 (CCl_2F_2), weaker but globally significant emissions of halon-1211 ($CBrClF_2$) and CFC-113 (CCl_2FCClF_2), and globally negligible emissions of CFC-11 (CCl_3F), carbon tetrachloride (CCl_4), and methyl chloroform (CH_3CCl_3). Given that 25% of contemporary CCl_4 emissions occur during the manufacture of CFC-11 and CFC-12, our observations of only weak CCl_4 emissions in mid-2001 corroborate the reported shutdown of Russian CFC production in 2000. In light of modern global emissions estimates for CFC-11, CFC-113, and halon-1211 that are inadequate to account for their measured atmospheric burdens, Russian emissions of these ODSs in 2001 were too weak to play a major role in their recent emission shortfalls.

Development of new calibration scales for CH_3Br and CH_3Cl

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Abstract

Atmospheric and oceanic mixing ratios of CH_3Br and CH_3Cl have been measured by CMDL since 1994. Efforts to develop calibration scales for these molecules began in 1993. Two gravimetrically-prepared standards served as the basis for the calibration scales from 1994 to 2001. During that time, it was discovered that CH_3Br and CH_3Cl mixing ratios can change with time in Aculife-treated aluminum cylinders, particularly at ppt-levels. Efforts to improve the scales by preparing new standards in both Aculife-treated aluminum and stainless steel cylinders have recently been made. New standards were used to confirm that mixing ratios of CH_3Br in some of the original standards had changed with time. They also showed that one of the CH_3Br primary standards did not drift, and agrees well with the new primary standards. The scale change implies that CH_3Br measurements made during the mid-1990s and used to infer the CH_3Br budget were overestimated by 4-5%. CH_3Br sinks derived from these measurements were overestimated by similar amounts. It is anticipated that stable, robust scales can be maintained by periodically preparing new standards in stainless steel cylinders from various primary standards and by continuing to monitor the relative differences between standards.