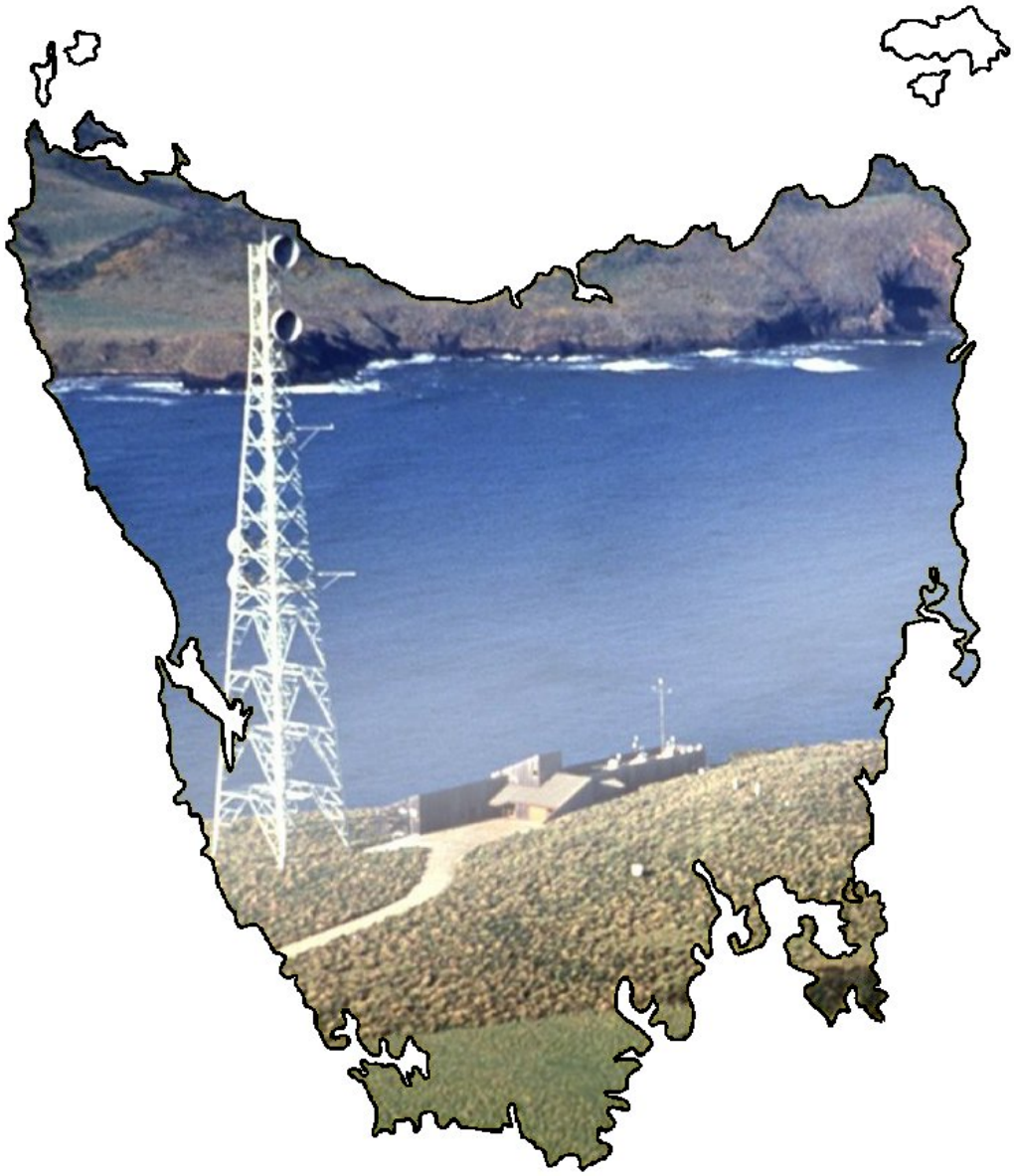
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Cape Grim Baseline Air Pollution Station
Annual Science Meeting 2005

ABSTRACTS



Edited by
Jill Cainey & Nada Derek

CSIRO Marine and Atmospheric Research
Aspendale, Victoria
8 – 9 December 2005

Cape Grim Baseline Air Pollution Station
Annual Science Meeting 2005

Thursday, 8th December		
Chair	***Jill Cainey***	
09:00	Convenors	General information on arrangements etc.
09:10	Greg Ayers	Welcome and opening of meeting
09:20	Roger Francey	Verification of global trends in atmospheric carbon dioxide stable isotopes
09:45	David Griffith	TCCON - the Total Carbon Column Observing Network
10:10	Ray Langenfelds	The effect of systematic measurement errors on atmospheric CO_2 inversions
10:35	**Morning Tea**	**Provided**
11:00	Rachel Law	The TransCom continuous experiment: Assessing model transport error at Cape Grim
11:25	Patrick Sturm	Fractionation at the air intake: Relevant to CO_2 measurements?
11:50	Colin Allison	Estimating emissions of HFC-134a and CFC-12 from the Melbourne transport fleet (2003-2005) based on observations in the Domain Tunnel
12:15	Paul Fraser	Past and future radiative forcing by long-lived greenhouse gases
12:40	**Lunch**	**Own Arrangements**
13:30	Michael Grose	Biogenic production of methyl halides by phytoplankton in Tasmanian Coastal waters – field measurements and culture experiments
13:55	Laurie Porter	Sources and sinks of methane, nitrous oxide, hydrogen and carbon monoxide from flux chamber experiments near Cape Grim, Tasmania
14:20	Paul Steele	Atmospheric carbon monoxide – measurement and calibration challenges
14:45	Cathy Trudinger	HFCs in Antarctic firn and the Cape Grim air archive
15:10	**Afternoon Tea**	**Provided**
15:40	Allen Goldstein	Chemical characteristics of North American outflow: Insights from Chebogue Point, Nova Scotia
16:05	Paul Krummel	AGAGE observations at Mt St Leonard
16:30	Stephen Wilson	Temperature effects on UV-B spectra measured at Cape Grim BAPS
16:55	Andrew Kleckociuk	Variability of ozone above Davis, Antarctica
17:20	**Close of Papers**	
17:30	**Poster Wine and Cheese Evening**	**CSIRO Marine and Atmospheric Research Canteen**
19:30	**Meeting Dinner**	**Comocean, 196 Como Parade West, Parkdale**

Cape Grim Baseline Air Pollution Station
Annual Science Meeting, 2005

Friday, 9th December		
Chair	***Jill Cainey***	
09:00	Convenors / Hosts	
09:10	John Gras	Post-frontal nano-particle enhancement at Cape Grim – is it important?
09:35	Melita Keywood	The influence of the baseline event switches on PM10 at Cape Grim
10:00	Kevin Rosman	Highly radiogenic lead in Southern Ocean aerosol and Antarctic snow
10:25	Wlodek Zahorowski	Radon observations in the Cape Grim mainland sector in 2001- 2004
10:50	**Morning Tea**	**Provided**
11:20	Rob Gillett	Comparison of formaldehyde and peroxide concentrations in baseline and urban air
11:45	David Etheridge	The use of baseline atmospheric composition data to verify geological storage of CO_2
12:10	David Worton	20th Century trends and budget implications of trihalomethanes and dihalomethanes inferred from North GRIP firn air
12:35	**Lunch**	**Own Arrangements**
13:30	Chair: Jill Cainey	Priority Science Goals Workshop
15:30	**Close of Meeting**	

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VERIFICATION OF GLOBAL TRENDS IN ATMOSPHERIC CARBON DIOXIDE STABLE ISOTOPES

Roger J. Francey* and Colin E. Allison

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Abstract

Understanding variations in atmospheric greenhouse gases on decal timescales is increasingly important in assessing the effectiveness of international efforts to reduce emissions resulting from human activities. However, maintaining calibration of the carbon dioxide (CO_2) stable isotope measurements ($\delta^{13}C$ and $\delta^{18}O$) over decadal timescales is non-trivial. In this paper we describe the detailed comparison of the two relatively independent CMAR Cape Grim CO_2 stable isotope programs over the period 1991 through 2004 to test the effectiveness of the process-based corrections and assignments we use. The resulting agreement between the two Cape Grim records, expressed as the average difference between running 90-day averages (to the smooth curves) over 14 years of data, of 0.005 ‰ ± 0.020 ‰ in $\delta^{13}C$ indicates that we have described and accounted for the main inherent sources of bias in the carbon isotope measurement. For $\delta^{18}O$ the differences are 0.024 ‰ ± 0.184 ‰, but flask storage and early standard assignment problems contribute to the large variation.

We have applied the process-based corrections and assignments to measurements made prior to 1992 and present an averaged Cape Grim record of $\delta^{13}C$ and $\delta^{18}O$ spanning more than two decades with precise error estimates for use in inversion analyses.

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TCCON - THE TOTAL CARBON COLUMN OBSERVING NETWORK

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Abstract

TCCON is a growing network of ground-based solar infrared remote sensing stations optimised to measure total column CO_2 with high precision and accuracy. The original drive for the TCCON stations comes from the need for ground validation of the Orbiting Carbon Observatory (OCO) satellite, but the network has meanwhile developed its own identity. TCCON measurements of CO_2 and O_2 (for normalisation) are made in the same near IR spectral bands as used by OCO, which is scheduled for launch in 2008. TCCON spectra can also be analysed for CH_4, N_2O and CO.

TCCON sites are currently in Ny Alesund Spitzbergen, Bremen Germany (PI Justus Notholt, Uni Bremen), Park Falls Wisconsin (Paul Wennberg, CalTech), Darwin Australia, and Lauder NZ (Brian Connor, NIWA). We operate the Darwin site, which was installed in August 2005. Wollongong will be added with a new ARC- funded FT-spectrometer in 2006.

We will describe the measurement protocols, first results, supplementary *in situ* measurement programmes proposed at Darwin and on the Ghan railway, and relationship to OCO and inverse modelling of sources and sinks of atmospheric CO_2 and other gases.

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THE EFFECT OF SYSTEMATIC MEASUREMENT ERRORS ON ATMOSPHERIC CO_2 INVERSIONS

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[3]CSIRO Marine and Atmospheric Research, Aspendale, Australia

Abstract

Estimates of surface-atmosphere CO_2 fluxes obtained by inverse modeling are subject to various sources of modeling and experimental error, both of which can be difficult to quantify. The two largest global atmospheric CO_2 measurement networks are operated by NOAA/CMDL and CSIRO. Both networks incorporate parallel, intra-laboratory measurements by different techniques at selected sites, and the two laboratories have additionally maintained a flask intercomparison program since 1991. The Cape Grim station has played a central role in these activities. Information gathered from these programs provides a basis for estimating experimental uncertainty, and its impact on CO_2 fluxes obtained using atmospheric inversions. We show that the magnitude and variability of inferred flux errors are generally small by comparison to the flux signals, and to errors introduced by the modeling technique.

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THE TRANSCOM CONTINUOUS EXPERIMENT: ASSESSING MODEL TRANSPORT ERROR AT CAPE GRIM

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Abstract

Over the last decade there have been a series of TransCom experiments focused around the assessment of transport model error in the context of CO_2 flux estimation from atmospheric concentration measurements. The early work comprised simple forward simulations (Law *et al*., 1996; Denning *et al*., 1999) while the more recent experiments have involved CO2 inversions at different time-scales (Gurney *et al*., 2002; Gurney *et al*., 2004; Baker *et al*., 2005). In each case the model output was used only at monthly timescales. Currently there is increasing interest in using continuous CO_2 data, particularly non-baseline data, in inversions. It is therefore important that we have a good understanding of transport model behaviour at diurnal and synoptic timescales. The present TransCom experiment is designed to do this. The experiment is currently in progress. A set of prescribed surface fluxes is input to the transport model and hourly concentration output are stored for a range of monitoring locations including Cape Grim. The model data are collected for 2002 and 2003. The talk will describe the experiment, the input flux fields and the available output data. We will highlight which locations in the Australian region are being sampled and will present some preliminary results for Cape Grim. Complete model submissions are due by the end of this year, after which the model data can be made available for collaborative analysis.

References

D. F. Baker, R. M. Law, K. R. Gurney, P. Rayner, P. Peylin, A. S. Denning, P. Bousquet, L. Bruhwiler, Y.-H. Chen, P. Ciais, I. Y. Fung, M. Heimann, J. John, T. Maki, S. Maksyutov, K. Masarie, M. Prather, B. Pak, S. Taguchi, and Z. Zhu. TransCom 3 inversion intercomparison: Impact of transport model errors on the interannual variability of regional CO_2 fluxes, 1988–2003. *Global Biogeochemical Cycles*, in press, 2005.

Denning, A. S., M. Holzer, K. R. Gurney, M. Heimann, R. M. Law, P. J. Rayner, I. Y. Fung, S. M. Fan, S. Taguchi, P. Friedlingstein, Y. Balkanski, J. Taylor, M. Maiss, and I. Levin. Three-Dimensional Transport and Concentration of SF_6: A Model Intercomparison Study (TransCom 2). *Tellus*, 51B, 266-297,1999.

Gurney, K. R., R. M. Law, A. S. Denning, P. J. Rayner, D. Baker, P. Bousquet, L. Bruhwiler, Y. H. Chen, P. Ciais, S. Fan, I. Y. Fung, M. Gloor, M. Heimann, K. Higuchi, J. John, T. Maki, S. Maksyutov, K. Masarie, P. Peylin, M. Prather, B. C. Pak, J. Randerson, J. Sarmiento, S. Taguchi, T. Takahashi, and C. W. Yuen. Towards robust regional estimates of CO_2 sources and sinks using atmospheric transport models. *Nature*, 415, 626-630, 2002.

Gurney, K. R., R. M. Law, A. S. Denning, P. J. Rayner, B. C. Pak, D. Baker, P. Bousquet, L. Bruhwiler, Y.-H. Chen, P. Ciais, I. Y. Fung, M. Heimann, J. John, T. Maki, S. Maksyutov, P. Peylin, M. Prather, and S. Taguchi. Transcom 3 inversion intercomparison: Model mean results for the estimation of seasonal carbon sources and sinks. *Global Biogeochemical Cycles*, 18, GB1010, doi:10.1029/2003GB002111, 2004.

Law, R. M., P. J. Rayner, A. S. Denning, D. Erickson, I. Y. Fung, M. Heimann, S. C. Piper, M. Ramonet, S. Taguchi, J. A. Taylor, C. M. Trudinger, and I. G. Watterson: Variations in modelled atmospheric transport of carbon dioxide and the consequences for CO_2 inversions. *Global Biogeochemical Cycles*, 10, 783-796, 1996.

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FRACTIONATION AT THE AIR INTAKE: RELEVANT TO CO_2 MEASUREMENTS?

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Abstract

The atmospheric Ar/N_2 ratio, measured by mass spectrometry, is a useful tracer to reveal fractionation effects, because no biogeochemical processes influence these inert gases on diurnal timescales. Surprisingly, Ar/N_2 measurements of atmospheric air continuously drawn through an intake tube showed a large diurnal variability (up to 100 per meg) which could be attributed to temperature variations at the intake that lead to diffusive fractionation of the sample air. Understanding and quantification of such artefacts is particularly relevant to high precision measurements of atmospheric O_2, because this effect is in the same order of magnitude as the real atmospheric O_2 variations. But it might also be detectable with LoFlo CO_2 measurements. Changes of about 100 per meg in Ar/N_2 would correspond to 0.03 ppm in CO_2 mole fraction.

An explanation of this effect is that during the day, particularly when the sun heats the intake tube, there builds up a small temperature gradient between the tube and the surrounding air. This leads to thermal diffusion with preferential accumulation of the lighter molecules in regions with higher temperatures. The isotopic ratios $\delta^{29}N_2$, $\delta^{34}O_2$ and $\delta^{36}Ar$ showed also small variations that are correlated with the temperature, providing compelling evidence of diffusive fractionation.

To assess the causes of the observed Ar/N_2 variations and to better quantify this effect, we conducted tests with different intake tubes and sampling flows. The temperature sensitivity of Ar/N_2 mainly depends on the gas velocity at the air intake. Experiments also showed that thermal fractionation at the intake is larger for black coated Dekabon tubing compared to intakes made of transparent plastic or stainless steel. A new air intake system where the intake orifice is shielded from solar radiation by a larger diameter tube and where a high flow rate of ambient air is drawn through the larger diameter tube may be most helpful for reducing thermal diffusion at the intake.

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ESTIMATING EMISSIONS OF HFC-134A AND CFC-12 FROM THE MELBOURNE TRANSPORT FLEET (2003-2005) BASED ON OBSERVATIONS IN THE DOMAIN TUNNEL

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Abstract

Automobile road tunnels have been used to derive integrated traffic emissions, emissions trends and emission factors for non-methane hydrocarbons and particles [Kristensson *et al*., 2004; Stemmler *et al*., 2005] and automotive refrigerants [Stemmler *et al*., 2004]. The Domain Tunnel in Melbourne is an ideal laboratory to study emissions from the Melbourne road transport fleet; outside-air flows into the tunnel at all times via the traffic exit/entry portals and is removed from the tunnel at measured rates through one exhaust stack. By analysing the air entering the tunnel and exiting via the exhaust stack, an integrated picture of vehicular emissions can be obtained.

Air samples were collected outside the Domain Tunnel and inside the exhaust stack ventilation shaft in 2003 (June 4 and July 31) and in 2005 (monthly except February) and analysed on the ADS GCMS system previously installed at Cape Grim as part of the AGAGE program and now located at CMAR, Aspendale. We present results from the analysis of the collected air samples and estimated emission factors for the refrigerants CFC-12 and HFC-134a from the transport fleet in Melbourne.

Reference

Kristensson, A., C. Johansson, R. Westerholm, E. Swietlicki, L. Gidhagen, U. Wideqvist and V. Vesely, Real-world traffic emission factors of gases and particles measured in a road tunnel in Stockholm, Sweden, Atmospheric Environment, 38, 657-673 (2004).

Stemmler, K., S. O'Doherty, B. Buchmann and S. Reimann, Emissions of the refrigerants HFC-134a, HCFC-22 and CFC-12 from road traffic: results from a tunnel study (Gubrist Tunnel, Switzerland), Environ. Sci. Technol., 38, 1998-2004 (2004).

Stemmler, K., S. Bugmann, B. Buchmann, S. Reimann and J. Staehelin, Large decrease of VOC emissions of Switzerland's car fleet during the past decade: results from a highway tunnel study, Atmospheric Environment, 39, 1009-1018 (2005).

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PAST AND FUTURE RADIATIVE FORCING BY LONG-LIVED GREENHOUSE GASES

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Abstract

Long-term measurements of long-lived greenhouse gases (CO_2, CH_4, N_2O, CFCs and other Montreal Protocol gases, natural chlorocarbons, HFCs, PFCs and SF_6) at Cape Grim and CSIRO GASLAB, from Cape Grim *in situ*, Cape Grim air archive and Antarctic firn air samples, has resulted in a unique record of the increase in greenhouse gases in the Southern Hemisphere over the past 2000 years.

The corresponding long-term record of radiative forcing from these greenhouse gases can be derived (Figure 1), using the simplified expressions for radiative forcing in the IPCC Third Assessment Report (Table 6.2, p. 358; Ramaswamy *et al*., 2001). The growth rate of radiative forcing reached a maximum in the 1980s and has since declined, largely due to the near-zero growth of CH_4 and Montreal Protocol gases over the past 5-10 years.

Radiative forcing scenarios (2000-2100) (IPCC TAR, Appendix II, 2001) have been published and when coupled to the radiative forcing records derived from atmospheric observations, they present a picture of the likely climatic impact of greenhouse gases, past and future. Some IPCC radiative forcing scenarios (for example CH_4) may be unrealistic, at least over the next 20 years, based on the past decade of observations.

The stable greenhouse gases are a major component of the radiative forcing picture, especially in the Southern Hemisphere. Nevertheless there are significant contributions to radiative forcing from aerosols and ozone (tropospheric and stratospheric) variations. The likely magnitude of these radiative forcing agents in the Southern Hemisphere will be assessed.

Reference

Ramaswamy, V., O. Boucher, J. Haigh, D. Hauglustaine, J. Haywood, G. Myhre, T. Nakajima, G. Shi and S. Solomon, Radiative Forcing of Climate Change, Chapter 6 in: Climate Change 2001: the Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, J. Houghton et al. (eds.), Cambridge University Press, Cambridge UK and New York, NY, USA, 349-416.

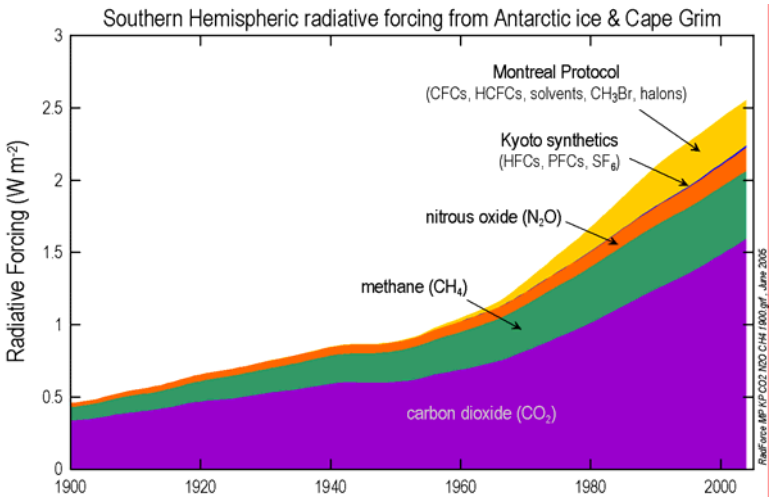


Figure 1. Changes in the Southern Hemisphere radiative forcing (Wm^{-2}) since 1750 based on greenhouse gas observations on ambient air samples at Cape Grim, from the Cape Grim air archive and from Antarctic firn.

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BIOGENIC PRODUCTION OF METHYL HALIDES BY PHYTOPLANKTON IN TASMANIAN COASTAL WATERS – FIELD MEASUREMENTS AND CULTURE EXPERIMENTS.

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Abstract

Methyl halides (methyl bromide, methyl iodide) produced biologically by phytoplankton in the ocean are important carriers of active forms of iodine and bromine to the atmosphere. In the atmosphere, these ions play important roles in ozone destruction, and iodated species have been suggested as initiators of new particle formation in the marine boundary layer. However, the characteristics of production of methyl halides are poorly understood. There has been an ongoing program investigating the production of methyl halides in coastal waters at Cape Grim and the surrounding area. Presented here is an update of the latest findings from field measurements and lab experiments, as well as future plans for the coming year.

Field data on the physical conditions, phytoplankton ecology and methyl halide production in the water column taken from a field site at Couta Rocks in 2003-04 are presented, with comments on seasonal patterns. Results from summer fieldwork are also presented, including transects performed at Woolnorth Point sampling from inshore out to 5 km offshore and measurements taken over 24 hours at Stanley. These measurements indicate significant spatial and temporal changes of methyl halide production, and methyl iodide production appears to be strongly influenced by kelp beds and tidal movement. Also, the methylation pathway within the phytoplankton cell was investigated in a phytoplankton culture flask experiment. Production of methyl halides was measured from Phaeocystis sp. under the influence of several biochemical inhibitors. Whilst not conclusive, the results indicate that these inhibitors did not have an effect, and the inferences about the biochemistry are discussed. Other experiments performed on phytoplankton communities in 'mini-cosm' chambers are also outlined. Future work for the coming year is outlined, including ongoing field measurements, work for the February field campaign and measurements to be taken aboard the Southern Surveyor cruise to Fremantle in March/April 2006.

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SOURCES AND SINKS OF METHANE, NITROUS OXIDE, HYDROGEN AND CARBON MONOXIDE FROM FLUX CHAMBER EXPERIMENTS NEAR CAPE GRIM, TASMANIA

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Abstract

Methane (CH_4), nitrous (N_2O), hydrogen (H_2) and carbon monoxide (CO) are trace gases with both biogenic and anthropogenic sources that are continuously monitored at the Cape Grim Baseline Air Pollution Station (CGBAPS). Methane and N_2O are significant greenhouse gases and H2 and CO are produced during the atmospheric oxidation of CH_4 and non-methane hydrocarbons. The identification and quantification of local soil sources and sinks provides useful information for the evaluation and interpretation of the Cape Grim measurements and can contribute to the understanding of regional budgets for these important species.

A series of flux chamber experiments were conducted from 1999 to 2002 at five sites within 20 km of CGBAPS, representing the major local vegetation communities. The 1999 to mid-2001 data and the flux chamber techniques are described in Cox (2001) and Cox *et al*., (2004).

The three sites chosen near CGBAPS were: (#1) improved farmland pasture (perennial ryegrass), (#2) soil and leaf litter under melaleuca scrub canopy and (#3) native tussock grass. The two other sites, located within 20km SE of CGBAPS, were: (#4) soil and leaf litter under the eucalypt dominated forest canopy near the Welcome River and (#5) beaded glasswort succulent vegetation of the coastal wetlands salt marsh at Robbins Crossing. The fluxes of CH_4, N_2O, H_2 and CO were measured at all sites throughout the period of the experiment.

The trace gas sources and sinks near CGBAPS are described, and quantification of the fluxes and their seasonalities are discussed.

For CH_4, sinks (loss of atmospheric CH_4 to the soil) was observed at most sites, with highest uptakes observed in the summer months.

For N_2O, fluxes ranged from negative (soil sink) to positive (emission to the atmosphere) values at all sites. The tendency was for soil sources in winter/spring and sinks in summer/autumn. The highest positive fluxes were observed at the improved pasture site.

For H_2, negative fluxes were observed at all sites, except the coastal wetlands where the tendency was for small sources to be observed. The soil sinks were largest at the dry soil sites during the summer months.

The largest CO sources were observed at the grass sites (pasture and tussock) and the coastal wetlands, with a tendency at all sites for maximum emissions in the summer months and uptakes in winter.

References

Cox, M, A regional study of the natural and anthropogenic sources and sinks of the major halomethanes, *PhD thesis*, School of Mathematical Sciences, Monash University, Melbourne, Australia 2001.

Cox, M., P. Fraser, G. Sturrock, S. Siems and L. Porter, Terrestrial sources and sinks of halomethanes near Cape Grim, Tasmania. *Atmospheric Environment*, 38 (23), 3839-3852, 2004.

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ATMOSPHERIC CARBON MONOXIDE – MEASUREMENT AND CALIBRATION CHALLENGES

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Abstract

Carbon monoxide (CO) is a key species in the chemistry of the Earth's atmosphere, responsible for removal of over half the concentration of hydroxyl radicals in the troposphere. CO is also recognised as an indirect greenhouse gas, because its influence on the hydroxyl radical can lead to an influence on the atmospheric lifetime of direct greenhouse gases such as methane.

Measurement of atmospheric carbon monoxide has presented some particular challenges. One of these is associated with the relatively large range of CO mixing ratios encountered in the troposphere. Under baseline conditions, CO in the extra tropical Southern Hemisphere varies seasonally from 30-75 ppb, while at high northern latitudes the seasonal variation is typically 75-200 ppb. Many remote sites also experience large positive excursions in CO mixing ratios (up to about 600 ppb), due to emissions of CO from biomass burning or from large urban/industrial centres. The range of CO mixing ratios requiring measurement is thus about 20. By contrast, the range of CH_4 mixing ratios experienced in such locations and conditions is less than a factor of two.

One approach to this particular challenge is to measure CO with different techniques, over a suitably wide range of CO mixing ratios. Such an experiment has been carried out at CSIRO Marine and Atmospheric Research, where three techniques were compared. The techniques were gas chromatography with a heated mercuric oxide detector, Fourier Transform InfraRed (FTIR) spectrospscopy, and vacuum ultraviolet fluorescence (the AeroLaser 5001 instrument). Results of the experiment will be presented.

Preliminary results will also be shown from experiments carried out to understand and quantify the production of CO in stainless steel cylinders.

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HFCS IN ANTARCTIC FIRN AND THE CAPE GRIM AIR ARCHIVE

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Abstract

Hydrofluorocarbons (HFCs) are being used as replacements for CFCs and HCFCs, for example in air conditioning, refrigeration, foam plastics and aerosol cans, because they do not damage the ozone layer. However, they are relatively potent greenhouses gases, and their concentrations are growing rapidly in the atmosphere. We will discuss measurements of HFC-134a, HFC-152a and HFC-125 in Antarctic firn air and the Cape Grim air archive to infer atmospheric histories for these gases. We will then use a 2-box atmospheric model to investigate their budgets, including comparison with estimates of their emissions.

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CHEMICAL CHARACTERISTICS OF NORTH AMERICAN OUTFLOW: INSIGHTS FROM CHEBOGUE POINT, NOVA SCOTIA

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Abstract

We present trace gas, particle and meteorological measurements from southern Nova Scotia during the summer of 2004, and use them to quantify the impact of U.S. pollution outflow and other sources on atmospheric composition at the site. In addition, we explore trends in regional trace gas concentrations over the past decade using historical data from Chebogue Point and Sable Island. The different sources controlling the composition of air arriving at Chebogue Point are identified and characterized using a factor analysis approach. The most important of these were U.S. outflow, local combustion, and biogenic emissions. Average levels of carbon monoxide and ozone in air coming from the eastern seaboard of the U.S. were 30 ppb and 20 ppb higher, respectively, than the average from other sectors. Total aerosol loading was higher by more than a factor of three during periods of U.S. outflow. Organic matter made up the highest proportion of the total aerosol mass during periods of primary and secondary biogenic influence, suggesting the importance of biogenic secondary organic aerosol.

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AGAGE OBSERVATIONS AT MT ST LEONARD

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Abstract

Regional pollution episodes observed in AGAGE data at Cape Grim have been used to estimate annual emissions (1994-2004) 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 commenced at Mt St Leonard (1100 m, 37.57°S, 145.53°E, 65 km north east of Melbourne CBD), at the head of the Yarra Valley, in June 2003. The site has a secure 30 m Telstra tower/Melbourne Water fire tower and a 10 m public-access observation tower. Public vehicular access to the site is restricted by a locked gate, 2 km north of the towers. Sampling is conducted from the observation tower and the samples have been analysed at Cape Grim on the AGAGE instruments. The initial Mt St Leonards results were presented at the Cape Grim Annual Science Meeting in 2003. This talk will present updated results from this sampling program and will compare these data to corresponding Cape Grim data under baseline conditions. The results will be evaluated with the aid of trajectory analysis.

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TEMPERATURE EFFECTS ON UV-B SPECTRA MEASURED AT CAPE GRIM BAPS

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Abstract

Environmental factors such as temperature have been identified as perturbing recorded UV-B irradiance, with effects being identified on both the spectrometers themselves and also on optical components such as the input diffusers. The identification and quantification of such effects has been challenging.

The impact of ambient temperature on the Cape Grim spectral radiometer SRAD were detected soon after it was installed, as there were clear changes in both wavelength calibration and spectral sensitivity with increasing temperature. As a consequence the spectrometer was temperature controlled (heated) using a variety of techniques from 1995 with a set point of 25°C.

While checks have shown that, in general, this heating system was sufficient to regulate spectrometer temperature on most occasions, it has been recognized that there may still be times when the temperature of the spectrometer varies. It has been found that short term changes in the measured dark current are a good surrogate for temperature. Using 5 years of data (2000 – 2004) periods potentially affected by a lack of temperature control have been identified. The dark current alters when hourly average temperature rises above 20°C. Over the time period investigated this represents a maximum of 240 hours/ year.

The data has been investigated more closely for evidence for changes in spectrometer sensitivity in the data record. This requires both warm conditions (> 20°C) and clear skies. In the 5 years of data record only one day had a sustained period where both conditions held! From the available data criteria have been developed to classify the severity of impact on individual spectra.

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VARIABILITY OF OZONE ABOVE DAVIS, ANTARCTICA

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Abstract

Since early 2003, the vertical distribution of ozone above Australia's Davis station in Antarctica (69ºS, 78ºE) has been regularly measured using ozonesondes by a programme jointly operated by the Australian Antarctic Division and the Bureau of Meteorology.

An ozone climatology for the troposphere and lower stratosphere has been produced from these measurements, which quantifies the amplitude and phase of the seasonal cycle as a function of altitude. These cycles are driven by well known chemical processes and large scale atmospheric circulation patterns. The measurements also reveal variability on a range of time scales, from rapid changes associated with wave processes, to longer-term variations related to the Antarctic ozone hole and the Quasi-Biennial Oscillation.

This paper presents an overview of the ozone climatology for Davis, and some examples of spatial and temporal variability of the vertical profile. In particular, global satellite and meteorological data are used to reveal details of the processes associated with these variations, which include wave-related changes in circulation near the edge of the polar vortex, mixing across the tropopause and long-distance meridional transport associated with the spring-time breakdown of the vortex.

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RADON-222 GRADIENT IN THE ATMOSPHERIC SURFACE LAYER BASED ON TOWER MEASUREMENTS

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Abstract

Radon-222 (radon) has long been recognised as a useful tracer for studying vertical mixing in the atmosphere. Results of such studies might lead to a significant reduction in systematic errors in the reproduction of diurnal and seasonal cycles in weather and climate prediction models on all scales.

For that purpose, ANSTO has been implementing two tower-based systems for continous measurement of radon gradients: the first system aims at vertical mixing in the surface layer, the second in the boundary layer. Each of the systems relies on a pair of 1,500 L radon detectors which have their inlets located at gradient-defining levels. The first system has a lower inlet at 2m and the higher at 50m, the second at 20 m and 200 m, respectively. The first system is located at ANSTO and uses the ANSTO meteorological tower. It has been operational since July 2005. The second system is located at the Cabauw site in the Netherlands, and is under construction. It will become operational in February-March 2006.



Figure 1. The 50m ANSTO meteorological tower and pair of 1,500 L dual flow loop, two filter radon detectors used for gradient measurements. Results are hourly averages of 30 minute readings. The sampling flow rate is ~80 L min-1 and the intake lines include thoron (220Rn) delay volumes >400L.

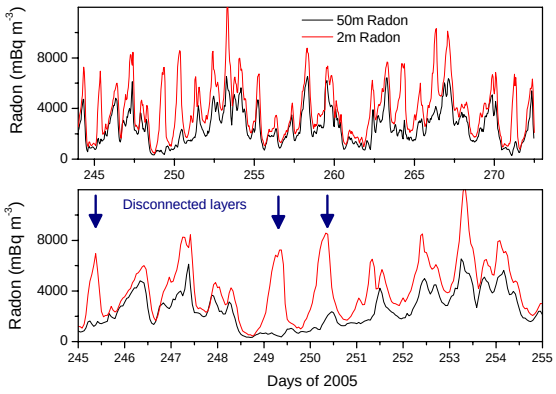


Figure 2. Comparison of 2m (red) and 50m (black) radon concentrations for all of September 2005 and a 10 day subset of that month. Close to the surface source, radon concentrations are enhanced. Radon concentrations also build up at night with the formation of the stable nocturnal boundary layer (NBL). On some nights, indicated by arrows, there is evidence that the local height of the NBL is below 50m.

USING INVERSE MODELLING TO INVESTIGATE POTENTIAL IR MEASUREMENT STRATEGIES FOR CONSTRAINING THE AUSTRALIAN CARBON CYCLE

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Abstract

CO_2 and methane are important greenhouse gases, both contributing in increasing amounts towards positive radiative forcing. It is hence important to gain maximum understanding of the carbon cycle in the atmosphere, and the scale of carbon trace gas sources and sinks, not only globally but also on a more regional level. The Orbiting Carbon Observatory (OCO) satellite, scheduled for launch in 2008, is designed for dedicated global mapping of CO_2. In order to investigate the usefulness of a variety of methods, including retrievals from satellite mapping, some preliminary inverse modelling using a Bayesian synthesis technique is performed using pseudodata generated to represent possible future measurement regimes. This study will focus on the ability of *in situ* measurements within Australia to reduce the uncertainties in Australian continental CO_2 flux estimates. The specific measurements investigated include a Ghan railway transect between Adelaide (34.9°S, 138.6°E) and Darwin (12.5°S, 130.9°E), and a number of continuous permanent sites. The reduction in flux uncertainties from additional measurements compared to a background inversion is examined, from which it is concluded that measuring on the Ghan railway is potentially worthwhile for reducing uncertainties associated with flux estimates.

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PFC EMISSIONS FROM AUSTRALIAN ALUMINIUM SMELTERS

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Abstract

Perfluorocarbons (PFCs) are very powerful and long-lived greenhouse gases that are emitted to the atmosphere predominantly from the global production of aluminium metal. They are included in the Kyoto Protocol 'basket' of gases, even though their cumulative contribution to past increases in radiative forcing due to the increases in long-lived greenhouse gases (CO_2, CH_4, N_2O, CFCs, HFCs, SF_6, PFCs) is less than 1%. This is because, once released to the atmosphere, their greenhouse impact is essentially irreversible, due to their multi-millenium atmospheric lifetimes, and because technologies exist, or likely could be developed, to significantly reduce their emissions.

Australian PFC emissions are included in the National Greenhouse Gas Inventory (NGGI), based on calculations using approved IPCC (Intergovernmental Panel on Climate Change) methodologies, involving estimates of Australian aluminium production on a smelter-by-smelter basis, and smelter-dependent PFC emission factors, obtained from an International Aluminium Institute (IAI) global survey of aluminium smelters.

Since early 2004, state-of-the-art PFC measurement instrumentation has been in operation at Cape Grim, in NW Tasmania (Figure 1), to monitor global PFC trends and estimate global PFC emissions (Fraser *et al*., 2005). However, three of Australia's six aluminium smelters, producing 40% of Australia's aluminium, are located within a 400 km radius of Cape Grim. Under the right weather conditions, PFC plumes from the Point Henry and Portland (Victoria) and Bell Bay (Tasmania) smelters are regularly observed at Cape Grim (Figure 1).

The magnitude and movement of these PFC plumes over SE Australia has been modelled using the CSIRO regional transport model (TAPM – The Air Pollution Model), incorporating smelter specific aluminium production and NGGI Australian-average PFC emission factors. Comparison of observed and modelled PFC plumes at Cape Grim suggests that the PFC emission factors for the SE Australian smelters are likely to be lower than the Australian average factors in the NGGI.

The installation at Aspendale of PFC measurement instrumentation in 2006 will significantly enhance the accuracy of PFC plume measurements, in particular for those from Point Henry (60 km from Aspendale).

This research is funded by CSIRO under its Light Metals Flagship initiative.

Reference

Fraser, P., P. Krummel, L. Porter, P. Steele, S. Baly, C. Rickard, B. Dunse and N. Derek, HCFCs, HFCs, PFCs, halons, CFCs, chlorocarbons, hydrocarbons and sulphur hexafluoride; the AGAGE *in situ* GC-MS-Medusa program at Cape Grim, 2004, in Baseline *Atmospheric Program (Australia)* 2003-2004, edited by J. M. Cainey, N. Derek and P. B. Krummel, Bureau of Meteorology and CSIRO Atmospheric Research, Melbourne, Australia, in press.

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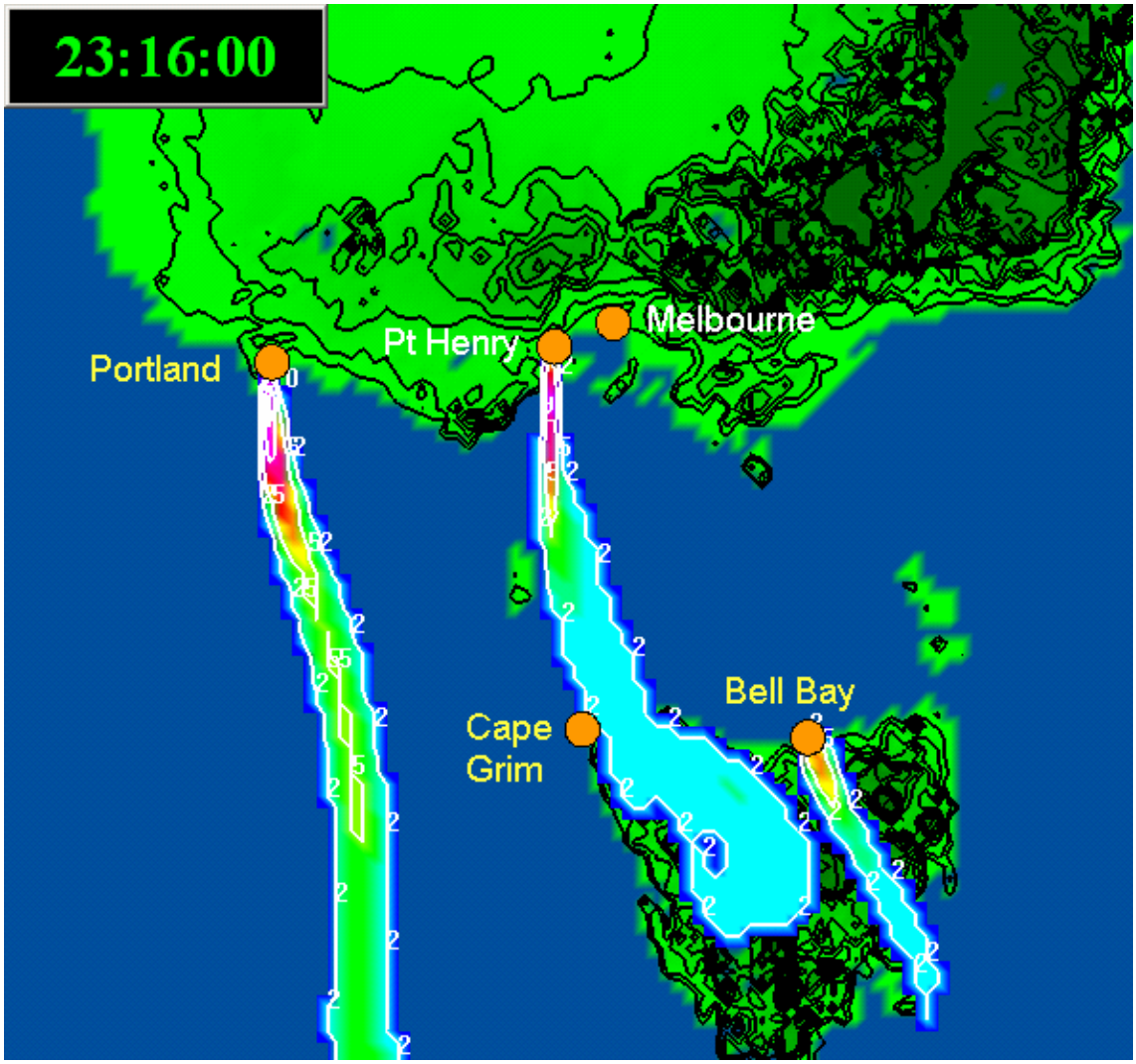


Figure 1. Location of Cape Grim and the SE Australian aluminium smelters and model (TAPM) derived PFC plumes.

CHANGES IN CONCENTRATIONS OF CO_2, CH_4 AND N_2O OVER THE PAST 2000 YEARS AND THEIR CAUSES

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Abstract

The concentrations of the major greenhouse gases carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) have increased significantly over the industrial period. We present new evidence of these increases and other changes and their causes over the past 2000 years from measurements of the air preserved in ice cores.

The measurements are on air from Law Dome (Antarctica), which is enclosed rapidly into bubbles, reliably recording past atmospheric composition. Advanced techniques of air extraction and analysis are used to precisely measure a large number of trace gas concentrations and isotopic ratios.

The results show major increases in CO_2, CH_4 and N_2O (29%, 150%, and 21% respectively) over the past 200 years and relative stability beforehand. Variations of up to 10 ppm CO_2, 40 ppb CH_4 and 10 ppb N_2O occur on decade to century timescales throughout the pre-industrial period.

Measurements of the isotopic composition ($\delta^{13}C$) of CO_2 and CH_4, combined with modelling of their sources and sinks, help to identify the causes of these changes. Anthropogenic emissions are the main cause of the increases over the past 200 years, or even longer for methane, whereas the effects of climate on natural sources are the main likely cause of the decade-century variability.

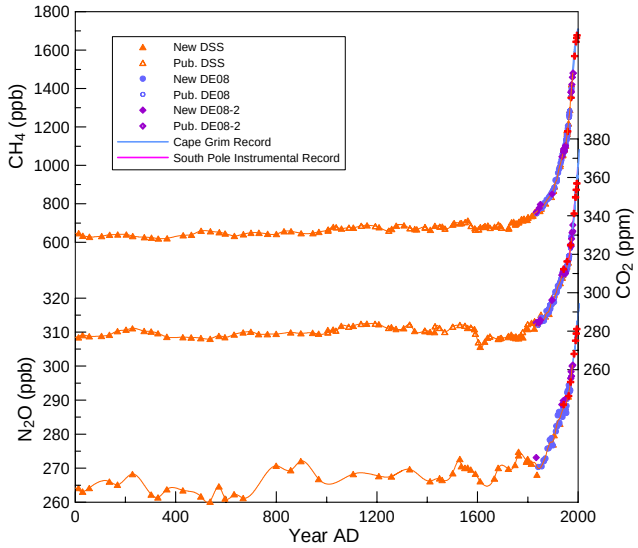


Figure 1. Concentrations of CO_2, CH_4 and N_2O over the past 2000 years.

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NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION (NOAA) ANNUAL GREENHOUSE GAS INDEX RELEASED

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Abstract

NOAA has developed and released for the first time this year its Annual Greenhouse Gas Index (AGGI). The AGGI is a readily understood measure of the climate forcing by long-lived, human-influenced greenhouse gases. These gases include carbon dioxide, nitrous oxide, and methane, as well as chlorofluorocarbons and their replacements.

All greenhouse gases included are precisely and accurately measured through the NOAA global, cooperative air sampling network. Indexed to 1.00 in 1990 (selected for its relevance to international agreements), the observation-dependent AGGI was 1.20 in 2004, representing a 20% increase since 1990. The annual increase in the index from 2003 to 2004 was 1.12%. Because the NOAA AGGI extends back to 1979, one can easily see that it has increased by ~50% since 1980, when it was 0.8, relative to a value of zero in 1750. NOAA announced this index in April of this year at the NOAA/CMDL Annual Meeting in Boulder, Colorado, and at the 2005 General Assembly of the European Geosciences Union. The index will be updated and reported annually.

The NOAA AGGI is designed to enhance the connection between scientists and society by providing a normalized standard that can be easily understood and followed. The contribution of long-lived greenhouse gases to climate forcing is well understood by scientists and has been reported by NOAA through a range of national and international assessments. Nevertheless, the language of scientists (for example, watts per square meter per year) often eludes policy makers, educators, and the general public. This index is designed to help bridge that gap.

[*] www.esrl.noaa.gov/gmd (Formerly NOAA Climate Monitoring and Diagnostics Laboratory)

INTERANNUAL VARIABILITY OF THE AIR-SEA CO_2 FLUX IN THE SOUTHERN OCEAN

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Abstract

We estimate the variability of the air-sea CO_2 fluxes in the Southern Ocean for the 1985-2003 period using the spatio-temporal distribution of atmospheric CO_2 measurements from 12 stations in the Southern Ocean and 43 stations worldwide. Our results show well-constrained variability of ±0.2 PgC/y correlating with the Southern Annular Mode (SAM), which indicates a predominant control of CO_2 flux variability by physical mixing and upwelling. We estimate that the intensification of the winds in the Southern Ocean since 1960 contributed to a reduction of the CO_2 sink efficiency by up to 0.2 PgC/y (-10%).

LAW DOME ATMOSPHERIC TRACE GAS RECORDS EXTENDED TO 2000 YEARS BP

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Abstract

High-precision multispecies trace gas measurements have been produced for the last 2000 years from air trapped in Law Dome ice. The new records of carbon dioxide (CO_2) and methane (CH_4) compare very well with the published Law Dome records of the last 1000 years. The new measurements confirm the changes observed in these records, fill in gaps in the sampling and extend the record to 2000 BP with high sampling frequency and high temporal resolution. Additionally, measurements of nitrous oxide (N_2O) and carbon monoxide (CO) have obtained for the past 2000 years. The new measurements confirm some variations in the published records, which are hard to explain with our current knowledge of the carbon cycle. The confirmation of the published CO_2 and CH_4 records indicates that the variations during the Little Ice Age period are indeed significant.

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ATMOSPHERIC BURDEN OF SOME OZONE-DEPLETING COMPOUNDS CONTINUES TO INCREASE

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Abstract

With the signing in 1987 of the Montreal Protocol on Substances that Deplete the Ozone Layer, the international community began a series of steps to reduce the emission of ozone-depleting compounds into the atmosphere. As a result of these efforts, the contribution of these gases to the atmospheric burden of ozone-depleting halogen continued to increase until 1993-94, when their collective trend reversed and began to decline (Montzka et al. 1996). This decline has continued over the past decade as anticipated by models of expected emissions.

Not all contributing gases, however, are decreasing in atmospheric concentration. Mixing ratios of chlorofluorocarbon-12 (CFC-12), for example, have leveled off, but the turnover is slow, owing to the long lifetime and continued release of this gas from reservoirs such as foams and older automobile air conditioners. Mixing ratios of the two major halons (H-1301 and H-1211) continue to increase, albeit much slower than in the past. H-1301, with an atmospheric lifetime of 60 y, is still used worldwide for lack of a suitable replacement, although its production ceased in developed countries in 1994 and was frozen in developing countries in 2002. Growth rates of shorter-lived (20 y) H-1211, which has replacements for some uses, have dropped some, but remain positive. The atmospheric mixing ratios of hydrochlorofluorocarbons, the intermediate replacements for CFCs, have been increasing rapidly over the past decade, but some are showing signs of leveling off. We examine here the current and potential future contribution of all of these gases to the burden of ozone- depleting halogen in the atmosphere, focusing on why they continue to increase.

[*] www.esrl.noaa.gov/gmd

TRENDS IN THE NITROGEN AND OXYGEN ISOTOPIC COMPOSITIONS OF TROPOSPHERIC N_2O AND POSSIBLE IMPLICATIONS FOR THE GLOBAL N_2O ISOTOPE BUDGET

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Abstract

We report measurements of N_2O isotopologues on 25 free tropospheric whole air samples collected and archived between 1978 and 2004 from Cape Grim, Tasmania (40.7°S, 144.8°E), as well as 11 firn air measurements from Law Dome, Antarctica. The measurements on archived air show significant decreasing trends in the nitrogen and oxygen isotopic compositions over the last 40 years and are the first direct observations of a historical change in N_2O isotopic composition in the late 20th century. The observed trends are larger than box model predictions [Rahn and Wahlen, 2000] and are similar to those derived from other firn air measurements [Röckmann *et al*., 2003]. Importantly, however, the direct measurements of atmospheric N2O appear to reveal detectable temporal variations in the isotopic trends which cannot be reliably retrieved a priori from firn air measurements. These variations, if significant above the measurement precision, may reflect changes in the relative source contributions of N_2O from the oceans or biomass burning during El Nino years, for example, and thus may provide a better mechanistic understanding of what environmental factors contribute to variations in the magnitude of N_2O emissions to the atmosphere. Here, we also investigate the apparent temporal variations in the isotopic trends using a box model similar to that of Rahn and Wahlen [2000] but updated with new knowledge of the fluxes of heavy N_2O isotopologues from the stratosphere to the troposphere from Park *et al*. [2004]. These preliminary results suggest that these new data and their analysis should provide important new constraints on the global N_2O isotope and concentration budgets. In general, these decreasing isotopic trends support the idea that the increase in the atmospheric N_2O burden is a result of agricultural activities that produce isotopically light N_2O.

References

Park S, E. L. Atlas, and K.A. Boering. Measurements of N_2O isotopologues in the stratosphere: Influence of transport on the apparent enrichment factors and the isotopologue fluxes to the troposphere. *J. Geophys. Res.*, 109, D01305, doi:10.1029/2003JD003731, 2004.

Rahn, T., and M. Wahlen. A reassessment of the global isotopic budget of atmospheric nitrous oxide. *Global Biogeochemical Cycles*, 14(2), 537-543, 2000.

Röckmann, T., J. Kaiser, and C.A.M. Brenninkmeijer. The isotopic fingerprint of the pre-industrial and the anthropogenic N_2O source. *Atmos. Chem. Phys.*, 3, 315-323, 2003.

THE ADVANCED ULTRACLEAN ENVIRONMENT (ACE) FOR PROCESSING METALS AT ULTRA-TRACE LEVELS

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Abstract

The increasing sensitivity and expense of modern analytical instruments demands that more attention be given to sample preparation if the expected gain in measurement quality is to be realized. A common problem with the measurement of elemental concentrations at ultratrace levels is contamination of the sample which can occur during its collection, processing or storage. We address the problem of contamination during sample processing by minimizing contamination from the laboratory air and by selecting suitable construction materials for the laboratory. This is realized with the ACE facility commissioned in 2004, which occupies about 400 square metres and is located at Curtin University of Technology. It includes 4 individual work areas, a chemical reagent preparation area and a cold laboratory intended for processing Polar ice and snow samples that may contain femtogram/gram concentrations of the elements of interest. All work areas are enclosed inside a dust-free exclusion space supplied with HEPA-filtered air and operated above the ambient atmospheric pressure. Air quality in each work area is maintained by frequent recirculation of the air through HEPA-filters. All work spaces achieve the Class 3 classification of air cleanliness (ISO 14644-1) in the as-built state. The ACE facility has a highly innovative design with low maintenance and versatile work spaces.

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Pb ISOTOPES AND CLIMATE: A 220 KY RECORD FROM THE EPICA DOME C ICE CORE

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Abstract

Deep ice cores obtained from central East Antarctica provide an insight into climatic conditions and aerosol provenance during the Holocene and previous glacial and interglacial periods. Previous studies have indicated that Lead (Pb) concentrations vary during glacial (colder) and interglacial (warmer) climate periods as a result of changing quantities of dust transported to Antarctica.

Samples were obtained from ice core sections drilled at Dome C as part of the European Project for Ice Coring in Antarctica (EPICA). Potentially contaminated outer surfaces of each core section were removed within a clean room supplied with HEPA-filtered air using apparatus cleaned in high-purity acids. The remaining pristine ice core samples were then analysed by Thermal Ionization Mass Spectrometry, with Pb and Ba concentrations determined by the Isotope Dilution method.

We report concentrations of Pb and Barium (Ba) and Pb isotopes in samples of the EPICA Dome C ice core dating to 220 ky Before Present. Ba data are used as a proxy of dust inputs, while deviations from crustal Pb/Ba ratios are interpreted as inputs of Pb from other natural emission sources, such as volcanism. If the dust deposited in Antarctica is comprised of multiple sources, then variations in the Pb/Ba ratio may also indicate changing dust contributions from different source areas. Pb isotopic compositions are compatible with a model of two major sources of natural Pb emissions: crustal particles, most probably originating from South America, and volcanic emissions from within Antarctica and/or the Southern Hemisphere.

We observe variations in Pb isotopic compositions over the past two climate cycles, with less-radiogenic Pb isotopic compositions during colder climate periods and more-radiogenic Pb isotopic compositions during warmer climate periods. Variations in the Pb isotope data and Pb/Ba ratios are consistent with decreased inputs of dust during interglacial periods, which then result in a greater proportion of radiogenic Pb from volcanism being observed.

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A NEW AIR-BORNE SAMPLER AND LAB COUNTING UNIT FOR VERTICAL RADON PROFILES IN THE LOWER ATMOSPHERE (<3000M AGL)

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Abstract

Vertical radon profiles measured with the help of airborne platforms can be used to address time-varying aspects of exchange and mixing processes over a wide range of altitudes within the lower atmosphere.

A system comprising an air-borne radon sampler (Figure 1) and a laboratory based counting unit (Figure 2) for measurement of vertical radon profiles has recently been constructed and tested at ANSTO. The sampler is capable of *in situ* extraction of radon from up to 300 L of air at a given altitude. It weights about 20 kg, consumes less than 200W power, and can be flown and operated using a light aircraft. A computer based controller allows the pilot to modify the sampling stragegy while airborne. A set of six samples for a single radon profile can be collected in about 2 hours.

The counting unit (Figure 2) is based on Lucas cells and is comprised of 20 independent channels which allow it to process and count at a sustained rate of 12 samples per day. The lower limit of detection is about 0.01 Bq m^{-3} for a three hour count.

The system was field-tested and then deployed for a two week field campaign at Meninge, South Australia.



Figure 1a. Sample tubes being changed on the ANSTO radon sampler during the Meningie field campaign. The sampler holds six charcoal traps which are hot flushed with nitrogen prior to use. Sampling is controlled remotely via a computer in the cockpit. Each trap is exposed for five minutes at a flow rate of 20 L min^{-1}. Where low concentrations of radon are expected, more than one exposure is used.

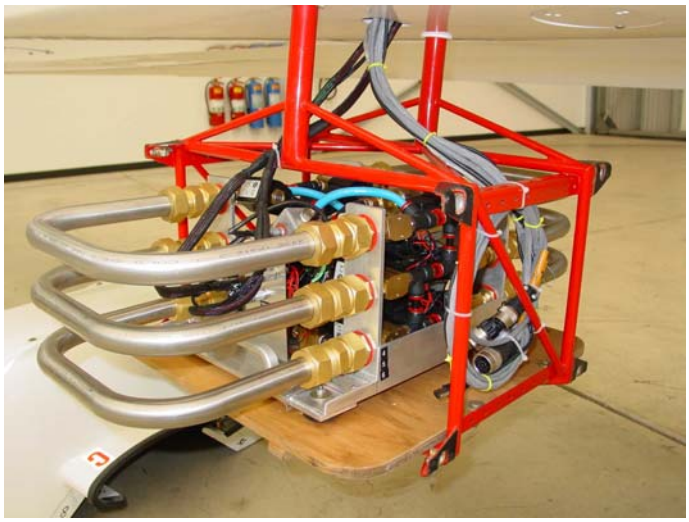


Figure 1b. ANSTO airborne radon sampler fitted to a wing pod rack of the Dimona motor-glider VH-EOS



Figure 2. The laboratory based radon counting rig. After exposure, charcoal traps are removed, sealed and couriered back to ANSTO where the sampled radon is extracted and analysed on a this multi-channel counting system.

POST-FRONTAL NANO-PARTICLE ENHANCEMENT AT CAPE GRIM – IS IT IMPORTANT?

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Abstract

Observations of nanoparticle concentrations (3-12 nm diameter) in clean post-frontal air at the Cape Grim Baseline Air Pollution Station show that enhanced concentration events occur throughout the year. For 1999-2000 these events were strongest in summer (~ 480 cm^{-3}), weakest in winter (~ 152 cm^{-3}) and of intermediate strength in spring (~ 325 cm^{-3}) and autumn (~ 183 cm-^{3}). Typically in events, nanoparticle concentrations peaked about 10 to 15 hours after frontal passage and events lasted for around 6 to 13 hours. The importance of these events to maintaining the background particle population is not immediately obvious, and coupled aerosol-transport models of sufficient detail to capture frontal processes do not yet exist. A number of arguments can be used to estimate the importance of these events. The approach to be discussed involves a simple model of the microphysical processes expected to drive particle evolution, for a Lagrangian parcel following frontal passage at Cape Grim.

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THE INFLUENCE OF THE BASELINE EVENT SWITCHES ON PM10 AT CAPE GRIM

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Abstract

During the lifetime of the Cape Grim program a number of general criteria have evolved to define clean air for collected aerosol and rainwater samples and to operate baseline event switch (BEVS). The main baseline switch (BEVS2) is activated when winds are between 190° and 280° (measured at the 10 m level) and particle concentration (CN) is less than 600 cm^{-3}. These conditions are encountered only 30% of the time, however, use of this fixed CN limit has persisted to maintain consistent records. The marked seasonal cycle in CN, with median concentrations of around 100 cm-3 in winter and 700 cm^{-3} in summer [e.g., Gras, 1995], as well as significant inter-annual variation, clearly indicate that a fixed CN level is less than ideal. Consequently, a supplementary baseline criterion and baseline switch (BEVS3) has been developed that uses the previous five year's CN data for the current month selected for a 50 m level wind direction between 190º and 280º. The CN threshold is based on the 90 percentile of CN hourly medians for the period interpolated using cubic splines to give daily values. BEVS3 was implemented in late 2001 after the Working Group recommended changes in the criteria used for operating the baseline switch for samplers making sample collections.

At Cape Grim, particles less than 10 μm (PM10) have been collected under baseline conditions (on BEVS 2) since 1981 using a high volume aerosol sampler (Hi-Vol). A study was initiated in December 2001 to investigate the possible effects of permanently changing the Hi-Vol sampling over to the new baseline switch, BEVS3. In this study, the mass and composition of aerosol collected using both baseline switches is being compared between a Hi-Vol operating on BEVS2 and a Hi-Vol operating on BEVS3. In this presentation the results of this study will be discussed as well as their implication for baseline event aerosol sampling at Cape Grim.

Reference

Gras, J. L. Particles, in *Baseline Atmospheric Program Australia 1992*, edited by A. L. Dick, and P. J. Fraser. Department of the Environment, Sport and Territories, Bureau of Meteorology in cooperation with CSIRO Division of Atmospheric Research. Melbourne, Australia, 35-39, 1995.

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HIGHLY RADIOGENIC LEAD IN SOUTHERN OCEAN AEROSOL AND ANTARCTIC SNOW

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Abstract

Southern Ocean aerosols were collected at the Cape Grim Baseline Air Pollution Station from onshore air under baseline conditions between February 1999 and April 2000. Thermal ionisation techniques (TIMS) and isotope dilution mass spectrometry (IDMS) were used to measure the isotopic composition and concentration of lead in the air giving concentrations as low as 0.6 ± 0.1 pg·m-3 but with an average of 11.0 ± 0.2 pg·m-3 over 12 months (May, 1999 – April, 2000). The range in isotopic ratios found was consistent with the mixing of lead from major population centers in the Southern Hemisphere in the mid to high latitudes, except for the presence of highly radiogenic lead in some samples.

Recent measurements of lead isotopes in snow from Law Dome, Antarctica show evidence of the intermittent arrival of highly radiogenic lead. This lead, which occurs at concentrations of ~0.3 pg.g-1 and has a 206Pb/207Pb ratio of ~1.31, may have the same geographical origin as the radiogenic lead detected at Cape Grim. This radiogenic lead could be a useful tracer for following the progress of air masses in the Southern Hemisphere and for assessing aerosol transfer to the Antarctic continent.

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RADON OBSERVATIONS IN THE CAPE GRIM MAINLAND SECTOR IN 2001- 2004

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Abstract

Cape Grim observations in the mainland sector have been analysed with increased frequency during recent years. There are a number of important features in this sector, which can be studied using hourly radon-222 concentrations. Similar features can be expected for other trace atmospheric species, especially those of terrestrial origin and atmospheric life times comparable to the half-life of radon. A number of such features are shown using the radon record at Cape Grim for 2001-2004.

Radon-222 distribution is strongly anisotropic (Figure 1 a), with mainland influence very well defined in the angular distribution of radon concentrations. The signal is much stronger in the mainland than in the baseline sector; e.g. the ratio of the respective medians has been as high as 68 in the period. Another characteristic feature occurs within the initial 24 hours following a change to the sector, when radon concentration distributions shift to higher values (Figure 1b). Monthly radon distributions vary strongly with a well pronounced peak in May-July (Figure 1c). This behaviour is primarily due to a seasonal variation in the time air masses spend over land before arriving at Cape Grim (Figure 1 d).

Back trajectories corresponding to high and low radon concentrations in the sector were used to delineate areas of extreme interaction of air parcels with land. The locations of resulting footprints vary strongly during the year. An attempt was also made to identify spacial variability of the radon source in the composite footprint corresponding to high interaction with land using a version of the Potential Source Contribution Function method.

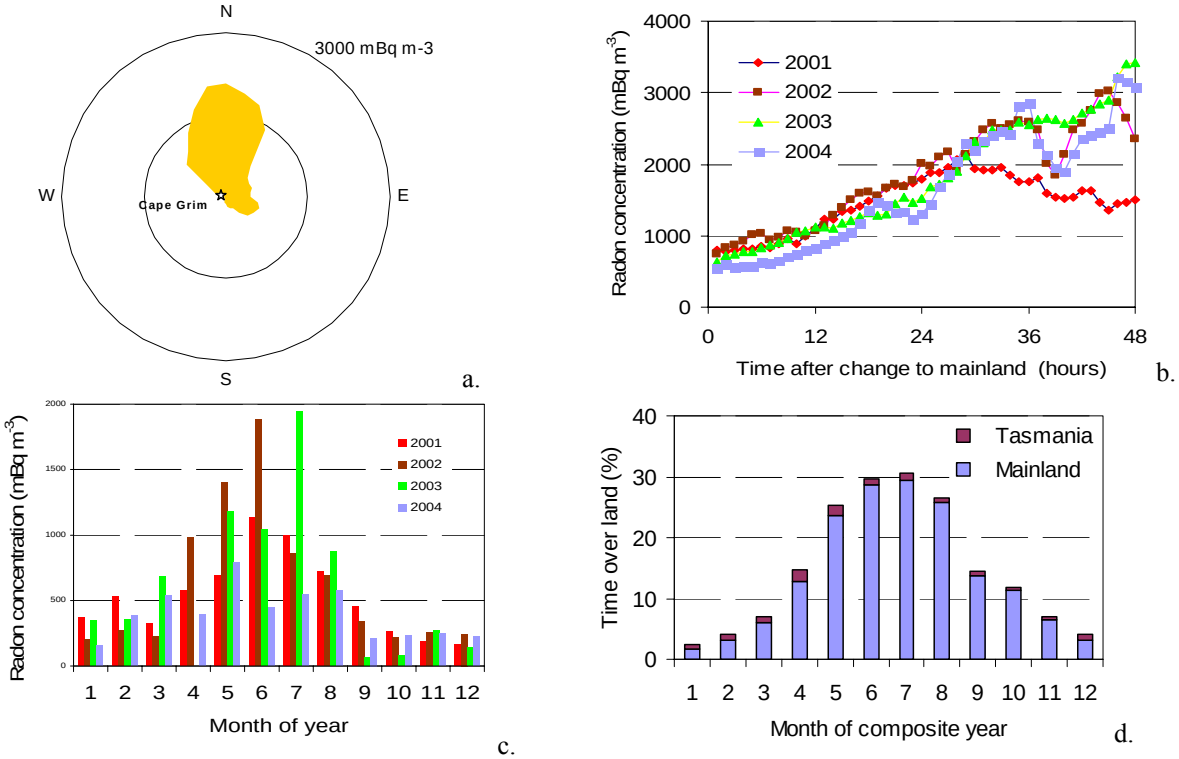


Figure 1. (a) Angular radon distribution (medians) for 2001-2004, (b) Radon concentration means in consecutive periods of 1 hour after the sector change to mainland, (c) Monthly mean radon concentrations and (d) Monthly estimates of the length of time spent by air parcels over land.

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COMPARISON OF FORMALDEHYDE AND PEROXIDE CONCENTRATIONS IN BASELINE AND URBAN AIR

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Abstract

In clean marine air baseline air at Cape Grim formaldehyde concentrations are produced from secondary sources, primarily from the oxidation of methane by hydroxyl radical, plus small contributions from the oxidation of alkenes and dimethyl sulphide by ozone or hydroxyl radical. The production of formaldehyde is balanced by loss physical loss processes such as photolysis and wet and dry deposition, and by chemical processes such as reaction with hydroxyl radical.

Hydrogen peroxide is produced almost exclusively in secondary processes from the termination of two hydroxy peroxy radicals, which are largely produced from the reaction of carbon monoxide with hydroxyl radicals. It is destroyed by physical processes, such as photolysis or wet and dry deposition, or chemically by reaction with hydroxyl radical.

In contrast to baseline air, formaldehyde is produced in urban atmospheres from secondary sources, plus a mixture of primary sources including motor vehicles, industry, domestic wood-burning and plant emissions.

This presentation will compare concentrations of formaldehyde and peroxides measured in baseline air at Cape Grim, with those measured at Aspendale in 'baseline' and polluted air. The measured concentrations of formaldehyde and hydrogen peroxide will be used to compare with outputs from the Australian Air Quality Forecasting System. In addition, the Australian Air Quality Forecasting System will be used to determine the relative contributions of secondary and primary sources of formaldehyde and peroxides in 'baseline' and polluted Aspendale air.

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THE USE OF BASELINE ATMOSPHERIC COMPOSITION DATA TO VERIFY GEOLOGICAL STORAGE OF CO_2

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Abstract

Carbon capture and storage, or geosequestration, will be required to retain the CO_2 in geological formations without leakage to the atmosphere. At stake are environmental health and safety, public acceptance, regulatory approval, carbon credits, and verification that geosequestration is an effective greenhouse gas control technology. Atmospheric monitoring is likely to be used together with below ground monitoring of injected gases. We outline atmospheric methods to measure gas emissions from geosequestration. Because CO_2 leaks would appear as small perturbations on an atmospheric background that varies due to global, regional and local fluxes, long term baseline atmospheric data may be needed.

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20TH CENTURY TRENDS AND BUDGET IMPLICATIONS OF TRIHALOMETHANES AND DIHALOMETHANES INFERRED FROM NORTH GRIP FIRN AIR

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Abstract

Four trihalomethane (THM; $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) and two dihalomethane (DHM; CH_2BrCl and CH_2Br_2) trace gases have been measured in air extracted from polar firn collected at the North Greenland Icecore Project (NGRIP) site. $CHCl_3$ was also measured in firn air from Devon Island (DI), Canada, Dronning Maud Land (DML), Antarctica and Dome Concordia (Dome C), Antarctica. All of these species are believed to be almost entirely of natural origin except for $CHCl_3$ where anthropogenic sources have been reported to contribute ~10% to the global burden.

A 2-D atmospheric model was run for $CHCl_3$ using reported emission estimates to produce historical atmospheric trends at the three firn sites, which were then input into a firn diffusion model to produce concentration depth profiles that were compared against the measurements. The anthropogenic emissions were modified in order to give the best model fit to the firn data at NGRIP, Dome C and DML. As a result, the contribution of $CHCl_3$ from anthropogenic sources, mainly from pulp and paper manufacture, to the total chloroform budget appears to have been considerably underestimated and was likely to have been close to ~40% at the maximum in atmospheric $CHCl_3$ concentrations around 1990, declining to ~19% at the beginning of the 21st Century. We also show that the atmospheric burden of the brominated THM's in the northern hemisphere have increased over the 20th Century while CH_2Br_2 has remained constant over time implying that it is entirely of natural origin.

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