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Composition of the atmosphere - abstracts of the fifth CAWCR Workshop 15 November - 17 November 2011, Melbourne, Australia

CAWCR Technical Report No. 044

Keith A. Day and Andrew J. Hollis (editors)

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FOREWORD

The Centre for Australian Weather and Climate Research (CAWCR) is a partnership between Australia's leading atmosphere and ocean research agencies – CSIRO Marine and Atmospheric Research (CMAR) and the Bureau of Meteorology. CAWCR, established in 2007, jointly manages the science capability within the Bureau and CMAR providing a single centre of research excellence. This year's CAWCR Workshop, *"CAWCR Atmospheric Composition Observations and Modelling and the Annual Cape Grim Science Meeting"* is the fifth Annual Workshop under the auspices of the Centre, continuing the series originating within the Bureau of Meteorology Research Centre.

The aims of the meeting are to: 1) understand the role of atmospheric chemistry and composition in global atmospheric change as expressed in the Australasian region and internationally; and 2) to provide a forum for atmospheric composition researchers from different disciplines (in-situ observations, remote sensing observations, modelling) to share ideas, enhance collaboration and develop a coordinated regional approach to characterising atmospheric processes in Australasia.

The key themes covered in this year's workshop are: (i) Chemistry-Climate interactions (aerosols, greenhouse gases, reactive gases); (ii) Budgets (carbon cycle, fluxes); and (iii) Emerging tools/opportunities (Australian observatories, satellites, re-analysis, new platforms).

A number of prominent scientists and experts from overseas, Australian research agencies and universities have been invited to give presentations. Keynote speakers include Professor Dr Martin Heimann (Max-Planck Institute for Biogeochemistry, Jena, Germany); Dr Olaf Morgenstern (NIWA Lauder, New Zealand); Dr Dale Hurst (NOAA's Earth System Research Laboratory, Boulder, USA) and Dr Michael Raupach (CSIRO Marine and Atmospheric Research, Canberra, Australia). The Workshop also includes the Annual Priestley lecture which will be given this year by Dr Stephen E. Schwartz (Brookhaven National Laboratory). We are grateful for these expert contributions and to all the participants' contributions to the debate and discussions.

We are particularly grateful to Intel for their generous support of this workshop.

Finally, we would like to thank the members of the organising committee for their efforts, comprising: Melita Keywood (Chair), Paul Krummel, Nada Derek, Clare Murphy, Peter Hurley, Bruce Forgan, Peter Rayner, Pep Canadell and Bronte Tilbrook. Meryl Wiseman, Val Jemmeson, Andrew Hollis, Keith Day, Mark Bervanakis and Anu Arora provided excellent administrative support.

Tom Keenan

Director

Centre for Australian Weather and Climate Research:

A partnership between the Australian Bureau of Meteorology and CSIRO

November 2011

THE CAPE GRIM STABLE ISOTOPE PROGRAM 1990-2011

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Abstract

CSIRO Marine and Atmospheric Research (CMAR) has been measuring the stable isotopic composition of atmospheric carbon dioxide ($\delta^{13}C$ and $\delta^{18}O$) at Cape Grim using two programs, the *in situ* program (CIA) and the flask program (CGO), for over thirty years. In the CIA program, CO_2 was extracted from baseline air at Cape Grim and sent to the CMAR Global Atmospheric Sampling Laboratory (GASLAB) in Aspendale for stable isotope analysis. In the CGO program, samples of air were collected in either 5.0 or 0.5 litre glass flasks and returned to GASLAB for analysis as part of the global flask network operated by GASLAB. While samples from both programs have been analysed using the same stable isotope ratio mass spectrometer (SIRMS), the measurement and calibration procedures used in these programs are quite different, essentially providing us with two independent records of both $\delta^{13}C$ and $\delta^{18}O$ in atmospheric CO_2 at Cape Grim. Having these two independent records has allowed us to identify, and correct for, many different analytical problems that may otherwise have passed un-noticed. Some of the problems addressed include calibration standard offsets and drifts, instrumental problems, and flask storage effects.

The CIA program ended in June 2009 and this presentation will summarise the comparison of the data from these two programs and introduce the results from the analysis of air collected at Cape Grim in 1.6 litre stainless steel canisters as a potential replacement for the CIA program. While this program does not maintain the independence of calibration and measurement protocols, it provides a larger air sample, by a factor of 3, and a different storage material, stainless steel, that allows some independence to be maintained.

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AEROSOL FORMATION OBSERVED DURING SMOG CHAMBER STUDIES OF THE PHOTODECOMPOSITION OF MONOETHANOLAMINE (MEA) IN NO_X AND AIR

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Abstract

The use of alkanolamines, such as monoethanolamine (MEA), to absorb CO_2 is one strategy widely considered to be a viable solution for CO_2 removal from fossil fuel combustion flue streams. Although this technology has been available since the 1930s, the impact of the process on emissions to the atmosphere has not received a great deal of attention. Given the scale of the carbon capture process and the mass of MEA required to facilitate CO_2 capture, investigations into the environmental impacts of fugitive MEA need to be expedited. The literature contains only a few limited studies addressing the atmospheric chemistry of MEA and the objective of this work was to assist in addressing this deficiency. MEA is very difficult to work with and injection strategies are required to overcome such difficulties. Aerosol formation under the conditions used appears to very rapid and light dependent. There is a strong correlation (R=0.992) with aerosol surface area and ammonia formation the latter which only forms while lights are on.

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TROPOSPHERIC POLLUTION OVER WOLLONGONG INVESTIGATED WITH THE EARTH-SYSTEM MODEL ACCESS

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Abstract

Earth-System models integrate the simulation of processes such as climate, atmospheric chemistry, oceans and land-surface interactions. Combination of systems produces a powerful tool for testing our knowledge of how all these systems interact. In Australia, a joint project between the CSIRO and the Bureau of Meteorology is to develop the Australian Community Climate Earth-System Simulator (ACCESS). Analysis of output is imperative in the model development process, in order to produce a model which most accurately represents the Earth-System.

This study focuses on preliminary results from the chemistry module of ACCESS, in particular tropospheric ozone and pollution precursor's carbon monoxide, nitrogen dioxide and formaldehyde. Increased concentrations of tropospheric ozone and precursors are of concern due to their detrimental effects on human health and vegetation. Enhanced pollution is usually found over urban and industrial areas, such as in Wollongong, NSW.

In this work, ACCESS results are compared with remote sensing retrievals from ground based Fourier transform Infrared measurements recorded at Wollongong over the period 1996-2009. Comparison with measurements improves our understanding of seasonal variability and background concentrations in the region. Further comparison of ACCESS results are completed with output from the global chemical transport model GEOS-Chem. Comparison between these different models, together with measurements, helps to interpret ACCESS output and to determine which processes are accurately captured.

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SEPARATING REMOTE FETCH AND LOCAL MIXING INFLUENCES ON NEAR-SURFACE RADON GRADIENT MEASUREMENTS

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Abstract

Predictions of weather and climate conditions are crucially reliant upon the fidelity of model parameterisations that represent the integrated behaviour of key physical processes responsible for transport and mixing in the atmospheric boundary layer. Distributions of trace gases and aerosols with respect to their natural or anthropogenic sources, as well as their removal through deposition, are also controlled by these processes. However, scientific understanding of many aspects of mixing and transport processes still requires substantial refinement, or even fundamental revision. In the stably stratified boundary layer vertical mixing processes remain poorly understood, particularly in very stable conditions when surface inversions can be extremely shallow and the thermodynamic structure of the lowest 50−100 m very complex. At the surface, for even simple investigations of atmospheric chemistry, there is a need to improve our understanding of the processes controlling the spatial/temporal variability in vertical exchange rates between the roughness elements (canopy/buildings) and the atmosphere above.

Two-point radon gradients provide a direct, unambiguous measure of near-surface atmospheric mixing. A 31-month dataset of hourly radon measurements at 2 and 50 m is used to characterise the seasonality and diurnal variability of radon concentrations and gradients at a site near Sydney. Vertical differencing allows separation of remote (fetch-related) effects on measured radon concentrations from those due to diurnal variations in the strength and extent of vertical mixing. With the help of model-derived back trajectories and boundary layer depths, we were able to characterise the pronounced seasonal variability in afternoon surface radon concentrations in the Sydney region in terms of air mass fetch, contact time with land, ABL dilution and regional variability of the radon source function. Influences of coastal sea breeze circulations and the local topography were identified, superimposed upon the dominant seasonal variations in regional circulation patterns.

Diurnal composites, grouped according to the maximum nocturnal radon gradient (ΔC_{max}), reveal strong connections between radon, wind, temperature and mixing depth on sub-diurnal timescales. Comparison of the bulk Richardson Number (Ri_B) and the turbulence kinetic energy (TKE) with the radon-derived bulk diffusivity (K_B) helps to elucidate the relationship between thermal stability, turbulence intensity and the resultant mixing. On nights with large ΔC_{max}, K_B and TKE levels are low and Ri_B is well above the "critical" value. Conversely, when ΔC_{max} is small, K_B and TKE levels are high and Ri_B is near zero. For intermediate ΔC_{max}, however, Ri_B remains small whereas TKE and K_B both indicate significantly reduced mixing. The relationship

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between stability and turbulence is therefore non-linear, with even mildly stable conditions being sufficient to suppress mixing.

BENZENE AND BTEX IN AIR IN URBAN AND RURAL REGIONS OF AUSTRALIA

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Abstract

We present a composite climatology of benzene, toluene, ethylbenzene and xylenes (BTEX) concentrations and ratios in urban and rural air in Australia based on measurements made over the last decade. Samplings were carried out at a number of urban locations (Sydney, Melbourne, Perth, Darwin and Launceston), and rural locations (Bringelly NSW, Wagga Wagga NSW, Ovens VIC, Burrup WA and Manjimup WA).

We use the distinctive BTEX source signatures of motor vehicle exhaust and biomass burning smoke to attribute the sources of the observed BTEX in these urban and rural locations. Motor vehicles are the most pervasive source and, on specific instances, there is clear evidence of biomass burning emissions. The motor vehicle emission signature is also examined for temporal trends.

The BTEX source signatures are compared with inventory emission signatures from the National Pollutant Inventory (NPI), with a particular focus on benzene. The NPI (2009) estimates “Burning/Wildfires” contribute only 1.6% of the total benzene emissions while motor vehicles, lawn mowing, solid fuel burning (domestic) and recreational boating making up 89% of the total national benzene emissions of 1.5×10^7 kg/y. Most likely the NPI neglects emissions from savanna fires in northern Australia and wildfires throughout the rest of Australia. If savanna burning is taken into account, the contribution of ‘Burning/Wildfires’ to benzene emissions is 4.5×10^7 kg/y or 75% of the revised total benzene emissions of 6.0×10^7 kg/y.

We provide our best estimate of the national budget of emissions of benzene and the concentrations of benzene and BTEX in Australian environments from these studies.

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PREDICTING FUTURE AIR QUALITY IN VICTORIA: MODEL VERIFICATION AND FUTURE PROJECTIONS

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[2]*EPA Victoria, Ernest Jones Drive, Macleod, VIC, 3085, Australia Abstract*

Abstract

A dynamical downscaling atmospheric modelling system has been set up to investigate future air quality trends (particularly for ozone, nitrogen dioxide and PM2.5) in Melbourne, Australia, for conditions of changing emissions and changing climate. An overview of the project is given in a companion paper (Walsh *et al*. 2011).

The coupled system consists of a comprehensive air emissions inventory for Melbourne and Victoria; a four member ensemble of climate trends from earth system models; a stretched grid atmospheric model for downscaling from synoptic to regional scale; and a meteorological/chemical transport model for downscaling from regional to urban scale, and for simulating multi-phase chemistry, including secondary particle formation.. The system incorporates climate-sensitive emission calculations, including the effects of temperature on wood heater emissions, tailpipe and evaporative emissions from motor vehicles, and biogenic emissions; and the dependency of sea salt emissions on wind speed.

System performance was assessed through a multi-stage process. 1) evaluation of the meteorological prediction components of the modelling system; 2) evaluation of the performance of the air emissions inventory primarily; 3/)evaluation of the performance of the chemical transport model (CTM) and the system as a whole. The system performance was generally found to be good, with nitrogen dioxide and temperature being most accurately modelled. On the other hand, peak concentrations of ozone and PM2.5 were slightly under-predicted in the summer. A comparison of observed and modelled PM2.5 components indicated generally good performance for all components except for organic carbon which was systematically under-predicted.

An ensemble of air quality projections were undertaken for decadal periods centred on 2030 and 2070 and compared to decadal simulations centred on 2000. The modelling suggests that, in the absence of emission controls, ozone concentrations will increase, leading to a 20–25% increase in population exposure. The outcomes for PM2.5 are mixed with annual population exposure increases of 4–7% mainly occurring because of increases in summer PM2.5 exposure. Winter-time PM2.5 exposure reductions are predicted and are associated with warmer temperatures and reduced woodheater usage. Peak concentrations of NO_2 were projected to increase by up to 10 ppb, and population exposure was predicted to increase by 3–5%.

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EVALUATION OF A GLOBAL AEROSOL MODEL PREDICTIONS OF AEROSOL OPTICAL DEPTH IN THE AUSTRALIAN REGION

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Abstract

Multi-phase chemistry in the atmosphere has a significant influence on climate. For aerosols, the globally averaged net radiative effect is negative (1.2 W m^{-2} or 75% of forcing due to the CO_2 increase since pre-industrial times) and 60% of this aerosol forcing is caused by aerosol-cloud interaction, the most uncertain of the anthropogenic forcings. These large uncertainties make it difficult to use the observed temperature record to constrain estimates of the earth's climate sensitivity. Hence, a better understanding of aerosol effects is essential in order to reconcile modelled and observed climate variability and climate change. Although growth of greenhouse gases is expected to eventually become the dominant driver of climate change during the 21st century, it will be difficult to predict regional climate change without improved knowledge of the climatic effects of aerosols.

Global Climate Models are important tools for understanding the influence of multiphase atmospheric chemistry on climate. Within ACCESS the UK Chemistry Aerosol Community Model (UKCA) is being developed to simulate and predict atmospheric chemistry and composition both for the globe and the Australian region. The importance of ground-truthing such a Global Chemical transport Model with observations has been stressed in a number of forums including the National Climate Framework.

We employed the Global Model of Aerosol Processes (GLOMAP http://www.env.leeds.ac.uk/research/icas/clouds/current/glomap.html) to simulate aerosol optical depth (AOD) across the Australian continent for August 2007 to July 2008 and compared these results to observations of AOD made in the Aerosol Ground Station Network (AGSNet) (Mitchell, Campbell *et al*. 2010).

We have used the mode version of GLOMAP, which is the aerosol scheme used by ACCESS UKCA (re-named to the mode-aerosol scheme in the UKCA computational platform). Our application of GLOMAP is forced by meteorology from ECMWF analysis fields and gas phase chemistry from an external global chemical transport model. This configuration has historically been used for isolating and investigating individual earth-system processes and doesn't include feedback between the aerosol and meteorological fields. AOD is an integrated measure of aerosol loading and results from the ability of particles to scatter and absorb radiation. Hence AOD has become an important parameter for the quantification of direct radiative forcing. In addition the retrieval of AOD from satellite-borne instrumentation such as MODIS means it is the most significant aerosol parameter for which there is global coverage – an important factor

when we consider the need for comprehensive datasets to verify the performance of global climate models.

AOD modelled by GLOMAP and observed by AGSNet at Darwin and Jabiru in northern tropical Australia and Birdsville and Tinga Tinganan in central Australia are compared in Fig. 1. Also shown in each panel is the Dust Storm Index (DSI) for each site - which is a measure of the frequency and intensity of wind erosion (McTainsh and Tews 2007). Large DSI at the two central Australian sites indicate high levels of dust storm occurrences. While significant gaps in the observational data are evident, GLOMAP under predicts AOD at tropical sites particularly during the 2007 dry season and over predicts AOD at central Australia sites during May 2008. Smoke from biomass burning is a significant source of aerosol to tropical Australia during the dry season. Under-prediction of AOD by GLOMAP suggests that the biomass burning emissions inventory utilised in this work underestimates the emissions for northern Australia in 2007 and 2008. Luhar *et al*. (2008) were able to precisely reproduce AOD over Jabiru and Darwin using TAPM (a limited-area meso-scale meteorological and chemical transport model) run with detailed burning emission fields developed by Meyer *et al*. (2008). Dust is a significant source of aerosol in central Australia. Over prediction of AOD by GLOMAP suggests that the dust formation module may require further refinement for Australian conditions. Finally comparing climatologies of observed AOD with climatologies of GLOMAP AOD may remove biases introduced by gaps in observational data sets (Mitchell *et al*. 2010).

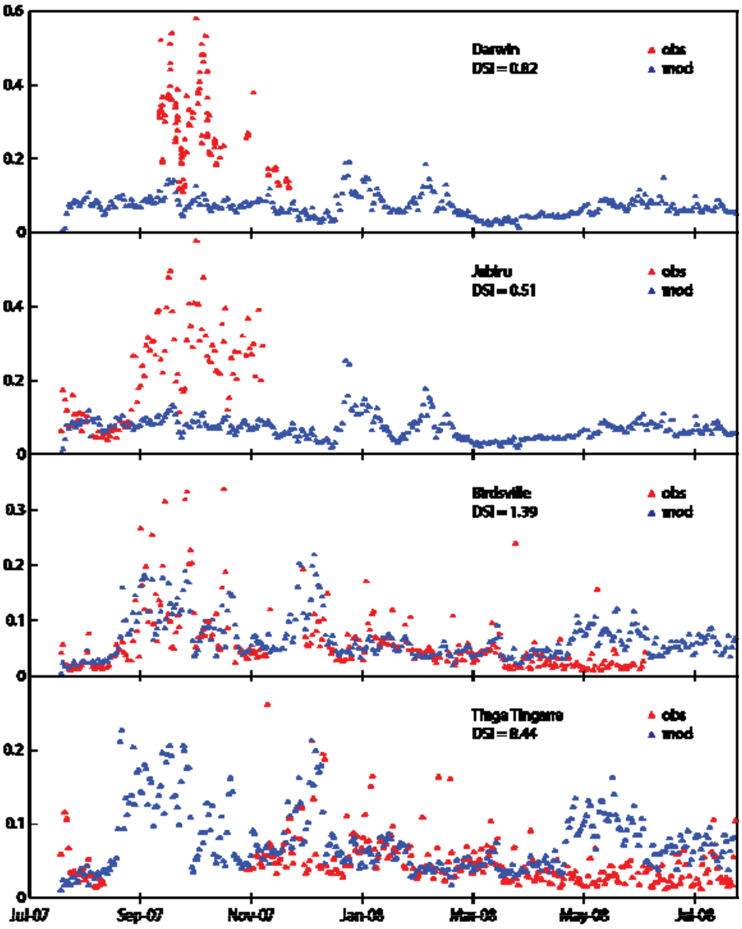

Fig. 1 Observed and modelled aerosol optical depth for selected sites in Australia. Also shown is the Dust Storm Index (DSI) for each site

On-going research will comprise process-modelling experiments where model components are challenged and informed by observational data of atmospheric chemical composition, aerosol chemistry and microphysics. These experiments form part of a long-term goal to determine the significance of long lived greenhouse gases, aerosols and reactive gases as drivers of radiative forcing in the Southern Hemisphere (SH) and Australasian region.

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DEVELOPING COUPLED STRATOSPHERIC CHEMISTRY CAPABILITY WITHIN ACCESS

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Abstract

The implementation of the UK Chemistry and Aerosol model (UKCA) within the Australian Community Climate and Earth System Simulator (ACCESS) enables coupled chemistry-climate simulations of the impact of stratospheric ozone chemistry on atmospheric composition, radiation balance and dynamics. We will show results from a simulation with fixed sea surface temperatures and increasing chlorofluorocarbon (CFC) concentrations from 1971 to 2009. Results show an Antarctic ozone hole consistent with satellite and ozonesonde observations, as do the simulated fields of other constituents such as N_2O and CH_4 with HALOE and CLAES satellite climataologies, however some biases exist. Comparisons with and temperature and winds fields from ERA reanalyses also show good agreement.

Globally, the simulations are reasonable, but the Antarctic ozone hole is too shallow and begins too early in the season. Temperatures tend to be slightly warmer than observations by around 10ºC. These biases are consistent with an overly weak Brewer Dobson circulation, which is driven by breaking gravity waves in the stratosphere. We will present simulations testing the effects of different parameter values for the gravity wave schemes within the UM. In addition, future plans for simulations coupled to the ocean model will be discussed.

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FLUX METHODS DEVELOPMENT AND APPLICATION TO THE MEASUREMENT OF THE AIR-SURFACE EXCHANGE OF ATMOSPHERIC MERCURY FROM NATURAL SOURCES OVER AUSTRALIAN ECOSYSTEMS

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Abstract

There are essentially no data on the emission and deposition of atmospheric mercury from natural sources over Australian environs. Moreover, there is an overall lack of data on natural sources and sinks for atmospheric mercury in the Southern Hemisphere. Australia presents a unique opportunity to study the natural emission/deposition/re-emission/biogeochemical cycling of atmospheric mercury.

Micrometeorological and dynamic flux chamber based Gaseous Elemental Mercury (GEM) air-surface exchange techniques are being developed and applied to the measurement of GEM flux. A full suite of environmental correlates are measured concurrently with the GEM flux (e.g., substrate properties, temperature, humidity, solar radiation, energy balance components, precipitation, other trace gases) to advance our understanding of climatic drivers and the impact of climate change on the mercury cycle. This poster presents some of the first GEM flux measurements from natural geogenic sources in Australia.

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TESTING ATMOSPHERIC MONITORING TECHNIQUES FOR GEOLOGICAL STORAGE OF CO_2

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Abstract

The success of CO_2 geological storage in mitigating climate change will depend on its ability to withhold large amounts of CO_2 from the atmosphere over centuries or more. Atmospheric techniques have been used to monitor Australia's first geosequestration project, the CO2CRC Otway Project, since its inception (Etheridge *et al.* 2011; Jenkins *et al.* 2011). These techniques have been developed to be sensitive (detecting small potential leakage signals against large and variable background CO_2 concentrations and fluxes), specific (attributing variations to sources using chemical and isotopic fingerprints and dispersion modelling) and practical (continuous remote operation) (Leuning *et al.* 2008; Luhar *et al.* 2009). A recent stage of the Otway project involved periods of controlled releases of injected gas at the surface that could mimic leakage. This provided a test of the original atmospheric scheme, complemented by additional measurements of CO_2 and CH_4 concentrations and carbon isotopes of CO_2.

Based on the experience at Otway and recent results from the new Arcturus baseline atmospheric station in Queensland, this presentation will consider the potential merits of atmospheric techniques for monitoring greenhouse gas emissions from emerging energy technologies such as geosequestration and coal seam methane.

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AUSTRALIAN AEROSOL AND CLOUD CONDENSATION NUCLEI (CCN)

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Abstract

Exploratory climate modeling suggests that aerosol effects are of comparable importance as greenhouse gases, as a driver of recent climate trends in the southern hemisphere, including Australia (Rotstayn *et al*. 2007, 2010). A 2008 CSIRO review considered the possible climatic effects of natural and anthropogenic aerosol located in the Australian region (Rotstayn *et al*. 2008). Observations and modeling suggest that various regional aerosol sources may be important, but systematic studies of their role in climate change and climate variability are currently lacking.

In addition, the aerosol indirect effects (or the effects aerosols have on cloud formation) are currently the largest uncertainty in the IPCC report estimate of anthropogenic induced climate change (IPCC 2007). There is a specific need to understand the processes involved with aerosol indirect effects and climate change in general on Australian regional aerosols such as dust emissions, bushfire emissions, Southern Ocean natural aerosol production, terrestrial biogenic aerosol and aerosol precursor emissions, transport and removal processes. A better understanding of aerosol effects is essential in order to reconcile modeled and observed climate variability and climate change.

To this aim, intensive ground-based measurements of ambient aerosols including cloud condensation nuclei (CCN) were made at three locations across Australia; a tropical site located at Gunn Point in the Northern Territory, an urban site located in a suburb approximately 22 km to the west of Sydney in New South Wales and a marine site located at the Cape Grim Baseline Monitoring Station located on the northwest tip of Tasmania.

A Scanning Mobility Particle Sizer (SMPS) spectrometer measured the size-resolved aerosol number concentration for particles between 15 and 750 nanometers. A nano SMPS measured the size resolved aerosol number concentration for particles between 4 and 150 nanometers at two of the three sites. An Aerodynamic Particle Sizer measured aerosol number concentration for particles between 0.5 to 20 micrometers at two of the three sites. A CCN counter measured the size resolved CCN number concentration for CCN between 0.75 and 10 micrometers, over a super saturation range of 0.1 to 0.9 %. The size-resolved chemical composition of aerosols was determined on samples collected with a cascade impactor, high volume and low volume samplers.

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The influence of important aerosol sources and processes to the Australian continent such as biomass burning, urban vehicle emissions, secondary formation and marine sources on CCN formation and regulation will be discussed in this presentation.

This work was supported by the Australian Climate Change Science Program.

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CAPE GRIM – A GLOBAL CARBON CYCLE CANARY?

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Abstract

At the time of the establishment of Cape Grim, design studies for a global CO_2 sampling network suggested that 1-2 sites were all that was necessary to monitor global trends (e.g WMO 1981). The choice of location, infrastructure and programs at Cape Grim were heavily influenced by the desire to be such a station. More than 30 years on, how well has that ambition been realised?

Figure 1 shows the five year trend in the annual accumulation of carbon dioxide in selected LoFlo data from Cape Grim show a near-monotonic decline in growth rate from 2.15 ± 0.05 ppm yr^{-1} in 2002 to 1.78 ± 0.05 ppm yr^{-1} in 2011. Five-year smoothing (Enting *et al*. 2006), is used in order to suppress the 3-5 year variability observed in the record and associated with ENSO and volcanic activity.

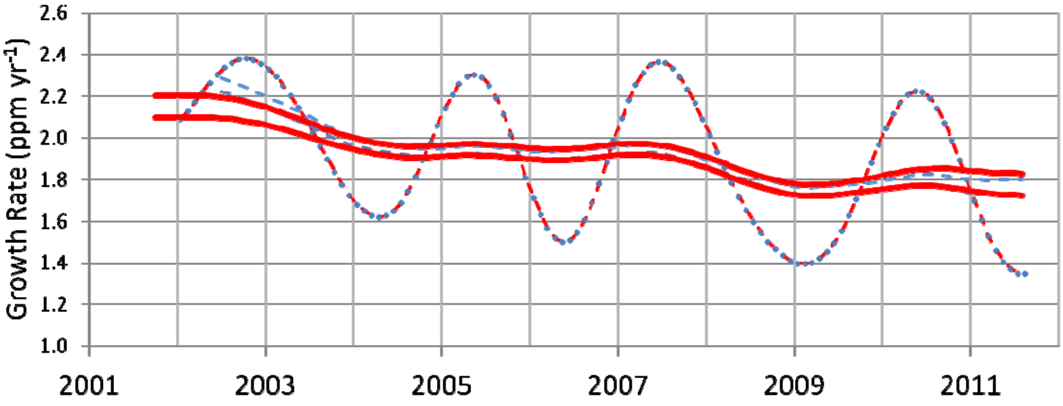

Fig. 1 CO_2 growth rate (1.8 yr) and uncertainty band for 5-year smoothing, in Cape Grim LoFlo data, selected for maximum spatial representativeness (>100° longitude, ~50° latitude, 8 km altitude).

In proposing this smoothed and differentiated record of CO_2 concentrations (routinely updated monthly) as an early indication of trends in the global carbon cycle, the following points need to be addressed:

1. Is the trend sensitive to measurement methodology?
2. What is the uncertainty in the trend, particularly near the end of the smoothed record?
3. What is the spatial representativeness of the Cape Grim data?

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4. How does the Cape Grim trend, and its uncertainty, compare with those measured at other globally-distributed sites?
5. In terms of providing a constraint on anthropogenic emissions, can ‘natural’ influences on the growth rate explain observed trends?

Some of these factors were addressed in Francey *et al.* (2010) using data through to 2008. That analysis is updated and extended to include data through to mid-2011.

Data Selection to distinguish global from regional (especially northern hemisphere) signals is identified as the major consideration in reducing global growth rate uncertainty; we use the scatter in monthly average measurements on flask air as a comparative measure of spatial representativeness. Compared to Cape Grim and sites further south, northern hemisphere (NH) mean trends are similar in sign, but slightly larger in amplitude (as expected since the major emissions are released in the NH and the exchange between hemispheres is slow compared to within-hemisphere mixing). But the northern uncertainties are too large to confirm the decreasing LoFlo trend, for example. We interpret the post-2002/3 declining trend in CO_2 growth as a more direct indication of changes in CO_2-induced climate forcing and ocean acidification than data with smaller spatial representation.

However, the slowing is in apparent conflict with the reported 30% increase in global CO_2 emissions due to human activity since 2000 (Le Quéré et al. 2010) and recent bottom-up estimates suggesting that the natural removal of atmospheric CO_2 by oceanic and terrestrial systems have slowed (e.g. Sarmiento *et al.* 2009; Pan *et al.* 2011). These factors all suggest an accelerating accumulation of CO_2 in the atmosphere, also an increase in inter-hemispheric gradient. Neither is observed, most significantly through a post-2000 period of low ENSO and volcanic activity. It will be demonstrated that recent modelling studies reporting decadal trends in the carbon sinks: a) underestimate uncertainty in FF emissions (R. Andres, CDIAC, personal communication), b) overestimate uncertainty in global CO_2 trends and c) have so many degrees of freedom that the mixing capacity of the atmosphere is not fully exploited.

Within the uncertainties of source and sink strengths and atmospheric accumulation, a simple solution was postulated by Francey *et al.* (2010), and reinforced here, involving small bias in early reported anthropogenic CO_2 emissions. With this assumption, a global mass balance persists throughout, the airborne fraction of fossil fuel CO_2 emissions remains relatively constant and human emissions track the mid-range of IPCC SRES socio-economic emission scenarios.

With regard to an on-going ‘canary’ role, there are few technical barriers preventing the placement of monthly-updated baseline selected Cape Grim LoFlo data on the web. Ideally this should be based on hourly baseline values selected on the basis of Rn^{222} values though several selection criteria give similar results. Smoothed trends with or without empirical suppression of inter-annual variability due to ENSO and explosive volcanoes could be easily included. These have proven a reliable indication of global trends with small uncertainty, and away from periods of unusual ENSO or volcanic activity (and in the absence of independent information on previously unidentified sink changes), a means of verifying global emissions.

Acknowledgments

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AN AUSTRALIAN GREENHOUSE GAS OBSERVATION NETWORK (AGGON)

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Abstract

Australian greenhouse gas (GHG) emissions are reported annually by the Department of Climate Change and Energy Efficiency (DCCEE, 2011) to the United Nations Framework Convention on Climate Change (UNFCCC). The emissions are calculated using so-called 'bottom-up' methodologies specified by the Intergovernmental Panel on Climate Change (IPCC).

The IPCC guidelines (IPCC, 2006) to estimate national GHG emissions recommend a series of verification options to assess the accuracy and uncertainty of the resultant emission inventories, including comparisons with emissions estimated by inverse modelling of '*atmospheric measurements at local, regional and on global scales'*.

This latter verification tool is only just starting to be deployed, as GHG measurement methods have improved and become more cost-effective, including the measurement of isotopic GHG data, and modelling techniques, with increased spatial resolution (down to regional), are evolving rapidly. Scientists have begun to argue that regulation of GHG emissions can only have integrity if verified by comparison with emissions derived from direct atmospheric measurements (Nisbet & Weiss, 2010).

Emissions estimated from atmospheric data have already being reported in national inventories to the UNFCCC by the UK (for methane - CH_4, nitrous oxide - N_2O and synthetic GHGs - SGGs), and by Australia (for SGGs) (DCCEE, 2011). In the recent (April 2011) submission by DCCEE to the UNFCCC, reporting the Australian National Greenhouse Gas Inventory (NGGI) for 2009, atmospheric observations from Cape Grim, Tasmania, were, for the first time, used to verify the Australian inventory emissions of SGGs (hydrofluorocarbons – HFCs, perfluorocarbons – PFCs and sulphur hexafluoride – SF_6).

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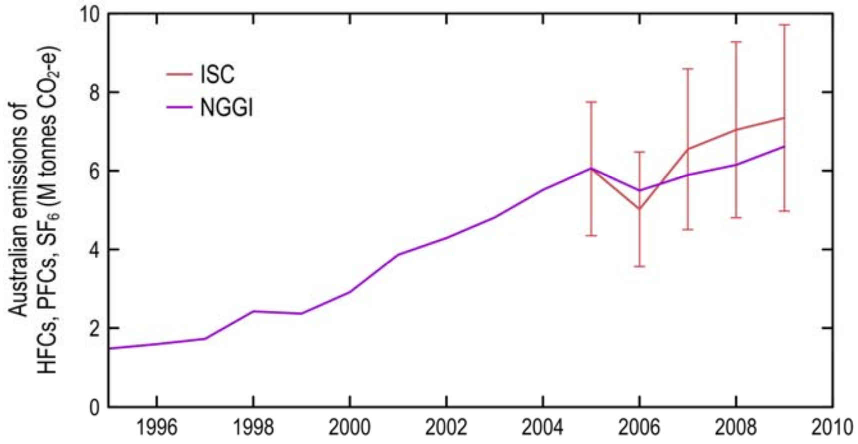

Fig. 2 Australian emissions (Mtonnes CO_2-e) of HFCs, PFCs and SF_6 in the NGGI (purple line) and derived from atmospheric observations at Cape Grim, Tasmania (red line, 1σ uncertainties) (DCCEE, 2011).

In order to achieve this 'atmospheric verification' for all Australian GHG emissions, in particular carbon dioxide (CO_2), CH_4 and N_2O, which have significant biogenic and anthropogenic emissions, the Australian atmosphere has to be measured at a relatively high spatial (in particular in the tropics) and temporal resolution via networks of ground-based stations, employing *in situ* (preferably via tall towers if continental) surface measurements, in conjunction with atmospheric column measurements (aircraft and/or remote sensing from the surface or space i.e. satellite-borne remote sensing). In addition, the modelling capability needs to be developed (RECCAP for example, Canadell *et al.* 2011) that can synthesize the resultant data fields, derive emissions and compare to 'bottom-up' budgets on a variety of spatial and temporal scales.

The pressures of emissions control legislation and the value of emission reductions, once a carbon-price is established in a carbon-trading market, could create strong incentives for mis-reporting of emissions. The 'top-down' approach to emissions verification requires a more intensive global (or national) network of monitoring stations than we currently have, but the cost will be small compared to the possible value of mis-reported emissions. Such verification may be critical to a revised and more potent UNFCCC regulatory framework that would seem necessary to bring global emissions of GHGs under control.

In an Australian context, with moves to a carbon-constrained future driven by carbon pricing and the adoption of a national strategy to deploy carbon capture and storage (CCS) as an emissions mitigation option, there will be a demand from government policy, financial markets, the legal community and public assurance for independent and verifiable estimates of emissions, as both national aggregates as well as emissions from targeted sectors such as energy, forestry, mining and agriculture.

These requirements cannot be met with the existing Australian atmospheric observational infrastructure, which needs to be expanded into an Australian Greenhouse Gas Observation Network (AGGON). The number and location (guided by network design tools – for example Law *et al.* 2004) of the GHG observing stations is GHG species dependent. Ideas will be presented on the size and shape, capability and cost of an Australian Greenhouse Gas

Observation Network and will be compared to emerging network designs in Europe and the USA.

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ATMOSPHERIC GREENHOUSE GAS RESEARCH AT CSIRO: A 40 YEAR ODYSSEY

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Abstract

This year, 2011, marks the 40th anniversary of the initial background greenhouse gas (GHG) measurements made by CSIRO scientists in Australia. In 1971, under conditions when the boundary layer and the free troposphere were mixing strongly, Graeme Pearman and John Garratt, members of CSIRO's Agricultural Meteorology team, measured near free-tropospheric levels of carbon dioxide (CO_2) over a wheat crop at Rutherglen, Victoria.

This lead to the establishment in 1972 of an innovative air sampling and CO_2 measurement capability (Pearman and Garratt, 1972), collecting air samples from the free troposphere over southern Australia (Tasman Sea, Bass Strait, Great Australian Bight) and analysing them on a Non-Dispersive Infrared (NDIR) CO_2 analyser at CSIRO's Division of Meteorological Physics, Aspendale (Fig. 1).

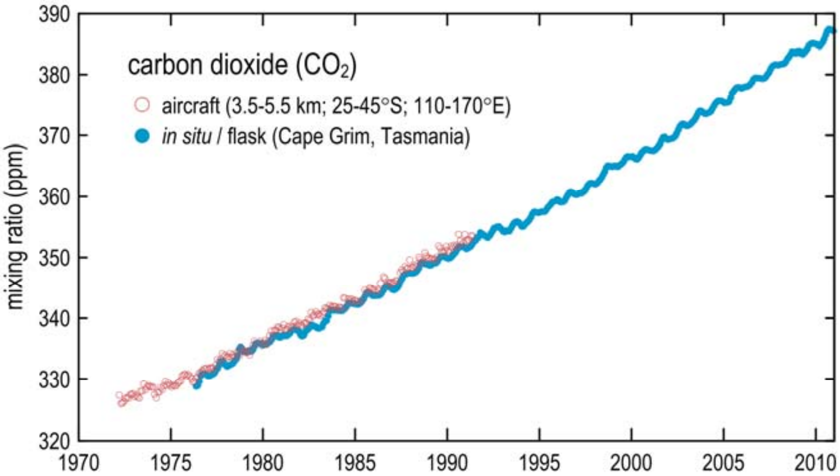

Fig. 3 The CSIRO record of CO_2 over southern Australia and at Cape Grim, Tasmania.

Since the ground-breaking work of Pearman and Garratt in 1972, the CSIRO GHG observational program has expanded in space, time and speciation (Fraser, 2007). The program operates the second largest global air sampling network for GHG observations in the world, including isotopic measurements, and the most comprehensive set of GHG species measurements in the world, including CO_2, methane (CH_4), nitrous oxide (N_2O) and approximately 50 synthetic GHGs (SGGs), such as chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs).

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The program has produced iconic 2000 year records of GHG concentrations and isotopic composition (Fig. 2), at unprecedented age resolution, precision and connectivity to modern, direct records, which have been used to derive accurate records of radiative forcing over the pre-industrial-industrial period. A major focus of CSIRO's GHG research has been at Cape Grim, arguably the most important baseline station in the Southern Hemisphere. The Cape Grim air archive has been studied by numerous CSIRO, national and international scientists/students to produce some of the most-used records of a wide range of GHGs since 1978.

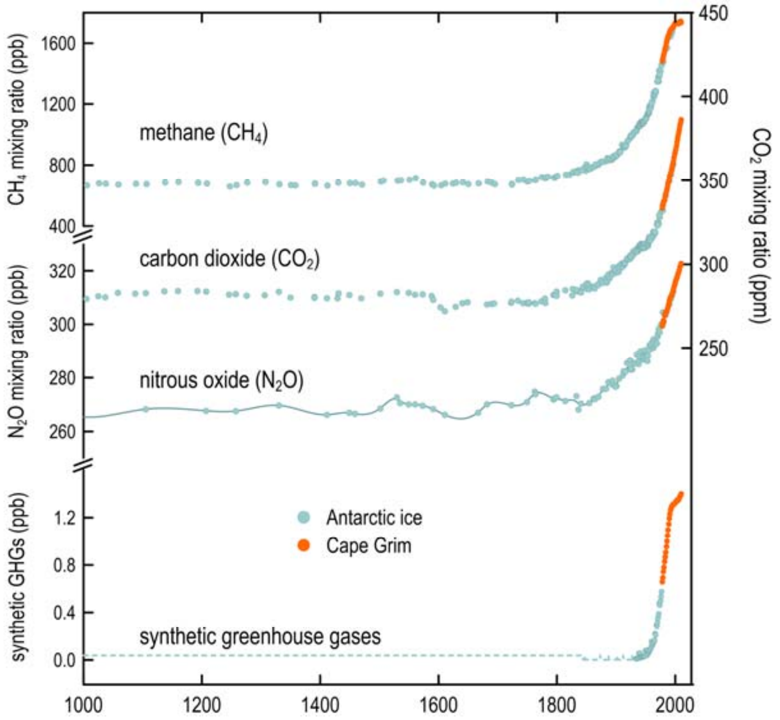

Fig. 2 Long-term observational records of all GHGs from Antarctic ice and firn air samples and from Cape Grim measurements.

CSIRO scientists involved in atmospheric GHG observations have collaborated with national and international modelling teams to derive emissions of GHGs on regional to global scales. Some of these emission estimates have been included as examples of 'top-down' atmospheric verification of emissions of SGGs in the National Greenhouse Gas Inventory (NGGI: DCCEE, 2011).

This paper will present a somewhat personal view of the history of GHG observational research at CSIRO.

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LONG TERM TRENDS IN OZONE IN THE SOUTHERN OCEAN MARINE BOUNDARY LAYER AND IN THE MID-LATITUDES FREE TROPOSPHERE OF THE SOUTHERN HEMISPHERE

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Abstract

Ozone in the troposphere has four important roles. Tropospheric ozone is a greenhouse gas, ranked third in anthropogenic radiative forcing after CO_2 and CH_4; ozone in the troposphere makes up an important fraction of the atmospheric shield against ultraviolet radiation particularly when ozone depletion events occur and when the total column abundance of ozone drops below 200 DU; tropospheric ozone drives tropospheric chemistry including the sink for gases such a methane, and increases in background ozone have impacts also on the occurrence of urban and regional photochemical smog, related health effects and crop damage.

There is very limited long term monitoring and few process studies of tropospheric ozone in the Southern Hemisphere. Due to the very different mixes of anthropogenic and natural sources, different regimes of tropospheric ozone may occur in each hemisphere.

Long term trends in tropospheric ozone, calculated from deseasonalised data, for the periods 1980 – 2009, 1990-1999, 1990 - 2009 and 2000 – 2009, where data permits, will be presented for four sites spanning the Southern Ocean. The sites and relevant details are:

Cape Grim Tasmania, 40.38ºS, 144.69ºE, 104 m asl, where surface ozone measurements from 1982 to 2010 will be presented including baseline ozone concentrations representative of the Southern Ocean marine boundary layer, and non-baseline representing regional influences.

Broadmeadows Victoria, Australia, 37.69ºS 144.95ºE where the ozone sonde data from 1999-2010 will be presented and trends calculated for the standard heights 0-1 km, 1-3 km, 3-8 km, and upper troposphere/lower stratosphere.

Macquarie Island, 54.50ºS 158.94ºE, where the ozone sonde data from 1994-2010 will be presented and trends calculated for the standard heights 0-1 km, 1-3 km, 3-8 km, and upper troposphere/lower stratosphere.

Davis, Antarctica 68.58ºS, 77.97ºE, where the ozone sonde data from 2003-2010 will be presented and trends calculated for the standard heights 0-1 km, 1-3 km, 3-7 km, and upper

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troposphere/lower stratosphere. A lower height of 7 km is used at this site for the upper bound of the middle troposphere layer because of the lower tropopause in winter.

Analyses of the contributions of various processes to the observed southern hemisphere tropospheric ozone ternds will be discussed. These include (a) dynamical effects including ENSO, SAM and the strength of the stratospheric/tropospheric exchange and (c) chemical processes including changes in biomass burning and the trends in methane in the southern hemisphere.

THE AUSTRALASIAN METHANE BUDGET: OVERVIEW AND MEASUREMENTS

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Abstract

Recent global trends in atmospheric methane concentrations have been enigmatic, in particular with a slowdown in the increase rate through the first decade of this century and a more recent acceleration of this growth rate. This paper will provide an overview and update of the global methane budget, present Australian measurements of both in situ and total column methane amounts, and put regional Australasian sources and sinks into the global context.

In Australia and particularly New Zealand, agriculture plays a major role in methane emissions, principally through cattle and sheep. We have developed and applied new techniques for determining methane emissions from free-ranging livestock, and these will be described.

Northern Australian tropical wetlands are also a major contributor to Australia's methane budget. Transects of surface concentrations taken on the Ghan railway between Adelaide (34ºS) and Darwin (12ºS) using a portable FTIR analyser consistently show a latitudinal gradient (increasing northwards) and enhanced methane concentrations during the wet season. These measurements and their interpretation through GEOS-Chem modeling will also be presented.

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COMMISSIONING OF SIFT-MS FOR AMBIENT MEASUREMENTS OF VOCS AT WOLLONGONG, NSW

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Abstract

The University of Wollongong has recently acquired a Selected-Ion Flow-Tube Mass Spectrometer (SIFT-MS) and is in the process of commissioning the instrument for measurements of Volatile Organic Compounds (VOCs) in ambient and smoke-affected air. SIFT-MS operates in a similar manner to Proton-Transfer Mass Spectrometry (PTR-MS), a technique that has been successfully applied to atmospheric monitoring of VOCs (Galbally *et al*. 2007; de Gouw *et al*. 2003). In SIFT-MS, three reagent ions (H_3O^+, NO^+, and O_2^+) are available, enabling the detection of a wide selection of VOCs, including light alkanes, alkenes, alcohols, aromatic hydrocarbons, aldehydes, ketones, as well as some carboxylic acids and inorganic species such as ammonia (NH_3), hydrogen cyanide (HCN), and carbon sulfoxide (COS). Although the SIFT-MS is in principle capable of measuring all the species listed above, we are currently testing whether detection of ambient concentrations will actually be achievable. Our aims are then to determine average ground-level ambient concentrations for a number of VOCs at Wollongong, NSW, and to analyse grab samples of smoke obtained during local hazard reduction burns.

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POLARSONDE: A SENSOR FOR SUPER-COOLED LIQUID WATER

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Abstract

A low-cost polarisation back-scatter sonde (Polarsonde) based on light emitting diodes is proposed as a means to detect super-cooled liquid water in clouds. This device is intended as an enhancement for standard radiosondes that measure pressure, temperature and humidity. A proof-of-principle experiment is described, and potential applications are discussed.

Introduction

Super-cooled liquid water in clouds is an aircraft icing hazard, and at present there is no technique in widespread, regular use for detecting its presence. The proportions of liquid and ice in mixed-phase clouds are also important in determining the radiative properties of clouds. Mixed phase cloud is included in models such as the ECMWF model, but the ice-fraction is calculated purely on the basis of temperature (ECMWF 2010). Studies of high latitude cloud with a cloud particle imager carried on a tethered balloon have shown that liquid can be present in more than one layer in a mixed-phase cloud (Lawson *et al.* 2011), a circumstance outside the scope of that parametrization. Recent lidar work has shown that the frequency of the liquid phase at temperatures below -15°C appears to increase with increasing southern latitude (Kanitz *et al.* 2011).

Other than by imaging cloud particles, Doppler or polarimetric radar is the technique usually used to detect super-cooled liquid in the interior of a cloud (Luke *et al.* 2010). Multiple band radar using a differential absorption technique has also been tried (Reehorst *et al.* 2008). Polarimetric lidar is able to detect mixed phase in optically thin clouds or at the proximal surface (Winker *et al.* 2010). However there is yet no relatively low-cost technique for profiling ice-fraction through a cloud.

Recent advances in light emitting diode (LED) technology mean that LEDs with quite high output powers (ca 400 mW) are available for very low cost (<$10). This raises the possibility of expendable back-scatter sondes as a means to detect super-cooled liquid in a cloud. The principle to be used is polarimetric; the backscattering of light from spherical liquid droplets is, neglecting multiple scattering, polarisation preserving. On the other hand back-scattering from ice-crystals alters polarisation. We thus envisage a package with a polarised LED and two detector channels, one for polarisation parallel to that of the LED, and one perpendicular. This

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package could be made sufficiently cheap and light to be used as an enhancement for regular radiosonde flights.

Proof-of-principle experiment

A proof of principle experiment was conducted using mists generated in the laboratory. Two types of mist were created; one warm made by an ultrasonic mister in water, and one cold made by adding liquid nitrogen to water. The mists were illuminated by a polarised LED with a beam spread of about 0.25 rad. The polariser in front of the LED was rotated slowly on a motor drive. The illuminated spot was viewed by a photodiode with a fixed polariser in front of it. Modulation of the LED current and lock-in detection of the photocurrent were used to improve the sensitivity. Figure 1 shows representative results of this experiment, using an amber LED. Similar results were obtained with a blue LED. The measure of depolarisation used is the 'traditional' one, $\delta = I_{\perp} / I_{\mathrm{P}}$, where the ratio is that of the photocurrent with polarisation perpendicular to that of the transmitted light, to that which is parallel. Strictly speaking this is not true depolarisation, but it is a simple measure to implement, and it adequately discriminates between scattering that changes the polarisation, and scattering that does not. The photocurrent in this experiment oscillates because the polariser in front of the LED is rotating and the peaks and valleys enable calculation of δ. In calculating δ, the background photocurrent is first subtracted.

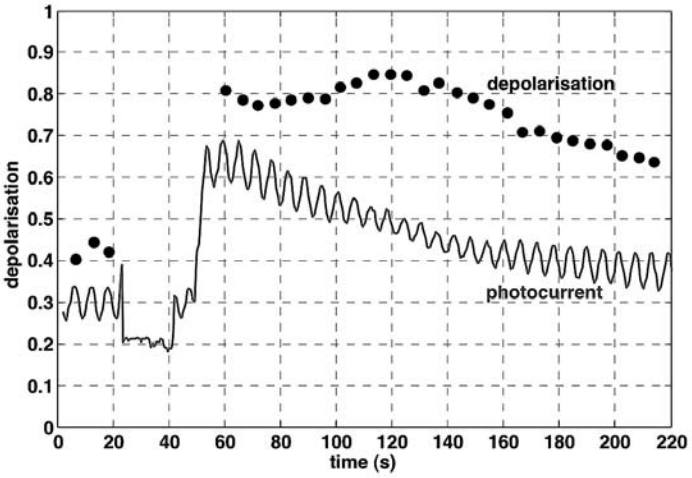

Fig. 1 Depolarisation and photocurrent for light scattered from laboratory mists. Between 0 and 25 s, the mist is warm. At 25 s the LED is blocked to establish the background photocurrent. At 50 s liquid nitrogen is added to the container to create a cold mist. The photocurrent is much higher after the addition of nitrogen because the amount of mist is greater and it is closer to the photodiode.

Discussion

The results of the proof-of-principle experiment give us confidence that spherical droplets of liquid water in a mixed-phase cloud can be detected. Whether this can be turned into a quantitative measurement of ice-fraction remains to be seen. The mists used had a greater optical density than typical clouds and so multiple scattering is an issue to be addressed. Also the mist container was approximately 500 mm x 800 mm, and scattering from the container was probably present. Thus testing in real clouds, with no background objects, is the next step. If a quantitative measure of ice-fraction is to be achieved, it is certain that this will require a correlation of depolarisation with other variables such as temperature, humidity, and total backscatter. These three at least will be available from the polarsonde - radiosonde combination.

A first prototype polarsonde has been constructed and will be tested with a Vaisala RS92 radiosonde on a tethered balloon. It is designed to use the Vaisala RSA921 interface, originally intended for ozonesondes, as the interface to the RS92.

Plans for further development involve construction of several prototype polarsondes and comparison of these with instrumentation for studying cloud. One appropriate comparison is with a cloud particle imaging device on a meteorological tower, and a second is to make balloon launches of the polarsondes at a location where appropriate lidars and radars are sited. One such location is Summit Camp in Greenland. Testing polarsondes on suitably instrumented aircraft is a further possibility. This has the advantage that suitable clouds can be actively sought out. The British Antarctic Survey plans a cloud measurement campaign using aircraft in 2013 in the Arctic. Funding to exploit invitations to site/use polarsondes in both of these places is being sought.

Acknowledgments

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THE AUSTRALIAN CONTINENTAL CARBON BALANCE (RECCAP-AUSTRALIA: REGIONAL CARBON CYCLE ASSESSMENT AND PROCESSES)

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Abstract

We present a synthesis of the Australian terrestrial carbon balance including monthly time series (1990-2009) of ecosystem fluxes (GPP, NPP, Soil Respiration) and stores (biomass, soil and litter carbon pools) and annual disturbance emissions (land-use change, fire). Monthly ecosystem fluxes are used to derive average seasonal cycles, interannual C flux anomalies and the time-averaged carbon budget. This work is providing a regional assessment of the Australian carbon balance. It is addressing the significant 5-fold uncertainty revealed in the most recent review of continental long-term mean Net Primary Productivity (NPP) (Roxburgh et al. 2004), and extends this study to include monthly dynamics of all components (fluxes and stores) of the terrestrial coupled carbon and water balances. The results are feeding into the global RECCAP ('REgional Carbon Cycle Assessment and Processes') effort, which aims to increase spatial resolution of the global carbon balance, hence improving attribution to processes and hot-spots regions essential to understand the future evolution of carbon-climate feedback. Emerging highlights are:

1. We produce a new continental NPP estimate of 1.7 GT Cy^{-1} (1990-2009). This estimate falls within the significant 5-fold range (0.67 to 3.31 GT Cy^{-1}) of long term NPP estimates reviewed by Roxburgh et al. (2004).
2. The average interannual variability of Australia's NPP (+/- 0.34 GT Cy^{-1}, 1 standard deviation) is larger than Australia's total anthropogenic greenhouse gas emissions according to the National Greenhouse Gas Inventory (0.16 GT Cy^{-1}).
3. Annually recurrent (mainly grassy) vegetation and persistent (mainly woody) vegetation account for roughly equal contributions to NPP across Australia.
4. Continentally, soil evaporation accounts for 60% of total evapotranspiration.

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OVERVIEW OF THE AUSTRALIAN COMMUNITY CLIMATE AND EARTH SYSTEM SIMULATOR (ACCESS)

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Abstract

In response to ongoing demand for climate projection capability and in recognition of the need of a national approach to climate modelling, a project to develop the ‘Australian Community Climate and Earth System Simulator’ (ACCESS) was commenced in 2006 to develop the next generation of Australian climate and earth system simulation capability. The partners in this project are the CSIRO and the Bureau of Meteorology though the Centre of Australian Weather and Climate Research (CAWCR) and participating Australian Universities, including linkage via the Centre of Excellence for Climate System Science. ACCESS aims to develop prediction/projection capability spanning the range of timescales from weather prediction, through seasonal prediction, to climate change projection on centennial time scales. It aims to support the Bureau of Meteorology in the provision of meteorological services, and the interests of natural resource management and climate impact and adaptation work. It further aims to support the Assessment Reports of the Intergovernmental Panel on Climate Change (IPCC) through the provision of appropriate climate projections. The initial components of ACCESS include those for the atmospheric, oceanic, sea ice and land surface. Components for the carbon and other key biogeochemical cycles, and for atmospheric chemistry are to follow. Eventually, the system is to incorporate or support the modelling of socio-economic processes. The atmospheric component is an implementation of the Hadley Centre HadGEM atmospheric model, the ocean component is based on the GFDL MOM4p1 code, the sea ice component is based on the LANL CICE4 code, the land surface model is the Australian community CABLE model. The system includes focus on both global and regional climate modelling, with the global modelling having the initial priority so as to facilitate participation in the IPCC Fifth Assessment Report and the Coupled Model Intercomparison Project phase 5 (CMIP5). The presentation will provide an overview of the status and scope of ACCESS, including linkages with related research areas and planned timelines.

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STRATOSPHERIC WATER VAPOR OVER BOULDER, COLORADO: TRENDS, UNCERTAINTIES, AND CLIMATE IMPACTS SINCE 1980

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Introduction

Stratospheric water vapor modulates Earth's climate directly through long-wave radiative processes. A decrease (increase) in the stratospheric water vapor burden radiatively cools (warms) the troposphere and warms (cools) the stratosphere. Even though the stratosphere is extremely dry (mixing ratios <10 ppmv) compared to the wet lower troposphere (up to 30,000 ppmv), small changes in lower stratospheric water vapor can have a profound impact on global surface temperatures. Solomon *et al*. (2010) concluded that the rapid ~10% (~0.5 ppmv) decrease of stratospheric water vapor in 2000-2001 reduced by 25% the decadal (2000-2009) increase in global surface temperature expected from well-mixed greenhouses gases.

There are two main sources of water vapor in the stratosphere: entry through the tropical tropopause (Brewer 1949) and the in situ oxidation of methane (CH_4) and molecular hydrogen (H_2) (Bates and Nicolet 1950). Air masses reaching the stratosphere through the cold tropical tropopause region are essentially freeze-dried. Methane and hydrogen in the stratosphere are oxidized to water vapor in reactions that inevitably yield 2 H_2O per CH_4 oxidized (leTexier *et al*. 1988). Convective overshooting in the tropics and cross-tropopause transport in the extra-tropics can also deliver water vapor to the stratosphere, but these sources are likely minor contributors to the global stratospheric burden. Other than recirculation the main loss mechanism for stratospheric water vapor is air mass dehydration in the Antarctic vortex (Douglass and Stanford 1982).

Water vapor abundance in the northern mid-latitude lower stratosphere (i.e., θ >380 K over Boulder, Colorado, 40 °N) is significantly influenced by water vapor variations in the tropical tropopause region, especially at the lowest mid-latitude stratospheric altitudes. These variations include a seasonal cycle, driven by seasonally varying tropical tropopause temperatures, and longer-term water vapor changes in the tropical tropopause region. Over Boulder, seasonal signals from the tropics diminish with altitude and are completely mixed out above 19 km (Fig. 1). The CH_4 and H_2 oxidation sources of water vapor become important above ~20 km and grow considerably with altitude.

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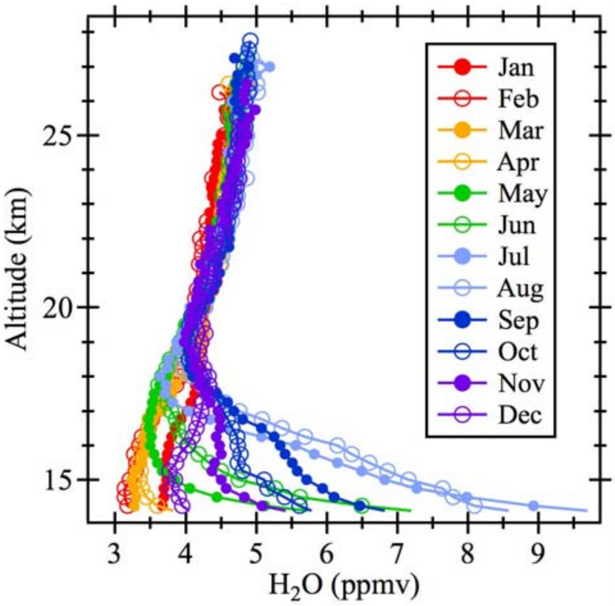

Fig. 4. The seasonal cycle of water vapor in the UT/LS over Boulder, Colorado. This seasonality, transported from the tropical lower stratosphere, is completely mixed out above ~19 km. (*from* Hurst *et al*. 2011).

Trends

The longest continuous record of stratospheric water vapor measurements in existence is from balloon-borne frost point hygrometers (FPHs) over Boulder (Fig. 2). The 31-year data record reveals a net increase of 1.0 ± 0.2 ppmv (27 ± 6%) in stratospheric water vapor mixing ratios since 1980 (Hurst *et al*. 2011). This long-term upturn is about three times the increase expected from tropospheric CH_4 growth (Dlugokencky *et al*. 2009; Rohs *et al*. 2006). Several other mechanisms that would also increase stratospheric water vapor have been postulated but not yet conclusively proven as significant contributors to the long-term increase.

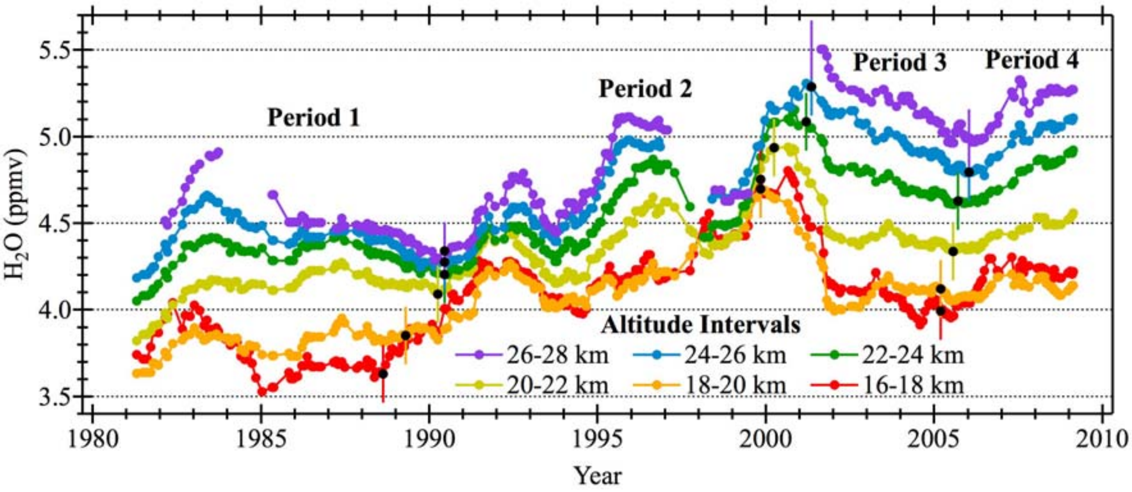

Fig. 2 Trends of stratospheric water vapor mixing ratios over Boulder, in 2-km altitude intervals. Each data point is a simple box-smoothed average (2-year box width). Gaps occur where the smoothing box fails to contain at least 12 data points. Black markers with colored vertical dashes depict the trend period boundaries for each altitude layer. (*from* Hurst *et al*. 2011).

Starting in late 2000 there was an abrupt ~10% decrease in lower stratospheric water vapor over Boulder (Figure 2), a prominent feature also seen in the HALOE stratospheric water vapor data over Boulder (Figure 3). After 2005 stratospheric water vapor started to increase again, and by 2010 the mixing ratios had recovered to their post-2000 levels, as presented in both the FPH and Aura MLS records (Figure 3). The similarity of the FPH- and satellite-based trends since 2000 adds confidence to these data sets and the trends they depict.

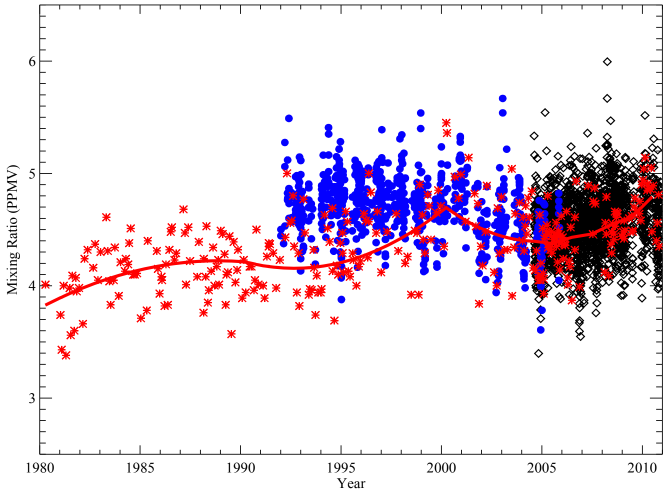

Figure 3. Stratospheric water vapor mixing ratios at 46 hPa over Boulder. Red markers and curves representing FPH mixing ratios and their trends are shown with HALOE v20 (blue) and Aura MLS v3.3 (black) mixing ratios. All HALOE mixing ratios were raised by 0.52 ppmv to better match the MLS and FPH data during the 1-year period of HALOE and MLS overlap. (*from* Rosenlof and Hurst 2011).

Uncertainties

Though the Boulder water vapor trends since 1980 are all statistically significant and, after 2000, are in quantitative agreement with satellite-based records (Figure 3), the trends from 1980-2000 are less certain. For example, HALOE mixing ratios indicate virtually no increase during 1992-2000 while the Boulder data show significant growth (Figure 3). Considerable efforts have been made without success to find a warming trend in tropical tropopause temperatures, or for that matter, a trend in anything that would explain the 1980-2000 water vapor increase over Boulder. Unfortunately the utility of comparing older satellite records with the Boulder record is greatly reduced by large (up to 50%) discrepancies between the water vapor measurements by different satellite-based sensors.

The agreement between trends in the FPH and HALOE records improves after 2000 when both show a similar sharp decline. Note that the HALOE mixing ratios in Figure 3 have been adjusted (see Figure 3 caption). The agreement between the FPH and Aura MLS records is much better, without adjustment, in terms of both the mixing ratios and trends.

There are also considerable uncertainties in estimates of the stratospheric water vapor burden. Significant disparities have existed for the past two decades, and still exist today, between in situ water vapor measurements by the FPH and those by the Harvard University Lyman-alpha instrument. At times the measurement discrepancy has been greater than 50%, propagating large uncertainties in stratospheric water vapor burden estimates. These large uncertainties severely limit the accuracy of the calculated radiative forcing by upper atmospheric water vapor.

Climate Impacts

The rapid ~10% (~0.5 ppmv) decrease in water vapor after 2000 was attributed by Randel *et al.* (2006) to anomalously cold tropical tropopause temperatures and increased tropical upwelling due to an increase in the Brewer-Dobson circulation. Reduced amounts of lower stratospheric ozone during 2001-2005, also a result of the increased tropical upwelling, may have exacerbated the lower stratospheric cooling (Randel *et al.* 2006). Stratospheric water vapor mixing ratios over Boulder were persistently low through 2005, then began to increase and by mid-2010 had nearly recovered to their pre-2000 values (Figures 2 and 3).

Solomon *et al.* (2010) evaluated the radiative forcing impact of this same decline in water vapor and, as described above, demonstrated its strong impact on global surface temperatures. Less emphasized in their work was how the net water vapor increase during 1980-2000 would have provided a positive feedback of ~30% to global surface temperatures during the 1990s.

It is clear from these examples that small deviations in the lower stratospheric water vapor burden can be both a response to and a driver of changes in the climate system.

Future

Our lack of understanding of the root causes(s) of past increases in northern mid-latitude stratospheric water vapor greatly limits our ability to predict future trends. The consensus of chemistry-climate models is that a warming climate will raise and warm the tropical tropopause, allowing more water vapor through the tropical cold trap. However, there are large disparities between different models' representations of past tropical cold point temperatures and water vapor entry mixing ratios (Gettelman *et al.*, 2010). Given our poor understanding of past water vapor increases, the large spreads in model simulations of past data, and large uncertainties in the future levels of tropospheric CH_4, it is currently not possible to confidently predict future trends in stratospheric water vapor.

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SYDNEY PARTICLE STUDY: OVERVIEW AND MOTIVATIONS

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Abstract

Studies of health impacts from atmospheric pollutants suggest that particles are currently one of the most significant pollutants with respect to human mortality and morbidity. However, reduction in particle concentrations through source regulation is challenging due to the large number particle sources (both natural and anthropogenic) present in an airshed, and the wide range of particle sizes and chemical species emitted. Additionally, secondary particles can also make a significant contribution to total particle exposure, particularly in the fine size fraction which is considered to have the largest impact on health. Being generated through photochemical processes (similar to ozone), a reduction in the concentration of secondary particles requires that source regulators also consider the relevant gas-phase precursors to these particles. Climate change projections for NSW suggest significant increases in the frequency of drought, increases in the frequency of hot days and increases in the frequency of high fire risk weather. This has important ramifications for air pollution and health, with atmospheric particle smog severity linked to the frequency of hot, sunny days, and with the highest particle pollution concentrations linked to the presence of bushfire plumes in the Sydney airshed. Particles and ozone are also coupled, with enhanced ozone concentrations often observed on bushfire days and with 50% or greater of fine particle mass potentially of photochemical origin.

The development of a long term control strategy for particles in Sydney can be informed through the use of comprehensive three-dimensional simulations of the atmosphere, sources and multi-phase phase chemistry. However the development of such modelling capability requires a good understanding of the contribution made by local and remote particles sources to the total particle exposure within the region. Such understanding requires detailed and high quality data sets.

We present here an overview of the Sydney Particle Study, a combined modelling and observation project which included an intensive field campaign of aerosol and aerosol precursor measurements carried out in Sydney during February 2011. We focus our discussion on the field campaign which combined sophisticated measurement techniques to produce a high quality data set of atmospheric composition observations. The campaign was a collaboration

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between CSIRO Marine and Atmospheric Research, NSW Office of Environment and Heritage, Queensland University of Technology and ANSTO. Data collected included criteria pollutant concentrations, aerosol microphysical properties, aerosol chemical composition (as a function of size, integrated over 4 hours and in real time), concentration of volatile organic compounds (integrated over 4 hours and in real time) and radon concentrations.

Continuous aerosol size distributions indicated the occurrence of secondary aerosol formation occurring in the afternoons on approximately 50% of the days sampled. Data analysis continues in order to understand the processes driving this secondary formation.

RADICAL CHEMISTRY IN THE REMOTE MARINE BOUNDARY LAYER

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Abstract

The remote marine boundary layer covering large areas of our planet is one of the cleanest atmospheric environments on Earth. It is thus an ideal location to study the basic photochemistry reactions occurring in the atmosphere largely unaffected by emissions. Furthermore, characterisation of the oxidation capacity in the marine boundary layer is important in order to understand the oxidation of marine volatile organic compounds (VOCs) and its impact on aerosol formation and the global ozone budget.

Here we present measurements of OH and HO_2 from the OOMPH campaign, which took place in March 2007 in the South Atlantic (28ºS-57ºS, 46ºW-34ºE) on the French research vessel Marion Dufresne operated by the French Polar Institute (IPEV). Using photolysis frequencies and relevant trace gas concentration data also available from this campaign, we assess our present understanding of the photochemistry in pristine air through comparison with previous measurements at different locations and with a simple box model.

When the wind was coming from behind sometimes emissions from the ship stack were detected. The impact of these emissions on the OH and HO_2 measured during the first few seconds of mixing with the clean marine air is also discussed.

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THE CARBON CYCLE IN ACCESS

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Abstract

The Australian Community Climate and Earth System Simulator (ACCESS) will be used to simulate the carbon cycle and its interactions with climate. This requires sub-models to simulate carbon exchange between the land and atmosphere and between the ocean and atmosphere. Land uptake of carbon by photosynthesis is simulated by the Community Atmosphere Land Biosphere Exchange (CABLE) model. CABLE also includes simplified plant and soil respiration functions but a more comprehensive treatment of these fluxes and their associated carbon pools is provided by CASA-CNP. CASA-CNP can also be used to simulate nutrient (nitrogen and phosphorus) limitation on carbon fluxes. The ocean carbon cycle is modelled using WOMBAT (world ocean model with biogeochemistry and trophic-dynamics). WOMBAT includes a two-component plankton model (phytoplankton and zooplankton) where the phytoplankton growth is controlled by phosphate and iron concentrations, light and temperature.

Two types of carbon-climate simulations are specified in the Coupled Model Intercomparison Project (CMIP5). The first type, Representative Concentration Pathways (RCP), prescribe atmospheric CO_2 concentrations and carbon fluxes are diagnosed but do not change atmospheric CO_2 concentration. The second type uses prescribed anthropogenic carbon fluxes and simulates atmospheric CO_2 concentration; different cases are performed with climate interactions switched on or off. We will describe progress in diagnosing carbon fluxes from ACCESS for RCP cases.

Atmospheric measurements of CO_2 contain important information about the carbon cycle. ACCESS allows CO_2 to be modelled as an atmospheric tracer. Extra atmospheric tracers, such as radon, can also be simulated for diagnostic purposes. One challenge for comparing simulated and observed concentrations is how the model output is sampled, particularly for coastal sites. This will be discussed in relation to Cape Grim.

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BIOMASS BURNING EMISSIONS FROM THE 2006 ROBBINS ISLAND FIRE, TASMANIA 41ºS

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Abstract

VOCs affect climate by driving formation of tropospheric ozone and secondary organic aerosol, (SOA) while aerosol has both direct and cloud albedo climate effects (through cloud condensation nuclei, CCN). The degree of radiative forcing from aerosol and tropospheric ozone is highly uncertain (IPCC 2007). Biomass burning is an important source of VOCs and aerosols in Australia. It is therefore crucial to understand the composition of smoke plumes and the processes within plumes that govern aerosol formation.

Measurements of reactive gases and aerosol were made at the Cape Grim Baseline Air Pollution Station from the 10 February to the 1 March 2006, as part of the Precursors to Particles (P2P) campaign (Cainey *et al*. 2007). For four days the station was impacted by a biomass burning plume from a fire on Robbins Island 20km east of the station. This fire gave a unique opportunity to examine the affect of the smoke plume on the composition of the air in this otherwise very clean marine boundary layer environment.

We present some observations including identities and concentrations of VOCs in the smoke plume, (measured using Proton Transfer Reaction Mass Spectrometry), ozone concentrations, and aerosol properties including CCN concentration, Condensation Nuclei (CN) concentration, black carbon, and size resolved aerosol distributions. Using these data the effect of biomass burning on VOC composition and aerosol properties are explored. In particular we explore the differences between the composition of fresh smoke plumes, in which primary VOCs are observed, and aged smoke plumes in which photochemically produced VOCs and ozone are observed. We also use aerosol size distributions to look for evidence of SOA formation and growth during these photochemical events and attempt to identify VOCs implicated. We use CO and CO_2 data to estimate Modified Combustion Efficiencies for the Robbins Island fire, and estimate VOC and aerosol Emission Factors. We also explore the effect of the biomass burning plume on the ability of aerosols at Cape Grim to form CCN.

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A greater understanding of the chemical composition and processes occurring within biomass burning plumes will ensure the accurate representation of reactive chemistry and aerosols in chemical transport models, as well as ground-truthing data retrieved by remote sensing technology.

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METHANE SIMULATIONS AT CAPE GRIM TO ASSESS METHANE FLUX ESTIMATES FOR SOUTH EAST AUSTRALIA

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Abstract

A transport model intercomparison for methane (TransCom-CH_4) has been run involving twelve models (Patra *et al.*, 2011). We contributed simulations using two climate models, CCAM and ACCESS. The CCAM simulations were nudged to NCEP analysed meteorology, which allows simulated atmospheric concentrations to be compared to observations on synoptic timescales. The ACCESS simulations were forced only with observed sea surface temperatures and are consequently not expected to match observed synoptic variations. The TransCom experiment involved simulating six CH_4 tracers (with different prescribed fluxes) along with SF_6, radon and methyl chloroform. We have analysed hourly model output for Cape Grim and find that the magnitude of the non-baseline signal differs, especially in winter, dependent on the CH_4 flux scenario used. The magnitude of the non-baseline signal also varies between models, although these differences can be reconciled when methane is scaled by model-simulated radon concentration. Comparison with observed CH_4, also scaled using radon, suggests that the CH_4 flux scenario with little or no wetland emissions in winter matches the observations. The observations also indicate an apparent extra source of CH_4 in October-November not seen in the model simulations. However this appears to be an artefact of this analysis method which assumes that radon emissions are known (and in this case constant in space and time). We have found that the discrepancy between model and observations in spring appears to be due to a poor simulation of radon, rather than CH_4. Observed radon shows a larger seasonality than modelled radon, which suggests that temporal and spatial variations in radon flux need to be considered. It would also be helpful to understand why the simulated CCAM and ACCESS radon (and non-baseline CH_4) concentrations differ in magnitude. Comparisons with Cape Grim output from the other participating TransCom-CH_4 models may provide some insight.

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CALIBRATION OF GREENHOUSE GAS COLUMN ABUNDANCES WITH IN SITU AIRCRAFT PROFILE DATA OVER WOLLONGONG, AUSTRALIA

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Abstract

Ground-based solar absorption measurements have been carried out in Wollongong, Australia in accordance with the Total Carbon Column Observing Network (TCCON) protocol since June 2008. Together with 14 other TCCON stations around the world, the network retrieves and analyses column concentrations of CO_2, CH_4, N_2O and CO. These trace gas amounts were calibrated against integrated aircraft profiles during the HIAPER Pole-to-Pole Observations II (HIPPO II) overpass over Wollongong.

Introduction

To complement in situ measurements, greenhouse gas monitoring from space, through satellites, were begun. Two key instruments are currently in orbit performing these measurements. The Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) on board the satellite ENVISAT and the Greenhouse Gases Observing Satellite (GOSAT). Satellites provide global coverage and instead of performing point measurements, space-borne measurements measure trace gas abundance from the top of the atmosphere to the surface of the earth. This is termed as the total column concentration. These satellite measurements require validation. This is provided by a system of ground-based high resolution Fourier transform infrared (FTIR) spectrometers known as the Total Carbon Column Observing Network (TCCON). TCCON measures solar absorption spectra from which column amounts of CO_2, CH_4, N_2O, CO, HF, H_2O and HDO are retrieved. The ratio of these column amounts with the retrieved O_2 brings about the column-averaged concentrations (X_{GAS}).

The TCCON site in Wollongong, Australia is located at 34.406ºS and at 150.879ºE with an altitude of 30 meters above sea level. It is situated on a narrow coastal plain bordered by the Pacific Ocean to the east and a steep sandstone precipice, called the Illawarra escarpment to the

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west. Approximately 82 kilometres to the north is Sydney and 8 km to the south is the Port Kembla steel works.

The instrument (a Bruker 125 HR Fourier transform infrared spectrometer) is currently located in the high resolution spectrometry laboratory of the Centre for Atmospheric Chemistry in the Halpern Chemistry Building of the University of Wollongong. By tracking the sun, it regularly records solar absorption spectra in the near-infrared as well as in the mid-infrared. In this paper, the focus would only be in the near infrared.

DC inteferograms are actually measured by the instrument. These interferograms are then corrected for source brightness fluctuations (Keppel-Aleks *et al.* 2007), Fourier transformed and the resulting spectra are analysed using GFIT. GFIT is a non-linear least squares fitting algorithm developed at NASA/JPL that retrieves column amounts of trace gases from solar absorption spectra (Toon *et al.* 1992). The spectral regions used for the retrievals are outlined in Wunch *et al.* (2010).

Results

Retrievals from the TCCON network are precise up to 0.25% or better for CO_2 as an example. However, due to inadequacies in the spectral linelists used, the accuracy of the retrieved columns is approximately 1%. This is insufficient for use in combination with in situ measurements for carbon cycle science. In order to make TCCON column measurements useful for these combined analyses, they must be calibrated to the World Meteorological Organization (WMO) in situ trace gas measurement scales. To achieve this goal, profiles obtained with in situ measurements aboard airborne platforms over TCCON sites are utilised (Wunch et al., 2010).

The first aircraft calibration of CO_2, CO, CH_4 and N_2O retrieved from the Wollongong TCCON site occurred in November 15, 2009. It involved collaborating with the second phase of the High-performance Instrumented Airborne Platform for Environmental Research (HIAPER) Pole-to-Pole Observations (HIPPO II) project aimed at measuring cross section concentrations of atmospheric gases essential to the carbon cycle from the north pole to the south pole and from the surface to the tropopause. The project uses a modified Gulfstream V (GV) business jet. Figure 1 shows the flight path of HIPPO II as it overpasses over Wollongong.

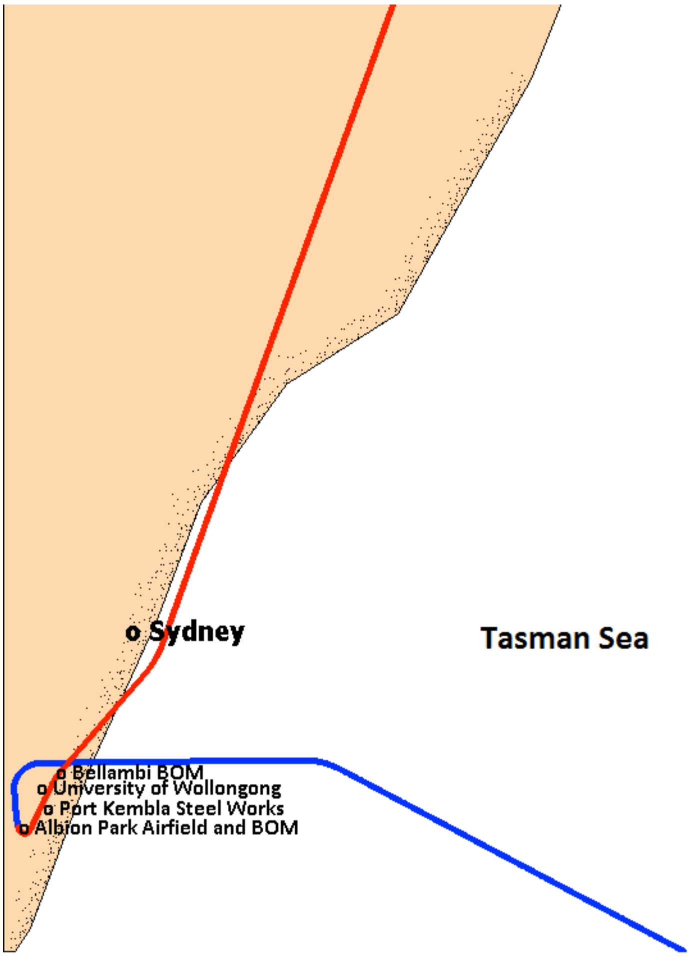

Fig. 1 HIPPO II Flight Tracks over Wollongong, Australia. The Gulfstream V began its descent from the Tasman Sea (blue), spiraled to the Albion Park airfield where it made a missed landing approach, then commenced its ascent (red) passing over the Port Kembla steel works, the University of Wollongong, the Bellambi Bureau of Meteorology (BOM) station and the city of Sydney.

The concentration profiles that are measured by HIPPO II are then integrated in a manner described in Wunch *et al*. (2010). They are then compared to the retrieved FTIR data. The calibration curves are shown in Fig. 2.

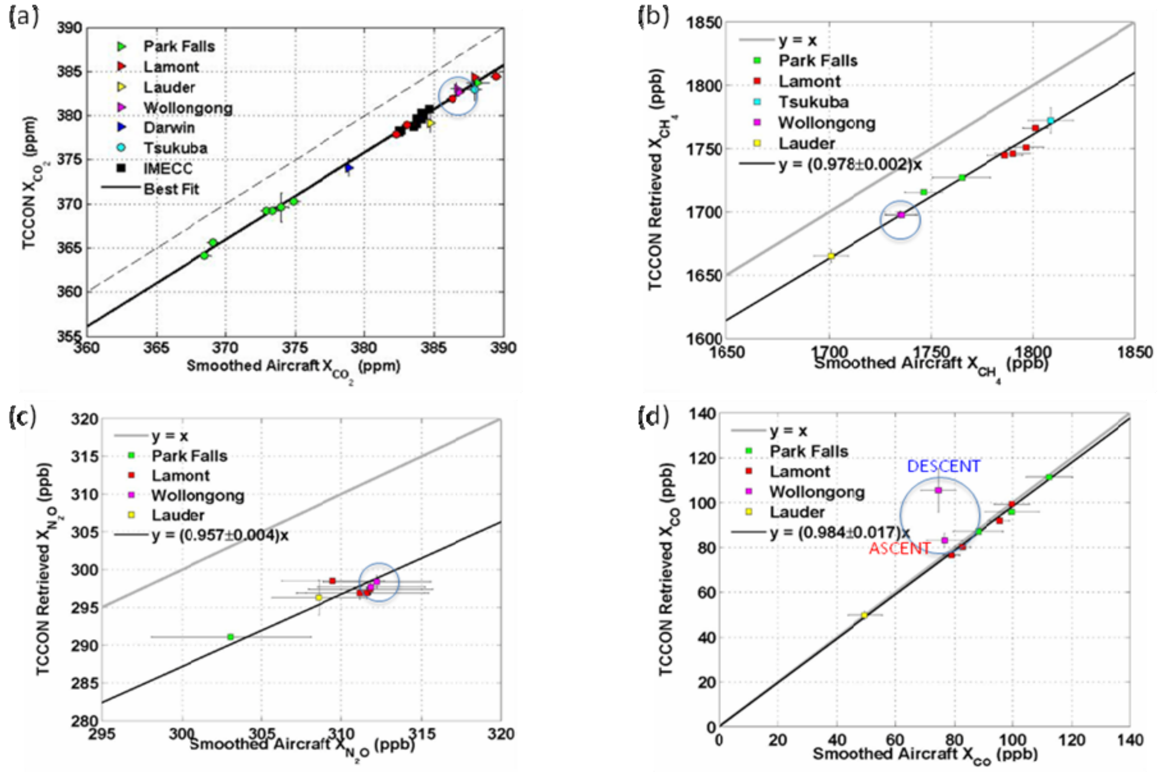

Fig. 2 Calibration Curves for: (a) CO_2; (b) CH_4 and (c) N_2O; and (d) CO for TCCON. Enclosed in the blue circle is the data for the Wollongong TCCON station.

From these calibration curves, the scaling factors for CO_2, CH_4, N_2O and CO were derived. These are outlined in Table 1.

Table 1 TCCON Calibration Scaling Factors

Greenhouse Gas	Scaling Factor
CO_2	0.989±0.003
CH_4	0.978±0.005
N_2O	0.958±0.010
CO	0.980±0.010

It can also be seen in Fig. 2(d) the deviation of the retrieved Wollongong CO data from the rest of the TCCON CO. From Fig. 3, the high CO data from the FTIR occurs when the winds come from the south to southeast direction. This direction corresponds to the location of the Port Kembla steelworks (see Fig. 1). It can also be noticed that the aircraft data is unaffected by this high CO. This will be further investigated in future work.

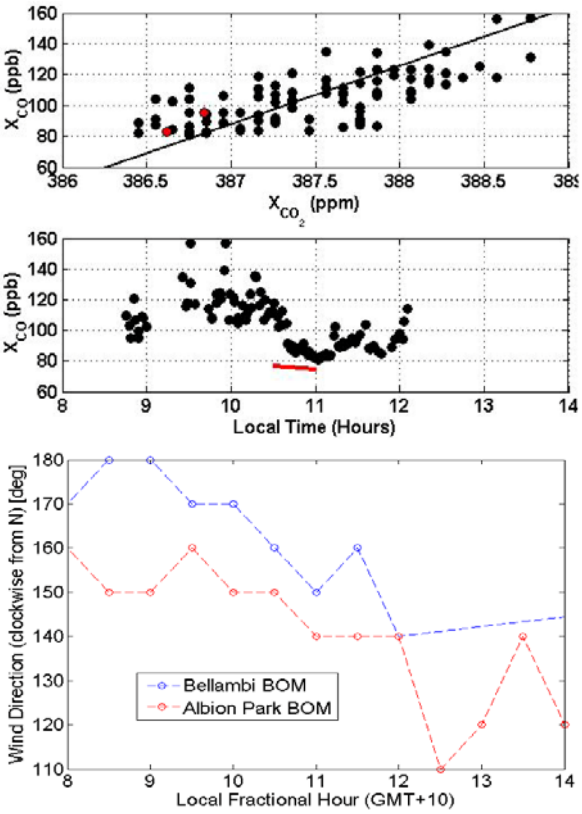

Fig. 3 Wollongong CO data: (top) correlation plot of X_{CO} and X_{CO2}. The black dots are the retrieved CO from the FTIR and the red dots are the derived CO from the aircraft; (middle) time series plot of X_{CO} from the FTIR. The red line corresponds to the aircraft overpass time; (bottom) wind direction data from the Bellambi and Albion Park Bureau of Meteorology (BOM) sites.

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A DYNAMICAL CORE WELL-SUITED TO TRACE-GAS MODELLING

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Abstract

A new dynamical core for atmospheric models has recently been developed in Australia, the Variable Cubic Atmospheric Model (VCAM), which is well-suited to the modelling of trace gases. VCAM is planned as a successor to the Conformal Cubic Atmospheric Model (CCAM), both being variable-resolution atmospheric general circulation models (GCMs) formulated on a cube-based grid. Unlike CCAM, VCAM is formulated using the flux form of the primitive equations of motion. VCAM thus preserves the globally-integrated mass of advected species, and by the use of total-variation-diminishing techniques also preserves well both maximum and minimum concentrations during advection. In addition, VCAM is formulated on the equiangular gnomonic-cubic grid, which is highly uniform in its unstretched manifestation.

The presentation will describe the formulation of VCAM, concentrating on the advective aspects. A number of solid-body-rotation test simulations possessing analytic solutions, will then be shown, to demonstrate the performance of the new dynamical core, in regard to its conservation and accuracy, for both smoothly- and sharply-varying trace-gas distributions.

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AMBIENT AEROSOL SAMPLING USING THE AERODYNE AEROSOL MASS SPETROMETER: INSTRUMENT DESCRIPTION AND FIRST FIELD DEPLOYMENT (SYDNEY PARTICLE FORMATION STUDY)

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Abstract

A Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS or short: AMS) is a state of the art instrument used for the on-line quantification and chemical characterisation of the submicron non-refractory aerosol components, as well as their chemically resolved size distribution measurements. The only ToF-AMS available in Australia is held at the International Laboratory for Air Quality and Health (ILAQH) at the Queensland University of Technology (QUT). The first field deployment of the ILAQH's AMS was during Sydney Particle Formation Study that took place at the NSW Office of Environment and Hertitage's Westmead air quality station in Sydney during February 2011. The principles of the instruments operation and some preliminary results from the study will be presented here.

Introduction

Atmospheric aerosols receive a great deal of attention due to their effects on human health, visibility and climate. Significant advances in aerosol measurement capabilities and instrumentation have been made in recent years. Among these, aerosol mass spectrometers are 'arguably, the most significant development in aerosol measurement in the past 20 years and show great promise for providing rich new insights into sources and chemical transformations of atmospheric aerosols' (McMurry 2000).

A compact Time-of-Flight Aerosol Mass Spectrometer (c-ToF-AMS; Aerodyne Research, Inc., Billerica, MA, USA) was used for the on-line quantification and chemical characterisation of the submicron non-refractory aerosol components during the Sydney Particle formation Study (February 2011). The term 'non-refractory' is assigned to those species that evaporate rapidly at 600^{o}C under high vacuum condition (~10^{-5}Pa) and in practice includes species such as ammonium sulphate and bisulphate, ammonium nitrate, ammonium chloride and organic compounds. The c-ToF-AMS consists of three main sections: the aerosol inlet, the particle-sizing chamber and the particle composition detection section. In the aerosol inlet section particles are sampled into the AMS through an aerodynamic lens that forms a narrow particle beam of ~100 μm diameter. The aerodynamic lens has 100% transmission for particles in the size range of 60 – 600 nm and partial transmission down to 30 nm and up to 1.5 μm (Jayne *et*

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al., 2000). Once particles exit the lens and expand into high vacuum chamber they acquire size-dependent velocity. These velocities (and, thus, sizes) are determined by measuring particle time of flight between a rotating chopper wheel with two radial slits and the detector. In the detection section, the particles impact onto the vaporiser, a heated, porous tungsten surface (~600^{o}C), where non-refractory aerosol components are flash vaporised and then ionized by electron impact. Positive ions generated in that way are then detected by the c-TOF-MS.

The c-ToF-AMS was deployed at the Westmead air quality station in February 2011. Data are available for two sampling periods: 10 – 15 February and 18 – 24 February. The instrument provided submicron particle mass loadings and their composition with a time resolution of 5 minutes. A particle collection efficiency of 0.5 was estimated to calculate the aerosol mass concentration.

Results

Figures 1 and 2 show time series of the mass loadings of the PM1 species as measured by the c-ToF-AMS for the time period of 10 – 15 February and 18 – 24 February, respectively. Note that due to instrumentation problems, the mass loadings of the second time period may be biased to lower concentrations; however, the relative change and ratio between the distinct AMS components was not affected. Figure 1 shows that the c-ToF-AMS mass loadings are substantially higher for the time period of 11 February (~9 am) – 12 February (~9 am). Increases in the mass loadings for this time period is characteristic for all c-ToF-AMS components (organics, sulphates, etc.), suggesting that their relative ratio has not changed during that time period. Increases in the c-ToF-AMS mass loadings for the time period of 11 February (~10 am) – 12 February (~8 pm) coincides with increases in ozone concentrations and solar radiation levels, which were the highest for that time period (maximum ozone = 54 ppb) suggesting new particle formation and/or growth, also indicated by particle number size distribution data determined using the principal of aerosol mobility. The spikes in the organic (Org) mass loadings may be due to appearance of combustion sources in the close proximity of the measurement site.

Fig. **6** shows elevated Org concentrations between 19 February (~11am) – 20 February (~11:30pm) when other c-ToF-AMS components remained low. This increase also coincides well with elevated ozone concentrations which were the highest for 19 and 20 February. In addition, Fig. 6 shows that there are three distinct events when sulphates and ammonium mass loadings increase that occurred during afternoon hours on 20, 21 and 23 February. During those time periods the wind was blowing from SE. A similar distinct event was also observed in the afternoon hours of 11 February (Fig. 1) and the wind during that period had ESE direction.

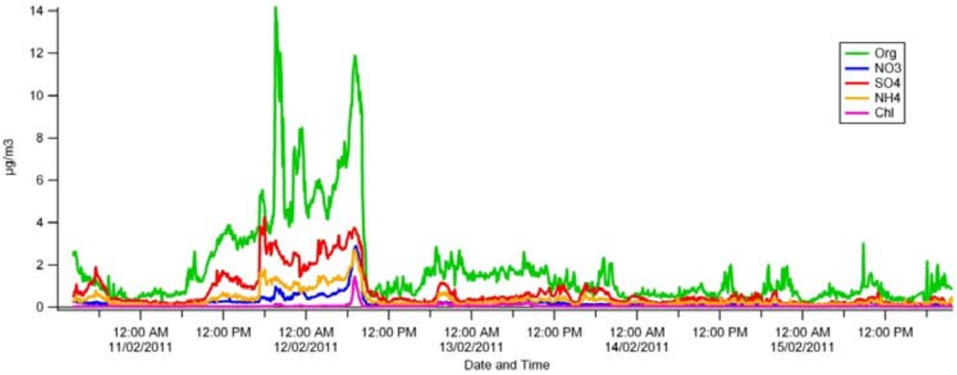

Fig. 5 Time series of the mass loadings of the non-refractory PM_1 species for the time period of 10 – 15 February 2011. Org = organics; NO_3 = nitrates; SO_4 = sulphates; NH_4 = ammonium; Chl = chloride.

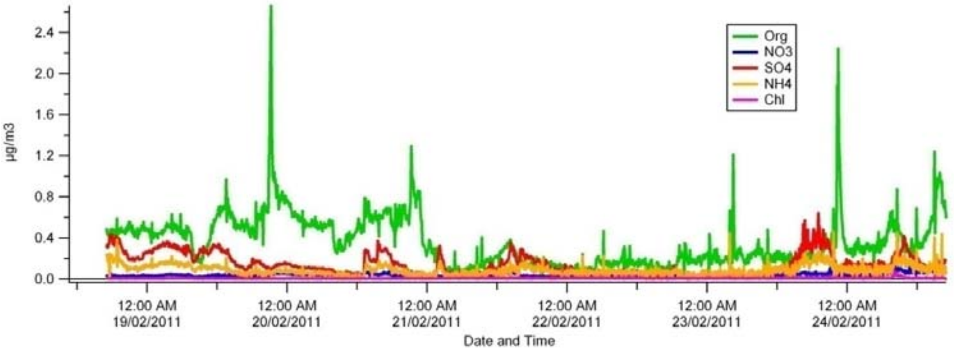

Fig. 6 Time series of the mass loadings of the non-refractory PM_1 species for the time period of 18 – 24 February 2011.

Electron impact (EI) ionization results in significant fragmentation which makes identification of molecular ions (i.e. exact species present in PM) impossible. Therefore, certain fragments (i.e. certain mass to charge ratios – m/z), specifically m/z44, m/z 57 and m/z60 have been proposed as markers for oxygenated organic species, hydrocarbon-like organic species and biomass combustion organic species, respectively (Alfarra *et al.* 2004). The abundance of certain peak is defined as: f_{xy} = *(m/z xy) / total organic mass.*

Based on these values further information about the nature of organic aerosol being sampled is available. For example, f44 ≈ 0.14 indicates that organic aerosol being sampled is oxygenated, which is typical for secondary organic aerosol (SOA). The summary of organic tracers, species they are related to and their average values are presented in Table 1.

Table 1. Summary of organic tracers (Ng *et al.* 2011).

Tracer (m/z)	Type of organic species	Average abundance (f_{xy}) values
43*	Total OA	0.05- 0.1
44	Oxygenated organic aerosol (OOA) - *SOA*	0.14
44	Low volatility oxygenated organics (LV-OOA)	0.16
44	Semi-volatile oxygenated organics (SV-OOA)	0.05
57	Hydrocarbon-like organic aerosol (HOA) - *POA*	0.07 – 0.08 (0.01 in OOA)
60, 73	Biomass burning organic aerosol (BBOA)	0.03

* m/z 43 has contributions from both oxygenated ($C_2H_3O^+$) and non-oxygenated ($C_3H_7^+$) ions it is a useful tracer for total OA.

The time series of f44 and f57 for the time periods of 10 – 15 February are presented in Fig. 7. f60 was not shown as it was lower than 0.005 throughout the whole sampling periods, indicating that biomass burning did not contribute to organic aerosol sampled during that periods Fig. 7 shows that there was a steep increase in f44 on 11 February around 8am from ~0.04 to ~0.12-0.14, indicating that there was an increase in oxygenated organic compounds (e.g. carboxylic acids, acyl peroxides), which are typical for SOA. At the same time, there was a steep decrease in f57 (from ~0.06 to 0.01), meaning that hydrocarbon-like compounds present in the aerosol had decreased. Increase in f44 (and decrease in f57) occurs around the same time as total mass loadings start to increase (Fig. 6).

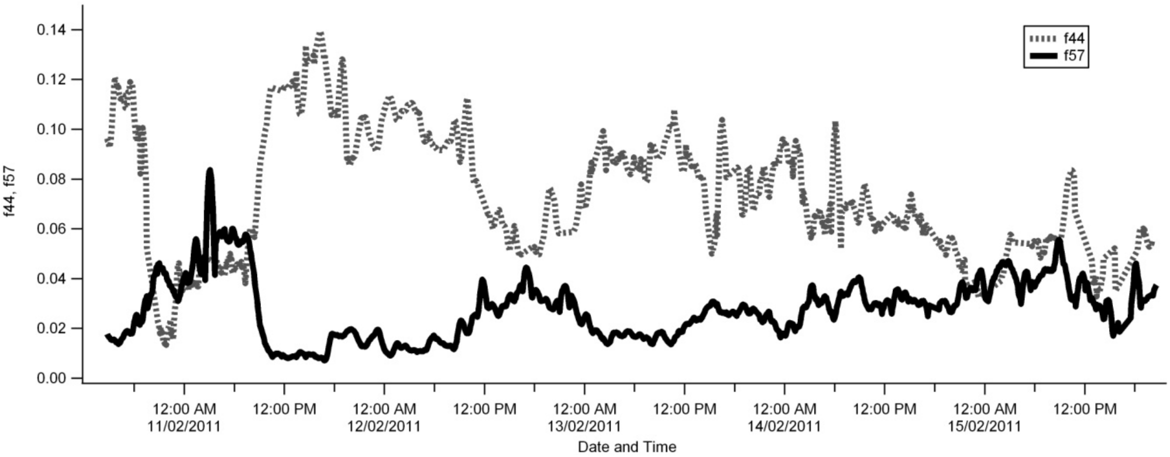

Fig. 7 Time series of f44 and f57 for the time period of 10 – 15 February 2011.

Acknowledgments

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CHARACTERISATION OF AEROSOLS OVER AUSTRALIA AND NEW ZEALAND AND EFFECTS ON SURFACE UV RADIATION

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Abstract

Aerosols play a key role in the radiation balance of the earth-atmosphere system, can play a significant role in atmospheric chemistry through heterogeneous reaction, and can have significant localised impacts on respiratory health. Through scattering and absorbing solar ultraviolet (UV) radiation, they can affect health indirectly by altering UV exposure (Lucas and Ponsonby 2002; Kalashnikova *et al*. 2007) and affect the availability of solar energy.

This study characterised aerosols at several sites in Australia and New Zealand using ground-based observations. Five aerosol classes were identified, including one class of bushfire smoke (Weber and Mills 2011). Of the sites studied, Darwin had the greatest aerosol concentrations as well as the most distinct seasonal trends. In particular, aerosol concentrations over Darwin were found to increase as the bushfire season intensifies (Weber and Mills 2011).

The optical properties of 'standard' aerosol types used in many radiative transfer models (e.g., libRadtran, Mayer and Kylling 2005) are based on northern hemisphere measurements (Shettle 1989). Coincident aerosol optical depth measurements and UV spectra collected at Darwin provide an opportunity to compare the UV to visible optical properties of the aerosols observed over Darwin with those of the "standard" northern hemisphere aerosols types.

Potential long-term health effects due to reductions in surface UV radiation at these sites were investigated using radiative transfer modelling, with the results expressed in terms of the effective sun protection factor (SPF) (Chee and Mills 2010). The modelled effective SPF due to aerosols is less than 1.12 – 1.3 on 95% of days at all sites using a range of northern hemisphere aerosol types (Chee and Mills 2010, Weber and Mills 2011). The highest estimate using the tropospheric aerosol type in the measurement period is 1.25, which occurred at Darwin (Weber and Mills 2011). The long-term averaged impacts on UV exposure and health are likely to be very small compared to typical lifestyle factors, such as the amount of time spent outdoors and the use of sunscreen and sun-protective clothing.

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INDOOR AIR QUALITY IN TYPICAL TEMPERATE ZONE AUSTRALIAN DWELLINGS

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Abstract

Indoor air quality is an important component of a person's total exposure to air pollutants and associated health outcomes. We report the results of a comprehensive study of indoor air quality in typical temperate zone Australian dwellings. Forty dwellings located over an 800 km^2 area in the south-east of Melbourne with a range of ages, materials and structures representative of Australian dwellings were selected. A range of indoor air quality pollutants were sampled both inside and outside for one week each in Winter/Spring 2008 and Summer/Autumn 2009. Information was collected on house characteristics, the surrounding areas and occupant activities during the sampling.

Weekly averaged CO_2, CO, NO_2, formaldehyde and other carbonyls had higher concentrations indoors compared with outdoors. Weekly averaged temperatures and water vapour mixing ratios also were higher indoors compared to outdoors. There were no significant differences between indoor and outdoor weekly average concentrations for $PM_{2.5}$ and PM_{10}. Elevated NO_2 concentrations were observed indoors during Winter/Spring whereas during Summer/Autumn concentrations outdoors were greater. Ozone concentrations were lower indoors than outdoors. Correlations and factor analysis showed that ventilation and activities associated with combustion and cooking were the major influences on indoor air quality. The indoor air quality results from this study were comparable with or lower than other Australian or overseas studies from the USA, UK and Hong.

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ATMOSPHERIC COMPOSITION RESEARCH IN TRANSITION: FROM OZONE HOLE TO CLIMATE CHANGE

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Abstract

In 1987 the Montreal Protocol was implemented to prevent dangerous anthropogenic damage to the ozone layer. Emission reductions agreed under the Protocol are causing the stratospheric chlorine and bromine loadings to decline. Consequently, polar ozone is expected to largely "heal" during this century. This development is widely hailed as a major success for international environmental protection, yet it may lead to the perception that further research into ozone chemistry is no longer needed. Ozone recovery will coincide with progressive climate change due to emissions of long-lived greenhouse gases. These changes will also affect the ozone layer. Recent research suggests that stratospheric ozone recovery will lead to a seasonal increase of tropospheric ozone, particularly in the Southern Hemisphere. We reassess this question, also taking into account the impact of ozone recovery on tropospheric photochemistry due to decreased actinic fluxes in the near-UV region. We find a substantial impact on the tropospheric ozone burden due to this photochemical effect. The tropospheric abundance of the hydroxyl radical, which acts as the principal detergent of the troposphere, is substantially decreased when stratospheric ozone recovery is taken into account, particularly in northern-hemisphere polluted regions. Associated with this is an increase of surface ozone which had not been modelled in earlier studies that did not account for the impact of ozone recovery on tropospheric photochemistry.

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ATMOSPHERIC CO_2 INVERSION VALIDATION USING VERTICAL PROFILE MEASUREMENTS OVER CAPE GRIM

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R. J. Francey, P. Tans and C. Sweeney

Abstract

The consistency of an inversion model with independent observations provides an important assessment of the reliability of the model and the resulting parameter (flux) estimates. Such an assessment of model consistency is achieved through a direct comparison (or validation) of a model with independent observations of a particular quantity (e.g. observed CO_2 concentrations).

We present the results of a validation of atmospheric inversions of CO_2 fluxes using four independent transport models: CCAM (Australia), LMDz (France), FRCGC (Japan) and TM3 (Germany). Each atmospheric inversion uses primarily surface observation data, combined with an atmospheric transport model, to estimate surface CO_2 fluxes. However, technical details of the four inversion models vary significantly. The model validation (or evaluation) then consists of running the optimized flux estimates through the forward model and comparing the subsequent model fit (simulated atmospheric CO_2 concentrations) to independent observations of CO_2. We use airborne observations of the vertical structure of CO_2, focusing here on vertical profiles collected over Cape Grim from 1990 – 2000. However, observed vertical profiles from other sites (e.g. Carr Colorado) were extensively used in the study.

Only one of the four inversion models (TM3) provided a consistent model fit to both the observed profiles and surface data used in the inversion at Cape Grim. This was not the case at other profile sites. A detailed analysis of the vertical structure as well as seasonal, temporal and inter-model variations in the model profile fit across the four models was completed. TM3 was identified as providing the most consistent model fit to the Cape Grim observed profiles by some measures, although this result did not extend to other profile sites. All four models displayed significantly different temporal and seasonal variations in their fit to the Cape Grim profiles, despite similar averaged model fit error statistics. At other profile sites, consistency across all four models in the inter-annual variations of the model profile fit suggest real variations in CO_2 fluxes visible in the vertical profile but not in the surface measurements.

Analysis of the CCAM inversion model was extended to assess the consistency of the model profile fit with different estimates of uncertainty in the inversion flux parameters. This assessment involved estimating the uncertainty in the model simulation of CO_2 arising from the estimated flux uncertainty. At Cape Grim, we found that errors in the CCAM model profile fit were broadly consistent with the flux parameter uncertainties provided by the inversion a posteriori covariance matrix. However, errors in CCAM model fit were not consistent with flux parameter uncertainties estimated by perturbing the surface observation network used in the CCAM inversion model.

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RATIONALE FOR A CLOUD PROGRAM DEVELOPMENT OVER CAPE GRIM

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Abstract

Climate model errors in the top of the atmosphere shortwave fluxes over the Southern Ocean are amongst the largest anywhere over the globe, exceeding 30 Wm^{-2} in some places. This is presumably due to our lack of understanding of the thermodynamical phase, and the microphysical and radiative properties of the different types of clouds occurring over the Southern Ocean. Although the Cape Grim site may be considered too far north to address the reasons for the main radiation bias over the Southern Hemisphere Belt, satellite active remote sensing reveals that this location shares some strong similarities in terms of cloud frequency of occurrence, multi-layer cloud occurrence, and supercooled water statistics. The Cape Grim location is also known to be characterized by very clean air, in contrast with other instrumented sites over the mid-latitudes. It would therefore be of great interest to build a reference ground-based atmospheric station that includes cloud characterization which in collaboration with the Cape Grim Particle Program would be similar to the EU CloudNET and US ARM programs. The aim of this presentation is to initiate discussion on including a cloud observation program at Cape Grim.

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CO_2, CLIMATE GOALS, AND FINITE-PLANET NARRATIVES: THREE VIGNETTES ABOUT THE EARTH SYSTEM

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Vignette: a word that originally meant 'something that may be written on a vine-leaf'

This talk offers short perspectives on three linked lines of work on the carbon-climate-human system. They are presented in order of increasing breadth.

1. ***CO_2 airborne fraction:*** The first line of work concerns trends in two related indicators of the response of the global carbon cycle to anthropogenic carbon dioxide (CO_2) emissions. The airborne fraction (AF), the fraction of total anthropogenic CO_2 emissions that remains in the atmosphere, is a measure of the ecosystem service provided by land and ocean CO_2 sinks in discounting anthropogenic emissions. The CO_2 sink rate, the uptake rate of CO_2 by land and ocean CO_2 sinks, is a measure of sink efficiency. By extending recent data and assessments on the budget of atmospheric CO_2 [Friedlingstein *et al.* 2010], it is found that the AF increased over 1959-2010 at a mean proportional growth rate nearly 0.4% yr^{-1} (5-95% confidence interval, significance P = 0.97) about an average value of 0.44. This new estimate reveals a stronger AF increase than earlier estimates (Le Quéré *et al.* 2009), primarily because of revisions to estimated CO_2 emissions from land use change. Over the same period, we find that the CO_2 sink rate declined at -0.8% yr^{-1} (P>0.999) about an average value of 1/37 yr^{-1}, equivalent to a decline of about 40% over 50 years. Both trends are robust when determined from multiple estimates of CO_2 emissions from land use change. Both trends potentially arise from two factors: (1) faster-than-exponential growth of CO_2 emissions; and (2) nonlinear responses of the carbon cycle to earth system changes. Both factors contribute to observed trends in AF and sink rate, but (2) is larger, indicating a declining CO_2 sink efficiency through nonlinearities in the carbon-climate system. Future trends both the AF and sink rate depend strongly on emissions trajectory: under high-emission scenarios the AF will continue to increase and the sink rate to decline more strongly. Under stabilisation scenarios the AF will decline, eventually becoming negative.
2. ***Reconciling the contributions of multiple greenhouse gases in climate targets:*** There are many different ways of quantifying the broad goal of 'avoidance of dangerous human interference with the climate system', including targets for limiting global warming, radiative forcing (RF), greenhouse gas (GHG) concentrations, GHG emissions in particular years, and cumulative GHG emissions ('carbon budgets'). One of the challenges in all these specifications is to relate the contributions of different GHGs, both long-lived (such as CO_2) and short-lived (such as methane). Here I introduce a recently-developed simple calculator for relating the various specifications of climate goal (Raupach *et al.* 2011). I will focus on a problem highlighted by the development of this calculator, that of relating the contributions of different GHGs. There is no unique answer to this problem because the outcome depends fundamentally on emissions history. The traditional approach of using Global Warming Potentials (GWPs) is not physically sound because warming does not depend strongly on integrated RF for any gas, short-lived or long-lived. Better metrics are obtained by considering (a) temperature, not RF (because it is closer to climate impacts), and (b) sustained, not pulse releases (because they are more realistic). This approach leads to an 'Enhanced Global Temperature Potential' (EGTP), in the spirit of the GTP defined by

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Shine (Shine *et al.* 2007; Shine *et al.* 2005). The EGTP uses realistic climate responses and accounts for time-varying emissions. Numerical values of the EGTP are not far from GWP values because of a transformation relating the warming from continuous emissions to a measure of integrated RF (the foundation of the GWP). Hence, the EGTP partly rehabilitates the GWP from its well-known problems by placing its formulation on a sounder physical foundation.

3. ***The role of narrative in shaping energy-water-climate futures:*** The final line of work is on a much broader level. The two centuries since the start of the industrial era has been a period of rapid and almost unbroken economic growth in much of the world, based upon exponentially increasing use of energy and water resources and the atmospheric commons. It is axiomatic that exponential growth cannot continue forever on a finite planet, leading to an emerging collision between the presently irresistible force of economic growth and the immovable reality of the finitude of Planet Earth. This collision takes many forms and will occur over many decades, but its effects on water resources and climate are already plainly evident. The inevitability of the collision has led to the a contest between two broad narratives about energy, water and climate in the 21st century, one framed around the paramount need for economic growth and the other around the paramount need to protect an increasingly fragile natural world. Many features of recent public discourse (including the acceleration of the news cycle and the echo-chamber effect of interactive social media) have driven these narratives to become progressively more mutually antagonistic and incompatible. Here I explore the idea that narratives (in the sense of stories that empower actions) are meme sequences that evolve through diversification, selection and adaptation. This memetic evolution can be understood and influenced, but not controlled. In shaping our shared energy-water-climate future, the evolutionary contest between growth and finite-planet narratives is just as important as the dynamics of the natural world. The future therefore depends upon the evolution of more subtle and resilient narratives about human-earth interactions, in which energy, water and climate are central. The evolutionary fitness test for these narratives is to empower a transition to a society that lives within the means of a finite planet and improves global wellbeing at the same time.

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INTEGRATING AUSTRALIAN RESEARCH ON ATMOSPHERIC COMPOSITION: COSTS AND BENEFITS

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Abstract

In this talk I will discuss the prospects and avenues for integrating Australian research on atmospheric composition. The case is rather different from that for the physical climate since, although both areas have large and diverse groups of stake-holders, research on physical climate has always been relatively centralized atmospheric composition research is spread Drawing on the successes and failures of these two projects I will try to deduce some lessons on whether and how to integrate atmospheric across many organizations. Using examples from Europe, I will sketch some of the costs and advantages of drawing the various communities together.

Finally I will sketch two possible pathways and some early steps. The first step is a proposed national meeting on atmospheric composition research to be held in the 2nd half of 2012.

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AMPLIFICATION OF ENSO-RELATED RAINFALL VARIABILITY DUE TO AUSTRALIAN DUST

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Abstract

The climatic effects of dust are attracting increased attention. In the Northern Hemisphere, dust is thought to modulate the inter-annual variability of tropical cyclones over the North Atlantic Ocean (Evan *et al*. 2006). A recent modelling study also suggested that dust exacerbated the famous “dust bowl” drought in North America in the 1930s (Cook *et al*. 2009). It is not yet clear whether Australian dust exerts significant effects on climate.

Recently we reported on an improved simulation of Australian rainfall variability in the CSIRO Mk3.6 Global Climate Model (GCM) compared to its predecessor (Mk3.5) and several international GCMs (Rotstayn *et al*. 2010). Our analysis led us to hypothesise that “active” dust (which interacts with the model’s hydrological cycle) might contribute to the improved simulation in Mk3.6 relative to Mk3.5. The argument was that by further suppressing convection over eastern Australia during El Niño events, and vice-versa during La Niña events, dust feedbacks may enhance rainfall variability there, in tune with the model’s natural El Niño Southern Oscillation (ENSO) cycle. Our hypothesis was based on qualitative arguments, since we did not have access to a pair of simulations in which only one thing (namely, dust) was changed. The purpose of the present study (Rotstayn *et al*. 2011) was to evaluate this hypothesis in a more mechanistic framework.

We will describe two coupled atmosphere-ocean simulations of modern-day climate. The first simulation (DUST) is a longer version of the run described by Rotstayn *et al*. (2010). The second run (NODUST) is otherwise identical, but has the Australian dust source set to zero. We focus mainly on the spring (SON) season, when the ENSO-rainfall teleconnection is strongest over Australia.

The ENSO-rainfall relationship over eastern Australia is stronger in the DUST run: dry (El Niño) years tend to be drier, and wet (La Niña) years wetter. The amplification of ENSO-related rainfall variability over eastern Australia represents an improvement relative to observations.

The effect is driven by ENSO-related anomalies in radiative forcing by Australian dust over the south-west Pacific Ocean; these anomalies increase (decrease) surface evaporation in La Niña (El Niño) years. Some of this moisture is advected towards eastern Australia, where increased (decreased) moisture convergence in La Niña (El Niño) years increases the amplitude of ENSO-

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related rainfall variability. The modulation of surface evaporation by dust over the south-west Pacific occurs via surface radiative forcing and dust-induced stabilisation of the boundary layer. The results suggest that (1) a realistic treatment of Australian dust may be necessary for accurate simulation of the ENSO-rainfall relationship over Australia, and (2) radiative feedbacks involving dust may be important for understanding natural rainfall variability over Australia.

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A REVISED ATMOSPHERIC δ^{13}C-CO$_2$ PALEORECORD COVERING THE LAST 200 YEARS FROM LAW DOME, ANTARCTICA

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Abstract

A unique record of atmospheric $\delta^{13}CO_2$ from Law Dome (Antarctica) ice covering the last 1000 years was published in 1999 by Roger Francey and colleagues at CSIRO, Aspendale (Francey *et al.*, 1999). Because of the characteristics of the Law Dome ice core, the record features relatively high intrinsic time resolution, small diffusional artefacts and overlap with modern direct atmospheric records and firn measurements. The record has yet to be improved because ice cores are the only natural archive to directly store samples of the past atmosphere in their bubbles and no better cores have been drilled or measured covering the last 1000 years. The CO_2 and $\delta^{13}CO_2$ records have provided a powerful constraint for models simulating the global C cycle (e.g.: Trudinger *et al.*, 1999). One of the most important conclusions one can draw from that dataset is that the CO_2 released into the atmosphere during the industrial period has a ^{13}C-depleted source ($\delta^{13}CO_2$ lower than the mean atmospheric value).

However, further measurements are needed to explain the causes of significant changes in the atmospheric CO_2 concentration (for example, during the little ice age, around 1600 AD (MacFarling Meure *et al.*, 2006)), which have since become the focus of studies of C-cycle variability (e.g.: Cox and Jones, 2008), as well as to extend the record into previous millennia.

While extending that record back in time and increasing its sample density through key periods, we have found a significant systematic difference from the published Law Dome record of the last 200 years. The precision and accuracy of our extraction and measurement techniques have been extensively tested at CSIRO ICELAB and GASLAB. Also, new firn records of $\delta^{13}CO_2$ (from Law Dome and South Pole) over the past century are now available, supporting the new ice core values. A revised firn model is used to make corrections for firn air diffusion and bubble close off.

Preliminary results will be shown focusing on the overlapping of our new ice measurements with the firn results. Potential causes of the differences between the previous and new ice core data and implications for extending the record back in time will be discussed. Finally, while the new record does not affect the interpretation of the source (depleted in ^{13}C) of CO_2 released into

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the atmosphere during the industrial period, possible consequences for global carbon cycle models will be briefly explored.

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INVERSION OF DOAS MEASUREMENTS TO PROVIDE DIURNALLY VARYING PROFILE INFORMATION

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Abstract

Differential Optical Absorption Spectroscopy has been used successfully to retrieve vertical profile information of diurnally varying species by combining complementary viewing geometries. Direct-sun spectra provide total column information, spectra obtained from zenith viewing geometries primarily provide stratospheric information, while spectra obtained from multiple azimuths at low elevation angles (the so-called Multi-axis approach), provide detailed boundary layer information. By combining these observations using optimal estimation, a complete characterization of their information content and retrieval smoothing errors can be achieved. As many of the species being measured are chemically or photochemically active, their concentrations change over the period for which they are being observed. This necessitates an inversion of measurements to vertical concentrations that is performed in both in altitude and time. The application of these techniques to measurements made at Lauder, Arrival Heights, along New Zealand coastlines and on remote first-year sea-ice regions of Antarctica, and applications in the tropical regions, are discussed.

Introduction

Differential Optical Absorption Spectroscopy (DOAS) has been widely used to remotely measure concentrations of a number of trace gases (Platt 1994, 1999). Species that can be retrieved include O_3, NO_2, BrO, SO_2, HCHO, CHOCHO, O_4, OClO and IO. Many of these species are naturally occurring, but O_3, NO_2 and SO_2 have important anthropogenic sources, and lead to degradation of air quality when found in high abundances in the lowermost atmosphere.

To derive column information from DOAS measurements, which are light-path averaged columns, a 2 dimensional and ideally 3 dimensional radiative transfer model is necessary (Hendrick *et al*. 2006; Wagner *et al*. 2004). The application of the NIWA Monte Carlo model (NIMO) (Hay *et al*. 2011) to interpret MAX-DOAS measurements of BrO and IO is discussed.

Enhanced concentrations of reactive halogen species, including bromine monoxide (BrO) and iodine monoxide (IO), in the marine boundary layer (MBL) are responsible for very efficient photocatalytic ozone destruction, as well as oxidation of gaseous elemental mercury and dimethyl sulphide (DMS). Many of the key processes involving these halogen species remain

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poorly understood. Although enhanced BrO concentrations (so called bromine explosion events) in the polar MBL are naturally occurring phenomena, areas covered by elevated BrO columns, as measured by the Global Ozone Monitoring Experiment (GOME) satellite instrument (Burrows *et al.* 1999), have been expanding, possibly due to anthropogenic influences on climate. Bromine availability in turn affects the deposition of mercury, a bio-toxin, from the atmosphere to the surface (Ariya *et al.* 2004; Holmes *et al.* 2010). Therefore, climate-induced changes in sea ice are likely to affect mercury levels in Antarctic ecosystems. Measurements and findings from 2 Antarctic field campaigns made on Ross Island (78°S) in the Antarctic support this theory.

As highlighted in the 2006 and 2010 Scientific Assessment of Ozone Depletion (WMO 2006, 2010) emissions of halogenated very short-lived substances (VSLS) and their degradation products (e.g. BrO) contribute significantly to the atmospheric bromine loading. These highly reactive radicals affect both tropospheric and stratospheric chemistry, and in particular drive catalytic ozone destruction reactions. If substantial amounts of the reactive halogen species are entrained into the base of tropical deep convective systems, they can be quickly transported to the tropical tropopause layer (TTL).

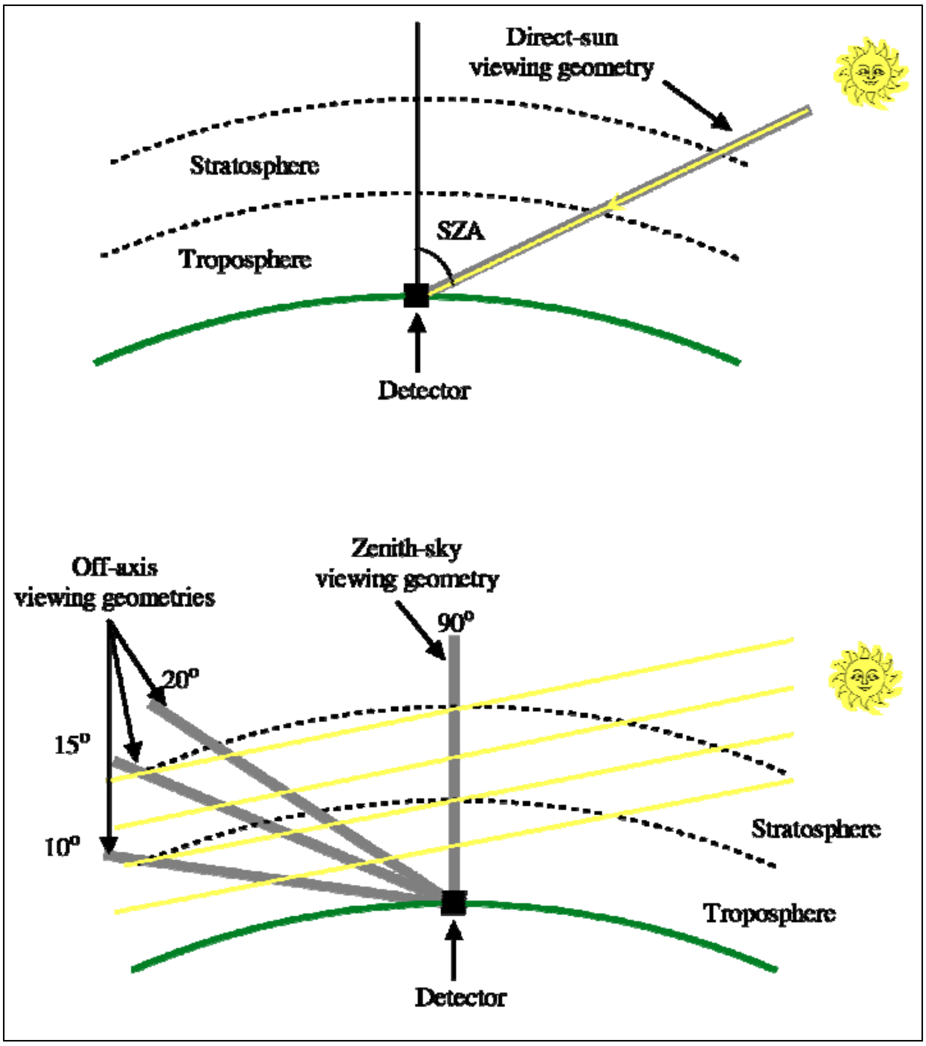

Fig. 1 The different viewing geometries used by ground-based DOAS instrumentation.

Results

Results for Max-DOAS measurements of IO and BrO observations conducted in Antarctica will also be presented. The entrainment of boundary layer bromine containing substances is shown to contribute to the stratospheric bromine budget, with a conceptual modeling study of TTL transport (Schofield *et al.* 2011). Measurements of emissions of bromine containing substances important in tropical convection entrainment, will be presented from several car-based measurement campaigns along the Malaysian (6ºN - 1ºN) and New Zealand (36ºS - 46ºS) coastline during 2009 to 2011 in collaboration with the University of Malaysia and University of Cambridge, UK.

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DISCOVERING THE IMPORTANCE OF AEROSOL SAMPLING MEDIA

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Abstract

The collection of aerosol samples on filter materials and the subsequent chemical analysis of the filters is a long-standing method for the determination of the chemical composition of atmospheric aerosols. While this method has revealed a great deal of information about the chemical composition of atmospheric aerosol, the disadvantages of the methods are well-recognised and primarily result from the change in aerosol chemical and physical properties that occur as soon as it is removed from the atmosphere. Examples include the positive and negative sampling artefacts in the presence of semi-volatile species (organic and inorganic) that partition between the gas and particle phase after the aerosol has been collected on the filter. In this work we discuss the negative ammonium artefact that results from the type of filter material used to collect marine aerosol at Cape Grim under the Cape Grim Multiphase Atmospheric Chemistry (MAC) Program.

The PM10 composition record that spans back to 1981 has been collected using high volume samplers on 10”x8” EMFAB filters composed of borosilicate glass fibres backed with a Teflon coating that strengthens the filter and prevents shedding of glass fibres, which particularly comprises the measurement of gravimetric mass on these filters. PM10 at Cape Grim is composed predominately of sea-salt, making it an alkaline aerosol. The presence of high sea-salt concentrations has been used to explain the absence of ammonium in PM10 since the weakly alkaline species is not required to balance acidity produced by the presence of sulfate in the presence of sea-salt alkalinity.

The PM2.5 composition record, derived from samples collected using a low volume sampler on 47 mm telfon filters, has a much lower sea-salt concentration than PM10 samples and displays a distinct seasonal cycle in ammonium concentrations that matches the cycle of non-seasalt sulphate. As part of a series of improvements to the MAC program PM2.5 samples were collected using a high volume sampler on 10”x8 “ EMFAB filters. Despite lower sea-salt concentrations measured in the PM2.5 fraction, ammonium was still absent in these samples. In addition, sodium concentrations on the samples were similar to the sodium concentrations measured on filter blanks so that a blank subtraction was required. Interestingly the very high concentrations of sodium measured in the PM10 samples meant that the blank sodium concentrations were not considered to be a significant issue.

These results suggest that the EMFAB filter material maybe leading to a deficit in the concentration of ammonium ion in the aerosol collected on the filter. The EMFAB filters have

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relatively high sodium blanks but no corresponding measured anion. The 47 mm Teflon filters have very low blanks for all water soluble ions. The pH of the blank 47 mm Teflon filters extracted in 12 mL of deionised water is 5.5 and the pH of a 6.25 cm^2 piece of blank EMFAB filter extracted in 10 mL of deionised water is 6.8. Bicarbonate can be estimated from the hydrogen ion concentration and for the 47mm Teflon filter is 0.02 µmol per cm^2 of filter and for the EMFAB filter is 20 µmol per cm^2 of filter and accounts for the missing anion on blank EMFAB filters. This amount of bicarbonate on the EMFAB filter would result in very high pH levels which cause ammonium to be converted to ammonia gas and lost from the filter.

These results highlight the importance of careful media selection for aerosol sampling.

THE CONTRIBUTION OF GROUND-BASED REMOTE SENSING MEASUREMENTS OF CARBON DIOXIDE IN THE SOUTHERN HEMISPHERE TO CARBON CYCLE RESEARCH

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Abstract

Over the past 7-8 years, precise and accurate estimates of the column average dry air mode fractions of carbon dioxide (XCO_2) and other major greenhouse gases have been derived from ground-based remote sensing measurements at the three operational Southern Hemisphere observatories in the Total Carbon Column Observing Network (TCCON): Darwin and Wollongong (Australia) and Lauder (New Zealand). In this paper we give a brief description of TCCON and the Southern Hemisphere XCO_2 timeseries. We then discuss specific contributions these Southern Hemisphere sites can make, and are making, to carbon cycle research through satellite validation, and through information they may reveal on CO_2 fluxes in regions of the globe that are poorly observed by the surface monitoring network.

Introduction

Accurate, quantitative estimates of surface fluxes of carbon dioxide (CO_2) and other important greenhouse gases, such as methane (CH_4), nitrous oxide (N_2O) and carbon monoxide (CO), are needed to understand the natural processes regulating atmospheric greenhouse gas concentrations (and hence predict future climate accurately), and to monitor compliance with emission reduction protocols (Kyoto and successors).

Surface fluxes of greenhouse gases cannot be measured directly at national to global scales. Atmospheric inverse models are widely used to infer what surface fluxes must have been, given measured atmospheric mixing ratios. However, flux inversions to date, based only on measurements from the surface in-situ trace gas monitoring networks, have significant uncertainties and limitations i) due to the sparcity and representativeness of the surface measurements and ii) because errors in modelled atmospheric transport are aliased into flux estimates derived in the inversion.

New, dedicated remote sensing measurements of CO_2 and CH_4 from space (Crisp *et al*. 2004; Kuze *et al*. 2009) will improve spatio-temporal data coverage and have the potential to reduce surface flux uncertainties significantly, provided they are sufficiently precise and accurate

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(Rayner and O'Brien 2001; Houweling *et al*. 2004). Because the error targets for the satellite remote sensing of greenhouse gases (e.g. ~0.3% (1 ppm) for CO_2 on regional scales) are so challenging, ground-based validation is essential.

The Total Carbon Column Observing Network (TCCON) is network of ~15 ground-based observatories around the world making routine, high resolution measurements of direct solar absorption spectra in the near infrared (Wunch et al. 2011a, http://tccon-wiki.caltech.edu). These spectra are analysed using standardized retrieval procedures to infer precise and accurate estimates of the column average dry air mole fractions (X_y) of CO_2, CH_4, N_2O and CO. Retrieved X_y are linked to the World Meteorological Organisation trace gas measurement calibration scales based on comparisons with co-incident aircraft measurements (Wunch et al. 2010). The typical network-wide clear-sky XCO_2 measurement repeatability is <0.1% 1-sigma. Historical between-station XCO_2 biases are typically <0.3%, primarily due to laser sampling errors (Messerschmidt *et al*. 2010). New hardware has recently been installed network-wide to address this problem, and should lead to significantly better site-to-site consistency. TCCON provide the primary validation for the operational Greenhouse Gases Observing Satellite, GOSAT (Morino *et al*. 2011) and future greenhouse gas satellite missions. The network targets for precision and accuracy also ensure the TCCON data can be used in their own right for carbon cycle research.

There are three operational TCCON sites in the Southern Hemisphere: Lauder, New Zealand (45.04ºS, 169.68ºE, 2004-present), Darwin, Australia (12.42ºS, 130.88ºE, 2005-present; Deutscher et al. 2010) and Wollongong, Australia (34.41ºS, 150.88ºE, 2008-present). A fourth Southern Hemisphere TCCON site at Reunion Island is expected to be operational in the coming year. We discuss some specific contributions these Southern Hemisphere sites can make, and are making, to carbon cycle research.

Results

The timeseries of the daily mean column average dry air mole fraction of CO_2 (XCO_2) acquired at Lauder, Darwin and Wollongong are illustrated in Fig. 1. The extra-tropical sites (Wollongong and Lauder) are characterised by a small seasonal cycle (peak to peak amplitude ~1 ppm) superimposed on the secular trend. The linear growth rate at the Lauder site over the six year period 2004-2010 is 1.79 +/- 0.06 ppm/year. This is slightly lower than, but still consistent with both the secular trend inferred from baseline surface CO_2 concentrations measured at Baring Head, New Zealand (41.41ºS, 178.87ºE) of 1.87 +/- 0.05 ppm/yr and the change in global mean CO_2 of 11.35 +/- 0.21 ppm (Conway and Tans, 2011) over the same time period. The seasonal variation is ~3 ppm peak-to-peak at the Darwin site, but is still much smaller than the observed seasonal variation in the Northern Hemisphere mid-latitudes (~10 ppm peak-to-peak).

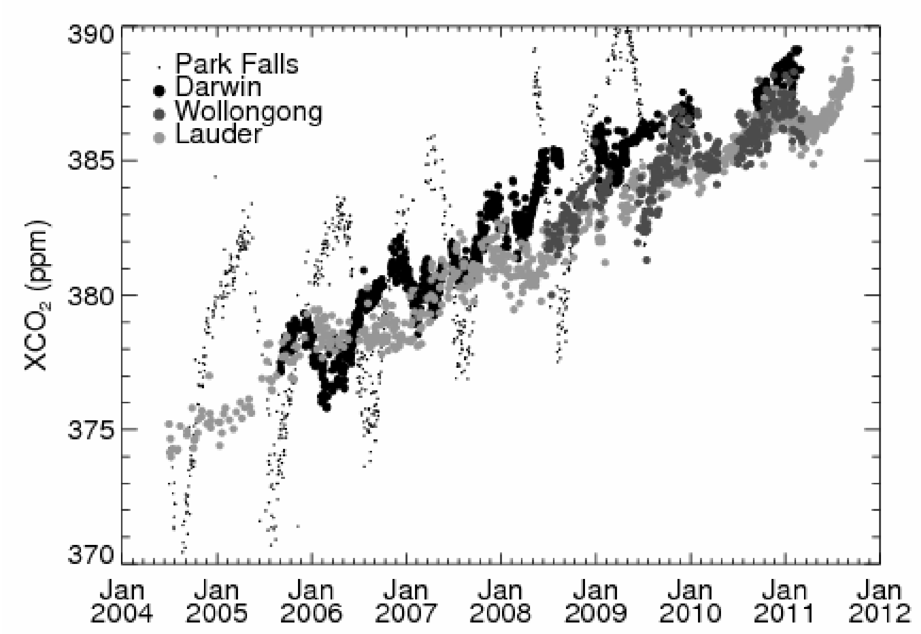

Fig. 8 Timeseries of the column average dry air mole fraction of CO_2 (XCO_2) acquired at Southern Hemisphere TCCON sites in Lauder, Darwin and Wollongong. A partial timeseries from the Northern Hemisphere midlatitude TCCON site in Park Falls, Wisconsin USA is also shown to illustrate the contrast between the amplitude of the seasonal cycle in XCO_2 in the two hemispheres.

Application to satellite validation

Low inherent variability of XCO_2 (due the predominance of ocean) in the Southern Hemisphere provides challenging tests of measurement and retrieval accuracy, both for TCCON and for satellite remote sensing measurements.

Wunch *et al.* (2011b) exploit the secular trend and low spatial and seasonal variability in XCO_2 observed at extra-tropical Southern Hemisphere TCCON sites to derive an a posteriori bias correction scheme for the NASA Atmospheric Carbon Observations from Space (ACOS) project retrievals of XCO_2 from GOSAT spectra.

We have also exploited low spatial and seasonal variability in Southern Hemisphere XCO_2 in our own work validating the National Institute for Environmental Studies (NIES, Japan) GOSAT XCO_2 and XCH_4 retrievals (Yoshida *et al.* 2011). We have characterised retrieval errors for co-located satellite and TCCON observations at the Australasian TCCON sites. We then assessed whether the retrieval error characteristics for the co-located data set are representative of the ensemble of NIES GOSAT retrievals over Australia (by statistical analysis of the GOSAT retrievals, given expected spatial and seasonal variability based on TCCON observations). Through this analysis we identified plausible candidates for the leading sources of satellite retrieval error. It appears likely that the treatment of aerosol in the current NIES retrieval algorithm is a significant source of error. In collaboration with the NIES GOSAT validation and retrieval algorithm developments teams, we will now use available aerosol measurements at the Southern Hemisphere TCCON sites in radiative transfer simulations to assess whether this improves agreement between GOSAT and TCCON measurements, to quantify errors due to incorrect treatment of aerosol in operational retrievals and, ultimately, to improve the NIES retrieval algorithm.

CO_2 fluxes from Southern Hemisphere land masses

Variations in TCCON XCO_2 on synoptic to seasonal timescales reflect hemispheric scale fluxes (Keppel-Aleks *et al*. 2011). Thus information on terrestrial biosphere and biomass burning CO_2 fluxes from Southern Hemisphere land masses (which are poorly observed by the surface monitoring network) might possibly be inferred from the Southern Hemisphere TCCON data. The seasonal variation of XCO_2 in the Southern Hemisphere timeseries is small, so clearly this will be challenging and highly dependent both on the accuracy and precision of the TCCON measurements (in particular, minimisation of sources of seasonally-dependent measurement biases) and accurate modelling of relevant transport processes.

We have performed TM3 forward model simulations using CarbonTracker 2010 analysed fluxes for the terrestrial biosphere and oceans, the Carbon Data Information Analysis Center (CDIAC) global and national fossil fuel emissions with within-country spatial distributions from EDGAR and GFED2 biomass burning emissions. Tracers were carried for each flux process for the TransCom regions (additionally, Australasia was split into four sub-regions: tropical and temperate Australia and the North and South Islands of New Zealand). These tagged tracer simulations have been used to understand the drivers of seasonal variations in XCO_2 and interpret differences between TCCON measurements and the CarbonTracker 2010 analysis at the Southern Hemisphere TCCON sites.

The tagged tracer simulations show the seasonal cycle in XCO_2 at the Southern Hemisphere TCCON sites is primarily due to the terrestrial biosphere, with a significant contribution due to biomass burning in the austral spring at the Darwin site. The terrestrial biosphere signal has a significant contribution due to inter-hemispheric transport of the Northern Hemisphere terrestrial biosphere flux imprint (damped and with a ~6 month phase lag) at all Southern Hemisphere sites. The combined terrestrial biosphere flux contributions from South Africa and South America make significant contributions (and of comparable magnitude) to the terrestrial biosphere signal at the extra-tropical TCCON sites (Lauder, Wollongong). At Darwin the South African and South American contribution has similar magnitude, but a different phase; contributions from tropical Australia are significant here too. Small differences between Lauder and Wollongong are associated with contributions from the temperate Australian biosphere.

With due consideration of the phasing and magnitude of the various contributions to the seasonal cycle of XCO_2 at Darwin and Lauder, we conclude the differences between TCCON measurements and the CarbonTracker 2010 analysis are potentially due to underestimates of South African and South American biomass burning emissions (with possible episodic discrepancies due to transport of South East Asian biomass burning emissions at the Darwin site).

Conclusions

High quality ground-based measurements of the column average dry air mole fraction of CO_2 and other important greenhouse gases have been acquired at the three operational TCCON sites in the Southern Hemisphere over the past 7-8 years. This data has had a unique and central role to play in the validation of CO_2 retrievals from the GOSAT satellite. Multi-site analysis of Southern Hemisphere TCCON timeseries and interpretation using tagged tracer modelling suggests they may also provide important information on CO_2 fluxes from Southern Hemisphere continents - regions which are poorly observed by the surface monitoring network.

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APPLYING HILBERT-HUANG TRANSFORM TO SURFACE GREENHOUSE GAS TIME SERIES DATA IN LAUDER, NEW ZEALAND

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Abstract

To accommodate the variety of data generated by nonlinear and non-stationary processes in nature, data analysis methods should be adaptive. The Hilbert-Huang transform (HHT) is a new method for the analysis of non-stationary signals in an adaptive manner. This allows the frequencies and amplitude inherent in a time series to be evaluated. The method consists of two parts: (1) the empirical mode decomposition (EMD); and (2) the Hilbert spectral analysis. The key part of the method is the first step, the EMD, in which the data are decomposed into time scale components, called intrinsic mode functions (IMF). The second step, the Hilbert transform (HT) is then applied. The Hilbert transform produces a localized time-frequency spectrum and instantaneous (time-dependent) frequencies of the modes. Since atmospheric and climatic phenomena are highly non-stationary and nonlinear, HHT would potentially provide more insights into their long term records.

In this study:

1. the HHT method is described;
2. Carbon Tracker's simulated surface mixing ratio of carbon dioxide (CO_2) from 2000 to 2010 in Lauder, New Zealand is used to examine the performance of HHT in time series analysis of long term greenhouse gas concentration records;
3. and the time series record of in situ observations of CO_2, CH_4, N_2O and CO from Lauder, New Zealand, taken during the period from the 2nd of May 2007 to the 31st, of December 2007 is utilised to assess the performance of HHT in measured data.

The results show that HHT can be applied for trend extraction and provides further insights to the time scales of changing daily and seasonal cycles.

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SOUTHERN OCEAN CO_2 NETWORK: CALIBRATION STRATEGY, INTERCOMPARISON RESULTS AND A PRELIMINARY EXAMINATION OF THE OCEANIC CO_2 SIGNAL AT MACQUARIE ISLAND

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Abstract

The Southern Ocean (south of 44°S) is a major sink of atmospheric CO_2, however a recent paper (Le Quéré *et al*. 2007) suggests that this sink may be shrinking, which would have serious implications for the global carbon cycle. Our ability to constrain the mean Southern Ocean carbon flux and its seasonality and interannual variability has been limited by the small number of Southern Ocean pCO_2 measurements, especially in winter. We are investigating whether the magnitude of and variations in the Southern Ocean carbon flux can be observed in the atmospheric CO_2 mixing ratio using a high precision network of continuous *in situ* CO_2 measurements.

This talk will outline methods used to address possible instrumental and site biases and to link data sets to a common, derived calibration scale. We will present results obtained from the cylinder intercomparison program (ICP) and preliminary data for an *in situ* comparison study between three instruments (a cavity ringdown spectrometer and a low and a high precision non-dispersive infrared (NDIR) CO_2 analyser) currently underway at Baring Head, New Zealand (41.4°S, 174.9°E) (Da Costa and Steele 1999; Francey and Steele 2003). This will more precisely link data collected at Southern Ocean sites Baring Head, Macquarie Island, Australia (54.5°S, 158.95°E), Cape Grim, Australia (40.68°S, 144.69°E) and Amsterdam Island (37.83°S, 77.55°E) and the calibration hubs located at CSIRO, Australia and LSCE, France.

An examination of the oceanic signal of the Macquarie Island record was also conducted. This signal was isolated from local biospheric and fossil events using a wind speed based filter (> 7 m/s) while CSIRO Conformal-cubic Atmospheric Model (CCAM) runs and HYSPLIT back trajectories were used to identify and remove land events. This ocean signal was then used to assess the seasonal cycles and interannual variability predicted by forward CCAM runs of biospheric and fossil tracers and ocean fluxes predicted by the REgional Carbon Cycle Assessment and Processes (RECCAP) project models.

Synoptic scale variations in oceanic signal were also calculated by removing the baseline. This residual was compared to four (baseline removed) ocean tracers. Overall regression statistics between the observed and model signals were poor ($R^2 \leq 0.25$). However months with significant oceanic flux spatial variability showed much larger correlations ($R^2 \sim 0.6$). Tracers based on more recent pCO_2 climatology and a biogeochemical ocean general circulation model

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matched observations more closely than those of the early climatology. This preliminary analysis suggests that models can be used to interpret the synoptic scale Southern Ocean CO_2 signal when strong spatial gradients exist in the oceanic fluxes. It also highlights the importance of observations for quantifying the Southern Ocean sink during periods of low flux spatial variability and suggests that the inclusion of these continuous in situ data sets may improve the accuracy of inversion based estimates of Southern Ocean sink strength and variability.

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PROGRESS TOWARDS MODELING TROPOSPHERIC CHEMISTRY USING ACCESS AND UKCA

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Abstract

The Australian Community and Earth Systems Simulator (ACCESS) is designed to underpin Earth Systems Modelling research in Australia. An important module of this project is the UK Chemistry and Aerosols (UKCA), which includes various reactive chemical gases and aerosol species (i.e. non-CO_2), which are needed to predict radiative feedbacks with the coupled climate system. In this presentation, we outline current progress and future plans for developing the tropospheric chemistry component of UKCA. Simulation results show the model sensitivity to changes in surface emissions when running the ACCESS with prescribed sea surface temperatures (i.e. non-coupled), as well as the sensitivity to radiative feedbacks with methane. Comparisons of the model results with AGAGE and CSIRO surface networks are made, as well as comparisons with chemical species reanalysis products. Further evaluation is to be facilitated by atmospheric nudging schemes and improved emission datasets.

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THE CSIRO/CAWCR COLLABORATIVE ATMOSPHERIC GREENHOUSE GAS OBSERVATION NETWORK FOR THE SOUTHEAST ASIAN - AUSTRALIAN TROPICAL REGION

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Abstract

The tropical regions play a major role in the global atmosphere through both natural and anthropogenic processes. Many of these processes and their impacts on future climate change are poorly understood, which is due largely to a deficiency of high quality atmospheric observation programs in these important regions.

To address this deficiency, a high precision atmospheric observation network for greenhouse gases (GHG) and related trace gas species is being expanded in the Southeast Asian-Australian region, in collaboration with partners in India and Malaysia. The primary objectives of the network are to:

1. Improve our global understanding of the forcing of climate change by providing observations of climatically active atmospheric constituents in the critically under-sampled tropical latitudes, and
2. Dramatically reduce the uncertainties in estimates of GHG emissions from Australia.

The Southeast Asian-Australian tropics and the tropics globally, are regions expected to be sensitive to future climate change due to vulnerabilities in the large carbon pools of tropical vegetation (subjected to biomass burning and deforestation) and draining of the tropical peatlands (Canadell *et al*. 2007).

The Cape Grim Baseline Air Pollution Station (CGBAPS) is one of only three designated GHG comparison sites ('super' sites) in the WMO/GAW program and is the only one in the Southern Hemisphere. CGBAPS is the central reference observation site for the existing Australian regional GHG network, including the proposed expansion to the Australian Greenhouse Gas Observation Network (AGGON). A key addition to this network is a new tropical atmospheric observation site established recently (2010) at Gunn Point in the Northern Territory (12.249ºS, 131.045ºE). This site incorporates high precision *in-situ* measurement and flask air sample collection programs for a range of GHG and related trace gas species. It is anticipated high precision atmospheric observations from this region should significantly improve the

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understanding of the tropical sources and sinks of the major anthropogenic GHGs (CO_2, CH_4, N_2O). High precision 'LoFLo' (NDIR) and 'Picarro' (Cavity Ring Down Spectroscopy) instruments are being used for the continuous measurement of CO_2, CH_4 and $^{13}CO_2/^{12}CO_2$.

The Gunn Point site is an existing Bureau of Meteorology Radar station (since 1997) and an Atmospheric Radiation Measurement site (ARM, funded by the US Department of Energy), operated by CAWCR. The site has been involved in numerous tropical meteorology field campaigns and experiments including: 'Mctex', 'TRMM', 'Dawex', and 'TWPICE'. This combination of research capabilities with both chemical composition and physical dynamical aspects of the tropical atmosphere provides a unique opportunity to develop a world class tropical atmosphere research capability.

The research program and preliminary data from this new site as well as those of collaborative programs at sites in the Asian tropical region at Cape Rama, India (NIO) and Danum Valley GAW station, Malaysia (MMD) will be discussed.

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TOWARDS SPACE BASED VERIFICATION OF CO_2 EMISSIONS FROM STRONG LOCALIZED SOURCES: FOSSIL FUEL POWER PLANT EMISSIONS AS SEEN BY A CARBONSAT CONSTELLATION

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Abstract

Carbon dioxide (CO_2) is the most important man-made greenhouse gas (GHG) that cause global warming. With electricity generation through fossil-fuel power plants now as the economic sector with the largest source of CO_2, power plant emissions monitoring has become more important than ever in the fight against global warming. In a previous study done by Bovensmann *et al*. (2010), random and systematic errors of power plant CO_2 emissions have been quantified using a single overpass from a proposed CarbonSat instrument. In this study (Velazco *et al*. 2010), we quantify errors of power plant annual emission estimates from a hypothetical CarbonSat and constellations of several CarbonSats while taking into account that power plant CO_2 emissions are time-dependent. Our focus is on estimating systematic errors arising from the sparse temporal sampling as well as random errors that are primarily dependent on wind speeds. We used hourly emissions data from the US Environmental Protection Agency (EPA) combined with assimilated and re-analyzed meteorological fields from the National Centers of Environmental Prediction (NCEP). CarbonSat orbits were simulated as a sun-synchronous low-earth orbiting satellite (LEO) with an 828-km orbit height, local time ascending node (LTAN) of 13:30 (01:30 p.m.) and achieves global coverage after 5 days. We show, that despite the variability of the power plant emissions and the limited satellite overpasses, one CarbonSat can verify reported US annual CO_2 emissions from large power plants (≥ 5 Mt CO_2 yr^{-1}) with systematic errors that are good enough to detect changes in trends of several power plant annual emissions. We additionally investigated two different satellite configurations using a combination of 5 CarbonSats. One achieves global coverage everyday but only samples the targets at fixed local times. The other configuration samples the targets five times at two-hour intervals approximately every 6th day but only achieves global coverage after 5 days. From the statistical analyses, we found, as expected, that the random errors improve by approximately a factor of two if 5 satellites are used. On the other hand, more satellites do not result in a large reduction of the systematic error. The systematic error is somewhat smaller for the CarbonSat constellation configuration achieving global coverage every day. Finally, we recommend the CarbonSat constellation configuration that achieves daily global coverage.

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AEROSOLS IN ACCESS CLIMATE MODELS

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Abstract

Aerosols play an important role in determining the state of the climate system. On a globally-averaged basis, anthropogenic aerosols partly offset the warming caused by greenhouse-gas increases over the industrial period, although the uncertainties involved are considerable (IPCC AR4, 2007). In my talk I will give an overview of aerosols in ACCESS models and present initial results from climate-model simulations being carried out for the IPCC's Fifth Assessment Report (AR5). The challenges involved in modelling and evaluating the global distribution of aerosols will be discussed. Dust uplift, in particular, is highly sensitive to the details of the land-surface scheme and the prevailing meteorology. A description of the ACCESS modelling system is given below.

The Australian Community Climate and Earth-System Simulator, known as ACCESS, is a collection of global climate and weather-forecasting models being developed jointly by CSIRO and the Australian Bureau of Meteorology in collaboration with the University community and the U.K. Met Office (UKMO). The ACCESS models are built around the Met Office Unified Model of the atmoshpere (the UM) coupled to the Australian Community Ocean Model (AusCOM) and either the CSIRO Atmosphere-Biosphere Land-Exchange system (CABLE) or the UK Met Office Surface-Exchange Scheme (MOSES). AusCOM is based on the GFDL MOM4p1 ocean model and the LANL CICE sea ice code. A number of configurations of the ACCESS climate model are being developed in parallel, based on different versions of the Unified Model and either the MOSES or CABLE land-surface scheme. Aerosols in ACCESS models are treated using the Unified Model's CLASSIC aerosol scheme, which stands for the Coupled Large-Scale Aerosol Simulator for Studies in Climate. An overview of the CLASSIC aerosol scheme and its performance in the different ACCESS climate model configurations will be presented.

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ATMOSPHERIC OBSERVATIONS AND EMISSION PATTERNS OF THE FOAM BLOWING COMPOUND HCFC-141B AND ITS REPLACEMENTS HFC-365MFC AND HFC-245FA FROM THE AGAGE NETWORK

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Abstract

The regulations of the Montreal Protocol and its subsequent amendments target the reduction in the use of halogenated compounds that harm the stratospheric ozone layer. Various applications (foam blowing, cooling, fire suppression) and various countries (Article-5 and non-Article-5) have undergone differing phase-out schemes since the implementation of the Protocol. In the foam-blowing sector, one of the major earlier used compounds, CFC-11 (CCl_3F), is now banned from usage globally. The phase-out of its main replacement, HCFC-141b (CH_3CCl_2F), is now underway, almost completed in non-Article-5 countries and an upcoming freeze in Article-5 countries in 2013 with a subsequent reduction in usage.

The two major replacements for HCFC-141b are the hydrofluorocarbons (HFCs) HFC-365mfc ($CH_3CF_2CH_2CF_3$) and HFC-245fa ($CHF_2CH_2CF_3$). While these compounds are not harmful to the stratospheric ozone layer, they are greenhouse gases with Global Warming Potentials (GWPs) of about 800 and 1000 (on a 100 year time frame), and atmospheric lifetimes of about 9 yr and 8 yr, respectively. Their large-scale productions started in about 2002 as shown from measurements of these compounds in archived air samples (Vollmer et al., 2010). Their global emissions for 2010 were estimated at ~3 kt yr^{-1} for HFC-365mfc and ~6.5 kt yr^{-1} for HFC-245fa, using atmospheric observations (Vollmer et al., 2010). There are no obligations to report HFC-365mfc and HFC-245fa to the United Nations Framework Convention on Climate Change (UNFCCC), presumably because their large-scale use was not expected when the convention came into place (e.g. HFC-245ca is listed, a compound that is only marginally used).

High-precisions two-hourly atmospheric observations of HCFC-141b, HFC-365mfc and HFC-245fa (along with a suite of other halogenated compounds) are available from the Advanced Global Atmospheric Gases Experiment (AGAGE) network, now also including the Chinese station Shangdianzi (~100 km north of Beijing) and some measurements from urban areas (Aspendale near Melbourne, Australia, and La Jolla, California, USA). These observations, along with other stations that cover footprints with regional emissions, allow for a better understanding of the regional emission patterns and may help to provide an estimate of the emissions and their transitions from one class of compounds to another. This is particularly useful for the above-mentioned compounds, for which bottom-up information (based on industry estimates) only exist in an aggregated way (e.g. HCFC-141b) or are completely lacking (HFC-365mfc and HFC-245fa). For example, the European stations Mace Head (Ireland) and

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Jungfraujoch (Switzerland) exhibit large HFC-365mfc concentrations above background but minor HCFC-141b pollution events, while Shangdianzi shows the opposite with virtually no HFC-365mfc and minor HFC-245fa pollution events.

While the observations at the AGAGE stations nicely show the transitional patterns from CFCs to HCFCs and to HFCs, the combined observations of HFC-365mfc and HFC-245fa also show the preference in the choices of these two compounds, which have similar application characteristics in the foam blowing sector. However the users' choices for HFC-365mfc or HFC-245fa has somehow been limited in some areas due to some additional regulations (e.g. fire-related safety issues) and this is shown in the relative magnitude of the pollution events at various stations. The most pronounced example are the relative pollution magnitudes for Aspendale compared to La Jolla showing much larger HFC-365mfc vs. HFC-245fa pollution events for Aspendale and the opposite for La Jolla. These observations lead to the assumption of largely differing emission ratios for the two HFCs and suggest that these ratios may potentially be used as air mass tracers allowing for the improvement of source attributions along with regional emission modeling efforts.

Finally, the observations from all stations suggest a recent leveling of the global emissions of HFC-365mfc and HFC-245fa. This is somewhat unexpected but could potentially be a temporary plateauing in a time where the Non-Article-5 countries have now completely switched from HCFC-141b to the two new HFCS, while the Article-5 countries have not yet started this transitional process. Future observations, particularly those capturing the Asian emissions, are expected to help in understanding the global and regional evolution of the emissions of these HFCs. They should also help in better understanding the discrepancies of the observation-based global emissions and projections by Vollmer et al., 2011, which suggest much lower near-future global emissions compared to those using independent information.

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PREDICTING FUTURE AIR QUALITY IN VICTORIA: OVERVIEW AND PROJECT DESIGN

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Introduction

Effective management of air quality requires a good understanding of pollutant emissions, dispersion, chemical transformation and deposition, together with insight into current and future trends, the factors behind these trends, and opportunities for influence and control. Climate change, technology improvements, population growth and various industry changes are amongst the major drivers of air quality trends. This extended abstract describes a 2-year project to estimate future concentrations of a range of air pollutants in Victoria, Australia, with an initial focus on the city of Melbourne. Uncertainties in prediction are a key challenge in this project, and will require careful attention.

Literature

A large body of literature now exists covering the effect of climate change and air quality. Much of this work is focussed on ozone, which is expected to increase in urban areas under a warmer climate (Walsh et al. 2009). Future particle concentrations are more uncertain (Jacob & Winner, 2008) due to the diversity of particle sources, and because of the influence of difficult-to-predict meteorological factors such as rainfall.
Studies of future emission trends have undertaken at both global and regional scales. For example, Wu *et al.* (2008) considered the separate effects of climate change and anthropogenic emission changes on air quality in the US, finding that greater emission controls may have to be in place to counteract the effect of climate change (the 'climate penalty'). The Future Air Projections project is the first Australian study to combine detailed modelling of future pollutant concentrations considering the effects of both climate change and emission trends.

Project Design

The project involves a number of significant research tasks:

- Development of a baseline emissions inventory for Victoria and Melbourne (year 2006);
- TAPM-CTM Model improvements & verification against measurements for Melbourne;
- Simulation of the effect of climate change only for two future decades (2030s & 2070s);
- Development of a 'most likely' future scenario, with emission inventories for 2030 & 2070;
- Development of an exposure model, accounting for population activity patterns;

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[*] For a detailed literature review, contact the corresponding author (sean.walsh@epa.vic.gov.au).

- Simulation of future air quality, accounting for climate change and ‘most likely’ emission changes, for two future decades;
- Sensitivity tests and source analysis to discern the most important driving factors affecting current and future air quality;
- Development of alternative future scenarios, considering factors such as carbon pricing, peak oil, and air quality policy options;
- Simulation of air quality under alternative futures, accounting for climate change;
- A feasibility study looking at how to model the effect of climate change on emissions from large scale dust and fire events.

The final step in the project will be an overall assessment of predicted trends, in terms of air pollution exposure and consequent health impacts.

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VERTICAL RADON-222 PROFILES IN THE ATMOSPHERIC BOUNDARY LAYER

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Abstract

Radon-222 (radon) is a naturally occurring radioactive tracer of air mass transport on different time and space scales. In particular, the vertical distribution of radon has been demonstrated to be useful for characterisation of exchange and mixing processes within the atmospheric boundary layer.

In 2006 we started a program of research, using radon-222 to advance our understanding of these processes as part of a broader goal to improve parameterisation schemes for vertical mixing in the lower atmosphere. Two types of experiments have been conducted. The first is based on continuous hourly estimates of radon-222 concentration gradients at two meteorological towers, one focussing on near-surface gradients (2-50m) recorded on a 50m tower at Lucas Heights in New South Wales (34.05ºS, 150.98ºE), and the other on boundary layer gradients (20-200 m) measured on a 213m tower at the Cabauw Experimental Site for Atmospheric Research in the Netherlands (51.971ºN, 4.927ºE). The second experiment type relies on the collection of high resolution radon-222 vertical profiles up to 4,000 m above ground level using radon samplers mounted on an instrumented motorised research glider.

In this presentation, we discuss selected results from a unique set of high resolution vertical radon profiles measured in 2007-2010 in clear and cloudy daytime terrestrial boundary layers over rural New South Wales. The profile examples reveal the characteristic structure and variability of three major types of daytime boundary layer: 1) dry convective boundary layers, 2) mixed layers topped with residual layers, and 3) convective boundary layers topped with coupled non-precipitating clouds. We demonstrate that important boundary layer processes are identifiable in the observed radon profiles, including ‘‘top down’’ mixing associated with entrainment in clear-sky cases and strongly enhanced venting and sub-cloud layer mixing when substantial active cumulus are present.

A related presentation (Chambers *et al*. 2011) outlines some recent results based on our radon gradient measurements at the Lucas Heights tower.

Reference

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