Atmospheric Composition & Chemistry Observations & Modelling Conference

incorporating the

Cape Grim Annual Science Meeting 2015

Abstracts

11-13 November 2015

hosted by

University of Wollongong

Murramarang Beachfront Nature Resort
South Durras, NSW, Australia



Edited by: N. Derek & P. B. Krummel

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Citation

Author, A. B., A. B. Author and A. B. Author, Abstract Title, in *Atmospheric Composition & Chemistry Observations & Modelling Conference incorporating the Cape Grim Annual Science Meeting 2015* [abstract], 11-13 November 2015, Murramarang, NSW, N. Derek and P. B. Krummel (eds.), Bureau of Meteorology and CSIRO Oceans and Atmosphere, Melbourne, Australia, page#, 2015.

Day 1: Wednesday, 11 November 2015

12:30	**Lunch**	**Poolside**
13:35	**Convenors**	**Welcome & general information on arrangements etc**
Chair	**Clare Paton-Walsh**	**Session 1 – Oral Presentations**
13:45	Britton Stephens	Atmospheric oxygen measurements over the Southern Ocean
14:00	Ian Galbally	What were the concentrations/mole fractions of ozone in the troposphere prior to 1970?
14:15	Jesse Greenslade	Tropospheric ozone over Melbourne, Macquarie Island and Davis
14:30	Matt Tully	Impact of approximations in the recommended Dobson algorithm on total column ozone measurements at four Australian sites
14:45	Paul Krummel	The 2015 Antarctic ozone hole
15:00	Paul Fraser	The Carbon Tetrachloride 'Mystery': Further Developments
15:15	Paul Fraser	Measurements of atmospheric trace species can change industrial practices that lead to GHG emissions
15:30	**Afternoon Tea**	**Poolside**
Chair	**Paul Krummel**	**Session 2 – Oral Presentations**
16:00	Robyn Schofield	AIR-BOX - Atmospheric Integrated Research facility for Boundaries and Oxidative experiments
16:15	Blagoj Mitrevski	An alternative method for in situ atmospheric hydrogen measurement at Cape Grim
16:30	Alan Griffiths	Increasing the accuracy and temporal resolution of two-filter radon–222 measurements by correcting for the instrument response
16:45	Alastair Williams	Universal baseline characterisation of air masses using radon
17:00	David Etheridge	Monitoring regional emissions of methane with continuous concentration measurements and inverse modelling and application to coal seam gas
17:15	Sarah Lawson	Coal seam gas and air quality in the Surat Basin, Queensland: A new two- year monitoring program
17:30	Melita Keywood	IGAC update and discussion
18:30	**Dinner**	**Bistro**

Day 2: Thursday, 12 November 2015

08:00	**Breakfast**	**Bistro**
Chair	**Sarah Lawson**	**Session 3 – Oral Presentations**
09:00	Peter Rayner	The Clean Air and Urban Landscapes Hub: What is it and why should I care?
09:15	Jeremy Silver	Modelling emissions and transport of rye-grass pollen in SE Australia
09:30	Clare Walter	Cleaner Air, Less Cancer
09:45	Fabienne Reisen	Air quality impacts of the Hazelwood mine fire
10:00	Kim Oanh Nguyen Thi	Emission characterization for rice straw field burning in Southeast Asia
10:15	Maximilien Desservettaz	Results from the June 2014 Gunn Point campaign, including emission factors of greenhouse gases and particulates from savanna fires
10:30	**Morning Tea**	**Poolside**
Chair	**Stephen Wilson**	**Session 4 – Oral Presentations**
11:00	**Melita Keywood**	**Cape Grim Particle Program 2004-2015**
11:30	John Ogren	Is there bias in the estimated climate forcing by black carbon aerosols?
11:45	Simon Alexander	Clouds and aerosols at Cape Grim observed with lidar

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Chair	Stephen Wilson	Session 4 – Oral Presentations……continued
12:00	Luke Cravigan	Sources of cloud condensation nuclei inferred from volatility and hygroscopicity measurements over the Southern Ocean
12:15	Ruhi Humphries	Atmospheric aerosol formation over East Antarctic sea ice – possible Hg catalysed nucleation?
12:30	Peter Nelson	Characterisation of atmospheric fine particles using QEMSCAN and isotopic carbon measurements
12:45	**Lunch**	**Poolside**
13:45	**Paton-Walsh/ Krummel**	**Session 5 – Poster Presentations** **Each presenter to give a 1-2 minute, 1-slide poster summary**
Christopher Caldow		Measurement of dissolved greenhouse gases (CO_2, CH_4, N_2O & CO) and their water-atmosphere exchange in inland waters
Peter Degorski		Constraining the carbon cycle with carbon 13 observations
Maximilien Desservettaz		Effect of fuel loading on greenhouse gases emissions from fires in the CSIRO Pyrotron
Ian Galbally		Particles in Western Sydney: Model-observation verification
Ian Galbally		Tropospheric Ozone Assessment Report: Global metrics for climate change, human health and crop/ecosystem research – a new global collaboration
Ruhi Humphries		The CAPRICORN Project – investigating cloud-aerosol interactions over the Southern Ocean
Wenwen Huo		Using atmospheric radiocarbon to estimate fossil fuel sources: A test case with a known source
Nicholas Jones		Trends in CCl_4 from a network of total column measurements
Alireza Kharazmi		Phototautomerization: A new pathway to formation of organic acids
Sarah Lawson		First data from the new Cape Grim VOC monitoring program
Katrina Macsween		Identifying the potential influence of climate change on mercury air surface exchange
Khalia Monk		Assessing the accuracy of WRF in simulating meteorology, NSW
Travis Naylor		Methane, nitrous oxide and ammonia emissions from manure stockpiling by the swine and poultry industries of Australia
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Clare Paton-Walsh		Clean air and urban landscapes – Towards a clean air plan for Western Sydney
Paul Steele		Tropospheric hydrogen – an update based on measurements from Cape Grim, the CSIRO global flask network and Antarctic firn air
David Etheridge		Atmospheric abundance and global emissions of perfluorocarbons CF_4, C_2F_6 and C_3F_8 since 1900 inferred from ice core, firn and atmospheric measurements
Steve Utembe		Particulate characterisation study of Western Sydney using WRF-Chem
Marcel van der Schoot		Developments in the CSIRO Australian Greenhouse Gas Observation Network (AGGON)
Callan Wilcox		Understanding the primary oxidation of terpenes
Stephen Wilson		Water in the visible: Retrieving water vapour column amounts from sun photometry
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16:30	Matthieu Miller	New developments in measuring reactive mercury in the atmosphere
16:45	Doreena Dominick	Time variation patterns of CH_2O and NO_2 monitored by MAX-DOAS, PTRMS and NO-NO_2-NOx instruments during Measurement of Urban, Marine and Biogenic Air (MUMBA) Campaign
17:00	Kathryn Emmerson	Evidence builds for a biogenic field campaign in Australia
17:15	Louisa Emmons	Characterizing emissions and chemical evolution from aircraft
17:30	Jenny Fisher	Organic nitrate chemistry and its implications for nitrogen budgets: Insights from aircraft and ground-based observations in the southeast US
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09:00	Kaitlyn Lieschke	Decadal-scale trends and variability in atmospheric composition over Wollongong, Australia
09:15	Guang Zeng	Modelling tropospheric composition in the Southern Hemisphere
09:30	Matthew Woodhouse	Modelling 20th century atmospheric composition
09:45	Andrew Zammit-Mangion	Atmospheric trace gas inversion with spatial statistical models
10:00	Zoë Loh	What can we learn from comparing the Cape Grim and Casey Picarro records of atmospheric CH_4 and CO_2?
10:15	Chris Waring	Total depletion of methane in cave atmospheres
10:30	**Morning Tea**	**Poolside**
Chair	**Marcel van der Schoot**	**Session 8 – Oral Presentations**
11:00	Joel Wilson	An AirCore system for measuring vertical profiles and ground-based sources of greenhouse gases in Australia
11:15	David Pollard	Initial results from an AirCore campaign at the Lauder TCCON site
11:30	Voltaire Velazco	Australian CO_2 'landscape' from TCCON and Lagrangian transport modelling
11:45	Xuanze Zhang	Response of terrestrial carbon cycle to climate variability and atmospheric CO_2: Numerical sensitivity experiments using the land-surface model CABLE v2
12:00	Nicholas Deutscher	Assessing Australian biospheric CO_2 fluxes using GEOS-Chem and atmospheric measurements
12:15	Tilo Ziehn	Designing optimal greenhouse gas observing networks for Australia
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Atmospheric oxygen measurements over the Southern Ocean

B. B. Stephens[1*], J. D. Bent[1], R. F. Keeling[2], A. S. Watt[1], S. R. Shertz[1], C. Sweeney[3], S. E. Mikaloff-Fletcher[4], P. K. Patra[5] and M. C. Long[1]

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[2] *Scripps Institution of Oceanography, La Jolla, CA, USA*
[3] *University of Colorado, Boulder, CO, USA*
[4] *National Institute for Water and Atmospheric Research, Wellington, NZ*
[5] *Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan*

* corresponding author: Britton Stephens [stephens@ucar.edu]

Abstract

The HIAPER Pole-to-Pole Observations (HIPPO) campaign, which flew on the NSF/NCAR Gulfstream V (GV) research aircraft from 2009-2011, measured the vertical, latitudinal, and seasonal distribution of atmospheric oxygen (O_2) with unprecedented vertical extent and latitudinal coverage, including 5 flights extending as far as 67°S from Christchurch, New Zealand (Figure 1a). Subsequently, since 2012 we have been conducting continuous measurements of atmospheric O_2 from the NSF ship ARSV Laurence M. Gould, operating in all seasons between Punta Arenas, Chile and Palmer Station Antarctica, and resolving the seasonal and latitudinal O_2 variations over the Southern Ocean with even greater clarity (Figure 1b). These recent *in situ* measurement programs leverage a multi-decade global network of flask sampling stations, including Cape Grim Observatory, as well as earlier airborne flask sampling above Cape Grim. I will discuss the challenges in making these measurements and will present some of the insights we are gaining from them, including unique constraints on the thermal and physical forcing of Southern Ocean seasonal carbon exchange. Two upcoming field deployments will further advance our Southern Ocean atmospheric oxygen observing capabilities. In January and February of 2016, the O_2/N_2 Ratio and CO_2 Airborne Southern Ocean Study (ORCAS) will conduct 6 weeks of flights on the NSF/NCAR GV, based out of Punta Arenas, Chile. Also this coming austral summer, colleagues at CSIRO will deploy an *in situ* O_2 analyzer, modelled after the Gould instrument, on board the R/V Investigator, providing unique opportunities for further collaborations.

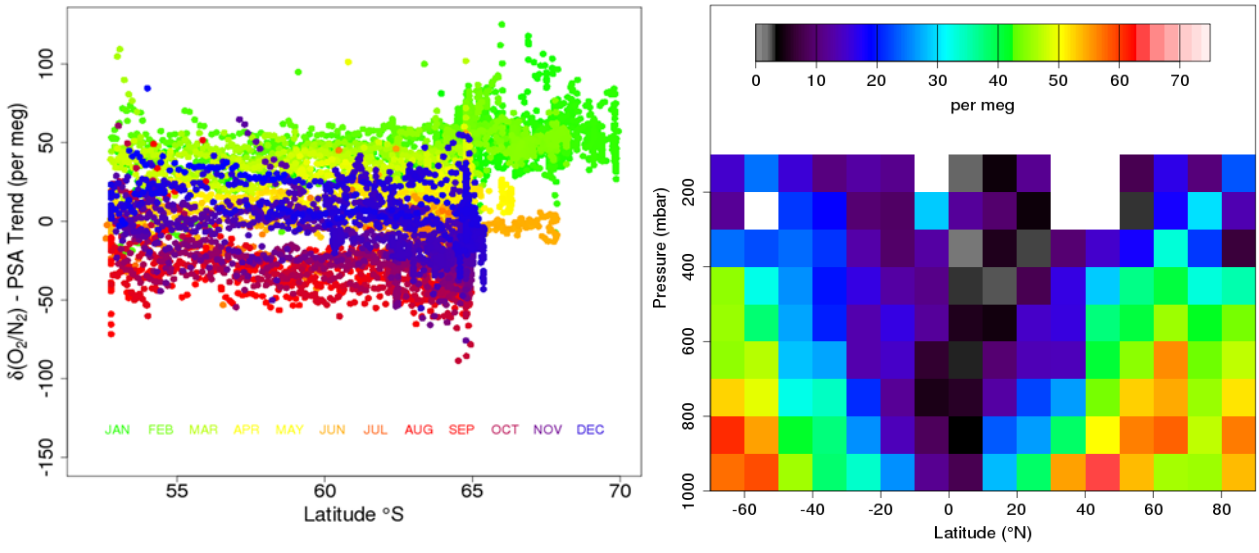


Figure 1. a) Seasonal amplitude of atmospheric potential oxygen (APO = O_2 + 1.1*CO_2), determined by binning and fitting with 1-harmonic, observations from the 5 HIPPO campaigns. B) Hourly observations of atmospheric O_2 between June 2012 and June 2015 from ARSV L.M. Gould.

What were the concentrations/mole fractions of ozone in the troposphere prior to 1970?

I. E. Galbally*

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* corresponding author: Ian Galbally [ian.galbally@csiro.au]

Abstract

One of the key challenges in atmospheric science is to model the changes in global temperature and climate that have occurred from the pre-industrial period to the present. One of the requirements to do this is a knowledge of the evolving atmospheric concentrations of climate forcing species during this period. These climate forcers include long-lived species such as carbon dioxide and nitrous oxide and short lived climate forcers such as black carbon and tropospheric ozone.

Tropospheric ozone is unique amongst these species in that it is a reactive gas and cannot be kept in cylinders and most probably does not persist in bubbles in ice cores. Hence no current measurements of past concentrations are possible. Therefore the history of the atmospheric concentrations of tropospheric ozone must be derived from measurements made at the historic time being considered. This means that the observational record for tropospheric ozone is probably more uncertain than that of other climate forcers.

Most of the observations of tropospheric ozone before the 1970s were made with measurement techniques and monitoring setups that are not traceable to modern measurement standards. The challenge is to devise methods for evaluating these early observations so that the uncertainties in the observations are understood and quantified. Four sets of criteria are proposed that will be used to evaluate these early datasets. These sets of criteria fall under the headings:

- Suitability of the measurement technique
- Effective sampling of the outside atmosphere
- Representativeness of the measurements
- Consistency of past observations with current understanding.

These sets of criteria are applied to descriptions of pre-1970 tropospheric ozone measurements. A sample of techniques used during the period, 1845 – 1970, will be evaluated. A preliminary assessment of the long-term record of tropospheric ozone will be presented.

Tropospheric ozone over Melbourne, Macquarie Island and Davis

J. W. Greenslade[1*], S. Alexander[2] and R. Schofield[3]

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[2] *Australian Antarctic Division, Hobart, Tasmania*
[3] *School of Earth Sciences, University of Melbourne, Melbourne, Victoria*

* corresponding author: Jesse Greenslade [jwg366@uowmail.edu.au]

Abstract

Tropospheric ozone is important for both air quality and climate change. Over the industrial period, tropospheric ozone has been estimated to exert a radiative forcing equivalent to a quarter of the CO_2 forcing. There are two sources of tropospheric ozone: stratosphere troposphere transport (STT) and photochemical production, with estimated source fluxes of 550 $Tgyr^{-1}$ and 5100 Tg yr^{-1}, respectively [Stevenson, 2006].

Using more than a decade of high vertical resolution ozone profiles through the troposphere measured by ozonesondes at Melbourne (145°E, 38°S), Macquarie Island (159°E, 55°S) and Davis (78°E, 69°S), we establish a quantitative method of classifying STTs as well as finding a lower bound on STT ozone flux. We will present an analysis of the seasonal height distribution and frequency of STTs.

Ozonesonde data are supplemented with ERA-Interim reanalysis [Dee, 2011] to enable construction of an STT exchange climatology. Some individual case studies will also be presented to illustrate a variety of synoptic scale conditions in which STTs can occur.

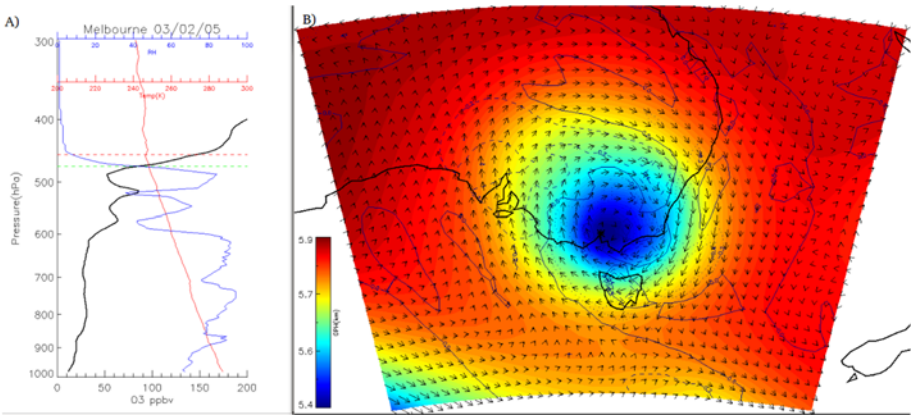


Figure 1. insert text

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Impact of approximations in the recommended Dobson algorithm on total column ozone measurements at four Australian sites

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Abstract

Observations of total column ozone made by the GAW network of Dobson spectrophotometers are processed by each operator using a standard algorithm, with the resulting processed data, rather than raw observations, being submitted to the World Ozone and Ultraviolet Data Centre and from there, available to data users. For simplicity, the official WMO algorithm uses a crude parameterised value of mean ozone height by latitude, and assumes a constant "effective ozone temperature" for all locations and times of year. These approximations potentially interfere with the comparison of Dobson measurements with those from other instruments, as well as introducing the possibility of a spurious ozone seasonal cycle or trend.

Here, daily ozone and temperature profiles from the MERRA reanalysis [Rienecker *et al*., 2011] are used to calculate the mean ozone height and effective ozone temperature at four long-standing Australian Dobson sites (Darwin, Brisbane, Melbourne/Airport and Macquarie Island) for each individual day from 1979 to 2014, also making use of the current state-of-the-art ozone cross-sections [Serdyuchenko *et al*., 2014], and the effect on the calculation of total column ozone investigated.

The effect on the calculated ozone of the annual cycle in temperature ranges from 2.5% at Macquarie Island to 0.5% at Darwin, but day to day variations can be twice this amount. The effect of the seasonal cycle in mean ozone height is negligible at Darwin but increases poleward, reaching 0.6% for measurements made two hours from local noon at Macquarie Island.

These results suggest the standard Dobson algorithm should be updated to incorporate reanalysis data in the ozone retrieval.

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The 2015 Antarctic ozone hole

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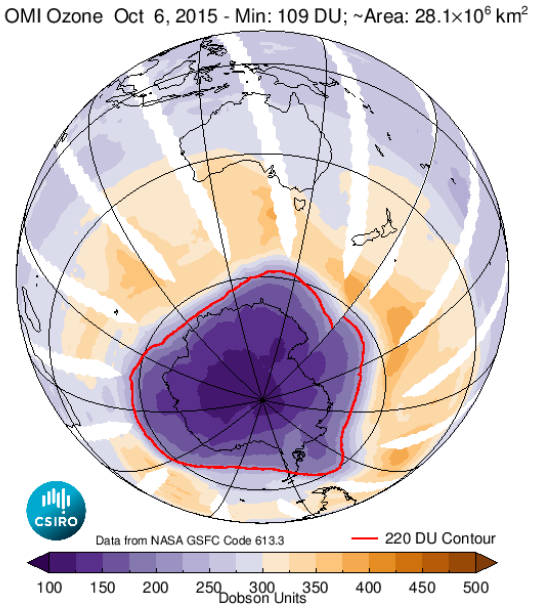
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Abstract

The 2015 ozone hole only started developing during the third week of August, which is the latest onset of the ozone hole that has been seen since the mid-to-late 1980s. However, record cold stratospheric temperatures and a very stable polar vortex have since seen the 2015 ozone hole become one of the biggest on record, at least in terms of its areal extent (3rd to 4th largest on record). Also, during October the ozone hole set new maximum area records for this time of year.

The development and recovery of the 2015 ozone hole will be shown via a set of metrics based on the Ozone Monitoring Instrument (OMI) on board the Earth Observing Satellite (EOS) Aura, and the OMPS (Ozone Mapping and Profiler Suite) instrument on the Suomi National Polar-orbiting Partnership satellite (Suomi NPP). Other observational results will be shown to complement these satellite data. The 2015 ozone hole metrics will be compared to the historical metrics, and these will be linearly regressed against Equivalent Effective Stratospheric Chlorine (EESC) data that are based entirely on Cape Grim Air Archive, Antarctic firn and AGAGE global measurements of ozone depleting substances (ODS). The year-to-year variability of the ozone hole does not reflect variations in the level of ODSs in the Antarctic stratosphere, which, based on surface observations, have fallen approximately 10% since their peak around 2000, or have fallen by approximately 18% since their peak around 2000 relative to 1980 levels of ODSs. The decadal variations in the ozone hole do reflect the long-term changes of ODSs in the Antarctic stratosphere and the results shown here suggest that ozone hole recovery has commenced, despite the 2015 ozone hole being relatively large.



The carbon tetrachloride 'Mystery': Further developments

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Abstract

Based on current levels of ozone depleting substances (ODSs) in the atmosphere, carbon tetrachloride (CCl_4) accounts for more than 20% of ODS emissions, weighted by their ozone depletion potential (ODP). This compares to less than 10% in the late-1980s, when ODS emissions were predominantly chlorofluorocarbons (CFCs, >70%). As noted in the last five *Scientific Assessments of Ozone Depletion (1998, 2003, 2007, 2010, 2014)* the observed rate of decline of CCl_4 in the atmosphere has been significantly less than that predicted based on expected production/consumption reductions under the Montreal Protocol (Figure 1) and this is due to emissions (up to 60 k tonnes/yr currently) not directly related to the production and use of CCl_4.

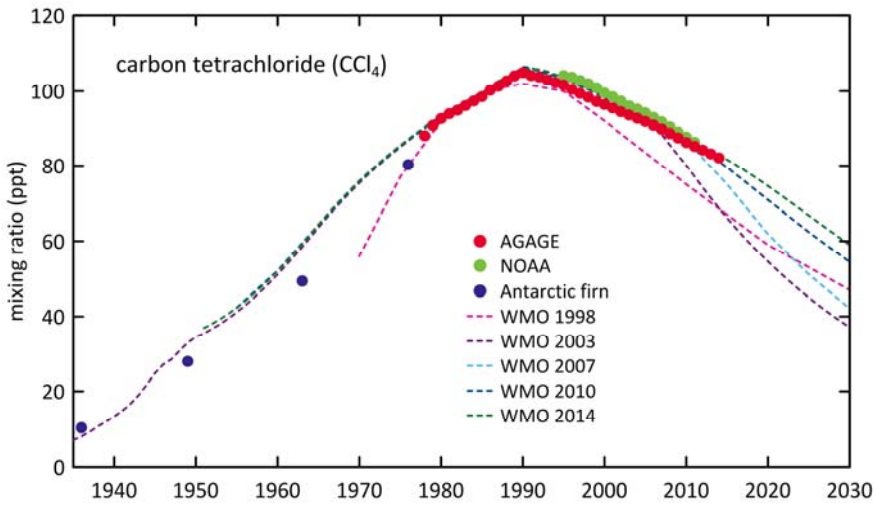


Figure 2. Annual mean baseline carbon tetrachloride concentrations (ppt) at Cape Grim, Tasmania, from AGAGE *in situ*, NOAA flask and air archive data (Fraser *et al*., 2014); also shown are Antarctic firn data (Sturrock *et al*., 2002) and scenarios of future CCl_4 concentrations based on expected reductions in production/consumption under the Montreal Protocol.

Cape Grim and Aspendale CCl_4 observations have shown continuing Australian emissions despite Australian consumption/production being effectively zero since the early-1990s. Both Cape Grim and Aspendale data suggest land-fills and/or toxic waste sites and/or chlor-alkali plants as possible unaccounted-for sources of CCl_4 which may be globally significant. The magnitudes of the currently identified sinks for CCl_4 (atmosphere, oceans, land surface) are important in assessing the disagreement between atmosphere-based 'top-down' and industrial-accounting ('bottom-up') estimates of global CCl_4 emissions.

SPARC recently (October 2015) held a Workshop in Dübendorf, Switzerland on the so-called CCl_4 'Mystery'. The outcomes of that Workshop will be included in this presentation.

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Measurements of atmospheric trace species can change industrial practices that lead to GHG emissions

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Abstract

In early 2000, W. Sturges (U. East Anglia) and co-workers reported in *Science* the first identification in the atmosphere of a rapidly growing, very potent greenhouse gas, CF_3SF_5, and speculated on its likely source [Sturges *et al*., 2000], possibly related to the use of SF_6 as a high-voltage dielectric. By late 2000, M. Santoro (3M), in an open letter to *Science*, suggested (Santoro, 2000) that the speculation on possible sources were likely incorrect and in fact the 3M chemical company was the likely major source of CF_3SF_5, a by-product of the production of perfluorooctanesulfonic acid (PFOS: $CF_3(CF_2)_7SO_3H$), which was a key ingredient in fabric stain repellants (e.g. 3M's Scotchguard®) and 3M fire-fighting foams. Santoro suggested that 3M had recently modified or curtailed PFOS production and this major (possibly sole) source of CF_3SF_5 emissions was closed down. Subsequent atmospheric observations and measurements on the Cape Grim air archive indeed confirmed that post-2000 CF_3SF_5 emissions were effectively zero [Sturges *et al*., 2012]. Although not publically acknowledged, this may have been an example of a chemical company taking action to restrict emissions of a chemical they produced as a by-product once that chemical had been found in the atmosphere.

There may be other examples. In 2014, J. Laube (U. East Anglia) reported in *Nature Geoscience* [Laube *et al*., 2014] on the first measurements (1978-2012) of HCFC-133a (CH_2ClCF_3) in the atmosphere, as found in the Cape Grim air archive, showing rapidly growing concentrations and emissions. Like CF_3SF_5, no purposeful end-product usage of HCFC-133a is known (it is toxic and carcinogenic), but it is known to be an intermediate product in the trichloroethylene ($CHClCl_2$)/perchloroethylene (CCl_2CCl_2) routes to the widely-used refrigerants HFC-134a (CH_2FCF_3), HFC-143a (CH_3CF_3) and HFC-125 (CHF_2CF_3). Following the 2014 publication, there has been a significant decline in HCFC-133a concentrations and emissions [Vollmer *et al*., 2015] post-2011, despite growing production of the HFCs. It would appear that the HFC production processes have been modified around 2011 to prevent inadvertent release of HCFC-133a to the atmosphere. The first public presentations (2011) of the discovery of HCFC-133a in the atmosphere [Laube *et al.*, 2011a,b] may have been a factor in bringing about these possible changes.

Strikingly similar global abundance and emission reversal patterns have been reported for the first time for HCFC-31 [CH_2ClF, Schoenenberger *et al*., 2015], which is an intermediate in the ever-growing production of HFC-32 (CH_2F_2) and is flammable and carcinogenic (hence not used in end-product applications). There appears to be no preliminary public reports on HCFC-31 in the atmosphere around 2011 when this reversal occurred. However it is possible that the industrial actions undertaken to reduce HCFC-133a emissions in the production of HFCs-125, -134a, -143a may have prompted similar actions to reduce possible emissions of HCFC-31 in the production of HFC-32.

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AIR-BOX - Atmospheric Integrated Research facility for Boundaries and Oxidative experiments

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Abstract

The AIR-BOX facility is currently being commissioned – it's a custom built shipping container – to provide mobile atmospheric chemistry observations. A consortium of University, CSIRO, ANSTO and AAD partners are involved and this facility will compliment the Australian atmospheric monitoring onboard the Marine National Facilities of the RV Investigator, RV Aurora Australis, and Cape Grim and Gunn Point sites. State-of-the-art observations of composition, physical parameters and aerosols relevant for international environmental treaties on air-quality, mercury, ozone depleting substances and greenhouse gases will be made.

AIR-BOX will simplify and expedite transport, safety, certification and instrument integration. Partners are involved in a variety of projects supported by the ARC, such as CoE for Climate System Science, CRC for Bushfires and e-research. Thus observations will be effectively disseminated to a wide community of end-users well beyond this team with the aim of being useful in in a wide range of applications extending to population health and biological studies.

AIR-BOX will provide a large suite of atmospheric composition observations drawing from the combined capability of the community. AIR-BOX will provide a platform to bring this capability together in a cost effective way. The following objectives are envisaged:

- Conducting remote and autonomous deployment
- Providing real-time data transfer and control
- Observing a wide range of physical and tracer measurements
- Providing flexible configuration

An alternative method for *in situ* atmospheric hydrogen measurement at Cape Grim

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Abstract

Cape Grim is one of the few sites globally where in situ measurements of atmospheric hydrogen (H_2) are routinely made. These in situ measurements of H_2 at Cape Grim began in 1993, and continue to the present time, as part of the AGAGE GC-MD (gas chromatograph-multiple detector) instrument system. The analytical method used for these H_2 measurements is based on the heated mercuric oxide detector (Trace Analytical), where reaction of the column-separated H_2 with the hot mercuric oxide releases elemental mercury which is detected by its absorption of UV light. This analytical method has been adequate to define the major features of atmospheric H_2 variations (trend, seasonal cycle), but its precision of ca. 1% has not been comparable to the 0.1% achieved for many of the other trace species measured at Cape Grim.

While hydrogen is not important as a 'direct' greenhouse gas, it is chemically reactive in the atmosphere, and thus worthy of study to fully elucidate the processes which produce and destroy it. One approach to this task is to examine correlations (short-term and long-term) between the variations in H_2 and those in other trace species. Improved precision of H_2 measurements is likely to make this task easier.

For making routine measurements of the major greenhouse gases, and some related trace gases in the atmosphere, there has been a strong, relatively recent uptake of new instrumentation based upon optical absorption techniques which use lasers as the light source. But these optical techniques are not presently suitable for gases such hydrogen. Here we present an alternative method for analysis of atmospheric hydrogen that has been implemented at Cape Grim since April 2015, as an additional GC 'module' on the GC-MD instrument system. It is based on pulsed discharge helium ionization detection and a prior gas chromatographic separation (GC-PDHID). This method has been operated in parallel with the previous method, allowing a very thorough inter-comparison experiment. Results of this inter-comparison experiment will be presented, showing that the GC-PDHID method can achieve a precision of 0.08%, with only a small non-linearity in detector response. The superior precision of the new method will allow better characterization of the hydrogen stability in high-pressure cylinders, and better propagation of hydrogen calibrations.

Some H_2 data will be presented, illustrating the major features of the variations at Cape Grim, and their correlations with selected species.

Increasing the accuracy and temporal resolution of two-filter radon-222 measurements by correcting for the instrument response

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Abstract

The two-filter, dual flow loop radon detector is one of the better instruments for continuous atmospheric radon observations. Nevertheless, in common with many radon detectors, the instrument has a slow temporal response with a one-half rise time of about 45 minutes. While not critically important at baseline stations, the instrument response limits the usefulness of radon observations at other sites. The problem is worth addressing because radon itself has almost ideal properties as a tracer of boundary-layer mixing, which means that better measurements make new kinds of studies possible. Here we show a Bayesian Markov Chain Monte-Carlo technique which can be used to correct for, or deconvolve, the instrument response, also with an estimate of the measurement error. There are three main advantages to deconvolution. First, half-hourly data can be extracted from historical radon observations, instead of the usual practice of down-sampling to hourly resolution. Second, radon observations become consistent with observations of other surface-emitted tracers (CO_2) and grab samples (Figure 1). Third, a source of bias in the daytime radon concentration is removed. This bias is present at inland sites under still, clear-sky conditions and its elimination is especially useful when radon is used directly as a model diagnostic.

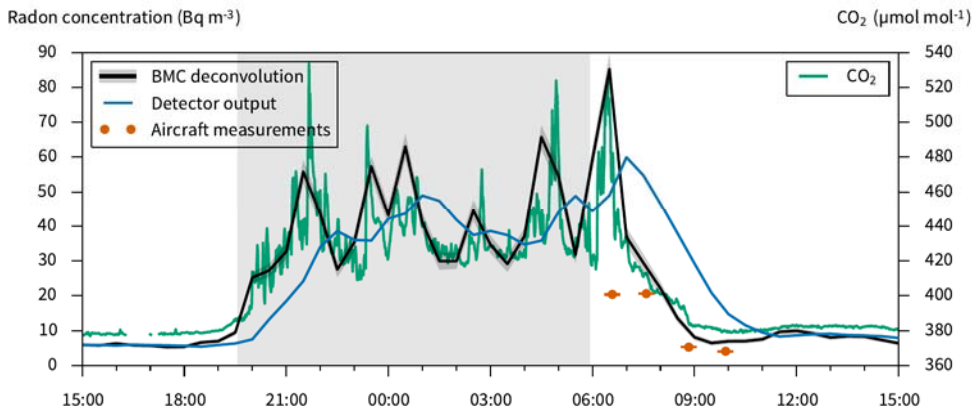


Figure 3. One day of observations made 2 m above dry grassland showing both the raw detector output and the radon time series corrected using Bayesian Monte Carlo (BMC) deconvolution. After correcting for the detector response, the timing of night time radon fluctuations match CO_2 fluctuations. In contrast with the raw detector output, the corrected time series is also consistent with grab samples from an aircraft flying 30 m overhead. Shading indicates night time.

Universal baseline characterisation of air masses using radon

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Abstract

A recent study is summarised [Chambers *et al*., 2015], in which we demonstrate the ability of atmospheric radon concentrations to reliably and unambiguously identify local and remote terrestrial influences on an air mass, and thereby the potential for alteration of trace gas composition by anthropogenic and biogenic processes. Based on high accuracy (lower limit of detection 10-40 mBq m^{-3}), high temporal resolution (hourly) measurements of atmospheric radon concentration we describe, apply and evaluate a simple two-step method for identifying and characterising constituent mole fractions in baseline air. The technique involves selecting a radon-based threshold concentration to identify the 'cleanest' (least terrestrially influenced) air masses, and then performing an outlier removal step based on the distribution of constituent mole fractions in the identified clean air masses. The efficacy of this baseline selection technique is tested at three contrasting WMO GAW stations: Cape Grim (a coastal low-altitude site), Mauna Loa (a remote high-altitude island site), and Jungfraujoch (a continental high-altitude site). At Cape Grim and Mauna Loa the two-step method is at least as effective as more complicated methods employed to characterise baseline conditions, some involving up to nine steps. While it is demonstrated that Jungfraujoch air masses rarely meet the baseline criteria of the more remote sites, a selection method based on a variable monthly radon threshold is shown to produce credible 'near baseline' characteristics. The seasonal peak-to-peak amplitude of recent monthly baseline CO_2 mole fraction deviations from the long-term trend at Cape Grim, Mauna Loa and Jungfraujoch are estimated to be 1.1, 6.0 and 8.1 ppm, respectively.

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Monitoring regional emissions of methane with continuous concentration measurements and inverse modelling and application to coal seam gas

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Abstract

Coal seam gas (CSG) offers potentially lower greenhouse gas emissions than other fossil fuels used to generate electricity. However, emissions during CSG production could offset any benefits due to the large global warming potential of methane. Quantifying methane emissions in CSG production regions poses difficulties due to the large variety, time variation and wide spatial distribution of possible sources. Here we present an atmospheric monitoring program to quantify regional methane emissions from the CSG production area of the Surat Basin in Queensland.

Two monitoring stations for measurements of gas concentrations and meteorology were installed to the south (Ironbark) and the north (Burncluith) of the CSG area, about 80 km apart. Their locations were guided by dispersion model (TAPM) simulations of emissions scenarios of existing and planned CSG industry sources. Source strengths for the simulations were estimated from mobile flux measurement surveys. The resulting two-station configuration aims to measure the upwind background and downwind source concentrations, optimised to the CSG source area and the dominant wind directions, so that enhancements can be maximised and accurately determined to infer emissions across the region. Measurements of eddy-covariance fluxes at Ironbark and meteorology at both stations will be used for the TAPM transport modelling in the inversions. Concentrations of carbon dioxide and carbon monoxide help identify methane emissions that are not related to CSG.

Measurements from the pair of stations have been made since July 2015. Preliminary results will be presented and the ability of the stations to monitor CSG emissions and the broader regional fluxes of greenhouse gases will be discussed.

Coal seam gas and air quality in the Surat Basin, Queensland: A new two-year monitoring program

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Abstract

In 2015 Origin Energy commissioned a two year ambient air monitoring program focused in the Surat Basin in Central Queensland, a region of significant coal seam gas (CSG) production. The monitoring is focused primarily in the Miles, Chinchilla, Tara and Condamine area which has the highest CSG production rate in the region. In addition to ambient air monitoring, the program will also include a detailed characterization of emission sources and an air quality modeling study. This is the first comprehensive air quality study to be undertaken in an unconventional gas production region of Australia.

CSIRO's role is to provide independent advice around the design, implementation and ongoing management of the program. CSIRO will summarize, interpret and report the data generated from the program, and will assess concentrations against predetermined investigation thresholds, compare concentrations with those from other Australian sites, and investigate emission sources.

Here we provide background information about the study and an overview of the study design and implementation. We provide an overview of Australia Pacific Liquefied Natural Gas (APLNG) Project's upstream CSG infrastructure (operated by Origin Energy) including gas wells, compressor stations, gas processing facilities and water treatment plants. An overview of the meteorology and terrain in the region will be given and selection of three ambient air monitoring sites will be discussed. We provide information on plans to incorporate air quality measurements at an additional two CSIRO sites in the Surat Basin, commissioned as part of the Gas Industry Social & Environmental Research Alliance (GISERA) Regional Methane Flux project.

We give an overview of measurements selected for the monitoring program, including carbon monoxide, oxides of nitrogen, carbon dioxide, methane, total non methanic hydrocarbons, speciated VOCs via passive samplers, PM2.5, PM10 and ozone. We review the reasons for selection of these measurement parameters. A brief comparison will be given between emissions and activities associated with CSG extraction in the Surat Basin compared to emissions and activities associated with unconventional oil and gas extraction in the USA.

The comprehensive air quality modeling study being undertaken by CSIRO will be discussed, which will be used to validate selection of monitoring sites, and will explore the impact of CSG production activities on primary and secondary pollutants in the Surat Basin. Finally, we discuss a VOC method intercomparison study which was undertaken and discuss how and when data from the program will become available.

The Clean Air and Urban Landscapes Hub: What is it and why should I care?

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Abstract

The Clean Air and Urban Landscapes Hub (CAUL) is part of the National Environmental Research Program. NESP is intended '*to improve our understanding of Australia's environment through collaborative research that delivers accessible results and informs decision making*'. As it approaches a year old, this talk will give an overview of CAUL's programme and progress and open a discussion of its place in the larger research landscape.

Modelling emissions and transport of rye-grass pollen in SE Australia

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Abstract

Hayfever (allergic rhinitis), which affects one in six Australians [ABS, 2010], is an upper airway allergic response to airborne allergens (e.g. pollen, dust, mould spores). Hayfever is closely linked to asthma, conjunctivitis and eczema, and these conditions have common triggers in many affected individuals [Bousquet *et al*., 2011]. Hayfever can lead to reduced quality of life, sleep loss [AIHW, 2011], lower productivity at work (among adults) and performance at school [Walter *et al*., 2001]. In more serious cases, combined onset of hayfever and asthma can lead to hospitalisation [AIHW, 2011]. The direct costs of hayfever and asthma are estimated at over $200 million and $650 million annually nationwide [AIHW, 2011; ACAM, 2011]. Exposure to grass pollen is believed to be the most widespread outdoor aeroallergen in Australia [AIHW, 2011], and in South Eastern Australia much of the allergenic burden is attributed to pollen from rye grass [*Lolium sp*.; Schäppi *et al*., 1998], which is a common pasture grass used for grazing livestock.

We are working to develop a modelling framework to simulate emissions and transport of airborne pollen. To this end, we have customised a version of the Community Multiscale Air Quality (CMAQ) Modelling System [Binkowski and Roselle, 2003], a limited-area chemistry-transport model developed by the United States Environmental Protection Agency. In this modified version, the gas-phase and particulate-phase scheme has been replaced by a single particulate type (rye-grass pollen). Emissions are parameterised as a function of land-use, rainfall, growing day, latitude, wind speed, humidity, vertical uplift and time of day. The meteorological drivers are produced by the Weather Research and Forecasting (WRF) Model [Skamarock *et al*., 2005].

We will present preliminary simulation results for southern Australia, and compare these with pollen observations from the Melbourne Pollen Count (courtesy of the School of Biosciences, University of Melbourne). We will discuss plans for optimising parameters within the pollen emissions module via inverse modelling, extending simulations to other regions and plant species, and simulating pollen under the projected future climate and land-use.

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Cleaner Air, Less Cancer

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Abstract

The World Health Organisation (WHO) estimates 1 in 15 deaths are attributed to outdoor air pollution. In Australia, our most recent analysis dates back to 2003 and estimates 3000 air pollution related deaths per year [Begg *et al*., 2007]. In the past two decades, large cohort studies have improved our understanding of particulate matter and its detrimental impacts (primarily cardio-respiratory and carcinogenic) on human health [Hamra *et al*., 2014]. Lung cancer is the leading cause of cancer related mortality in Australia [Cancer Australia]. Reductions in cigarette smoking have reduced the incidence of squamous-cell lung cancer however, lung adenocarcinoma is rising and affecting a significant non-smoking and younger patient population [Gabrielson, 2006]. Lung adenocarcinoma is a known impact of particulate matter, which is categorised as class 1 carcinogen [Loomis *et al*., 2013. Considering available global evidence, current domestic trends of particulate emissions [National Pollutant Inventory] and projected population demographics, the burden on our health system is likely to be substantial. Our legislation has failed to keep pace with scientific evidence and we are likely to be experiencing a much higher death toll than previous estimates. In order to protect public health, academics and health professionals need to lobby for the necessary changes.

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Air quality impacts of the Hazelwood mine fire

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Abstract

The Hazelwood mine fire was an unprecedented event that affected thousands of residents in the Latrobe Valley. The Hazelwood mine fire started on 9 February 2014 and was declared safe on 25 March 2015, burning over a period of 45 days. At the time of the event, little peer-reviewed publications were available to assess the impacts from such an incident. A large data set was collected during the Hazelwood mine fire by various parties to assess the impact on air, water, soil and human health.

The presentation will discuss the air quality impacts from the Hazelwood mine fire, in particular looking at key pollutants such as fine particulate matter, carbon monoxide, volatile and semi-volatile organic compounds and metals. The air quality impact will be assessed against non-smoke impacted periods and other major air pollution events such as the 2006/06 Eastern Victoria Great Divide bushfires.

Emission characterization for rice straw field burning in Southeast Asia

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Abstract

Rice straw (RS) field burning, commonly practiced in Asia, produces large amounts of toxic air pollutants but has not been comprehensively characterized. This study presents a comprehensive characterization of emission from RS burning using both *in situ* and laboratory hood experiments to simulate both spread and pile burning. The emission monitoring was done for 1) particulate matter (PM) and composition (EC/OC, water soluble ions, elements and levoglucosan), 2) gaseous species (CO_2, CO, SO_2, NO_2, BTEX and aldehydes), and 3) semi-VOC of (16 PAHs, 16 chlorinated pesticides and 14 PCBs). The emission concentration profiles of PM composition and semi-VOC were subsequently determined. Further, the emission ratio method was used to determine emission factors (EF) in the field spread burning experiments and the results were compared with those obtained by the hood experiments. The obtained EFs were used in the emission inventory (EI) for the field burning in Indonesia, Thailand and Vietnam.

Pile burning (in hood experiment) produced significantly higher PM EF (20±8 g kg^{-1} RS) than hood spread burning (4.7±2.2 g kg^{-1} RS). The majority of PM emitted from the field spread burning was $PM_{2.5}$ with EF of 8.3±2.7 g kg^{-1} RS burned. The largest fractions of total PM, EC and OC emissions from field burning were associated with $PM_{1.1}$. The most significant components in $PM_{2.5}$ and PM_{10} included OC, water soluble ions and levoglucosan. Relative abundance of some methoxyphenols (e.g., acetylsyringone), PAHs (e.g., fluoranthene and pyrene), organochlorine pesticides (OCPs) and PCBs may also serve as additional signatures for the PM emission.

Emission of gaseous pollutants and semi-VOC from the hood experiment burning dry RS (5% moisture) was lower than that from hood burning normal RS (20-30% moisture). EFs of all detected pollutants in the field burning were higher than hood burning owning to uncontrolled conditions in the field. The EFs of field burning in mg kg^{-1} RS were 760 for benzene, 230 for toluene, 510 for SO_2, 490 for NO_2, 260 for total PAHs (88% in gas phase), 0.11 for total PCBs (59% in gas phase) and 0.23 for OCPs (62% in gas phase). As compared to ambient air, RS smoke had significant enrichment of light PAHs, fluoranthene in PM and acenaphthylene in gas phase. Smoke had a higher proportion of benzene in BTEX than roadside air. Levels of PCBs, OCPs and aldehydes were higher in the burning smoke compared to ambient air, but there was no significant enrichment of particular compounds.

The EI results showed that RS field burning contributed substantially to the pollution load from biomass open burning in Indonesia, Thailand and Vietnam. The seasonality of the emission created more problems during the dry season.

Results from the June 2014 Gunn Point campaign, including emission factors of greenhouse gases and particulates from savanna fires

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Abstract

In June 2014 a measurement campaign took place at Gunn Point in the Northern Territory, Australia, aimed at characterising the emissions from early dry season savanna fires. The campaign was especially focused on understanding aerosol composition and size distribution. Equipment deployed to measure aerosol properties included a multi-angle absorption photometer, a nephelometer, a cloud condensation nuclei counter, a condensation particle counter, two scanning mobility particle sizer, two aerosol mass spectrometers (one a time of flight instrument), a multi-axis differential optical absorption spectrometer, a volatility-humidity tandem differential mobility analyser and two high volume aerosol samplers (one PM10 and one MOUDI). In addition there were measurements of mercury in both gas and aerosol phase. Complementary measurements of trace gases were provided by a proton transfer reaction mass spectrometer, a volatile organic compounds sequencer, a Fourier transform spectrometer, an ozone analyser and a nitrogen oxides monitor.

This presentation will present results from the Fourier transform spectrometer, the scanning mobility particulate sizer, the beta attenuation monitor. In particular individual fire events have been identified and emission factors calculated for CO_2, CO, CH_4 N_2O and aerosols (PM_1, PM_{10}, Aitken and Accumulation mode).

Cape Grim Particle Program 2004 to 2015

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Abstract

The Cape Grim Baseline Station has been producing high quality data and research outputs on the chemical composition and chemistry of the remote marine boundary layer for almost 40 years. The regular review of the science programs undertaken at Cape Grim contribute to this excellence. In 2015, it is the turn of the Particle Program to be reviewed.

The overarching goal of the Particle Program is to understand and quantify the Southern Ocean marine boundary layer aerosol and the processes that relate aerosol to climate change by investigating the nature, sources and processes of production and evolution of climatically important particles over the Southern Ocean. Climatically important particles may be comprised of sea-salt and organic compounds and include cloud condensation nuclei (CCN). The role of natural aerosol over the Southern Ocean in climate-change feedbacks remains an open issue.

Activities in the Particle Program fall under two categories; long term monitoring and research. While the aims of these two categories differ, they are related. It should be noted that the objectives and key scientific issues addressed by the Particle program closely align with those of the Multiphase Atmospheric Chemistry Program

The components of the Particle program that are reviewed here include aerosol microphysical research since 1999 and relevant collaborative programs. The Particle Program was last reviewed in 1999. Some achievements of the Particle Program include a 38 year record of particle number concentration, a 32 year record of CCN concentrations, a 24 year record of black carbon concentrations, and a 9 year record of aerosol scattering coefficients. In addition intensive campaigns were carried out in 2006 (P2P), 2007, 2011 and 2014. The results of these and other impacts of the Particle Program will be discussed. The review will cover (a) the Program scientific objectives; (b) discussion of existing activities and outcomes (c) work in progress (d) future plans and (e) relevance to GAW and Cape Grim.

Is there bias in the estimated climate forcing by black carbon aerosols?

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Abstract

The recent 'Bounding BC' assessment [Bond *et al.*, 2013] reached the conclusion that black carbon (BC) is the #2 most important climate-warming agent (behind CO_2), with an average forcing of +1.1 W m^{-2} (90% uncertainty bounds +0.17 to 2.1 W m^{-2}). This assessment used retrievals of aerosol absorption optical depth (AAOD) derived from sun/sky radiometer measurements (AERONET) to justify adjusting modelled BC column burdens upwards by a globally-averaged factor of 2.6. However, the verification of the AERONET AAOD retrievals relies primarily on short-term aircraft studies done under conditions of very high aerosol loadings (biomass burning, dust), and the retrievals have not been evaluated under the low optical depth conditions that prevail over most of the globe. In this talk, I will discuss comparisons of AERONET AAOD with in-situ measurements of aerosol light absorption coefficient obtained from light aircraft flying over sites in Oklahoma (SGP, 2006-2007) and Illinois (BND, 2006-2009). These comparisons, which were done in lightly-polluted continental air, show that the in-situ measurements of AAOD are substantially lower than the AERONET retrievals, and suggest that the up-scaled BC column burdens and resulting BC forcing may be biased high.

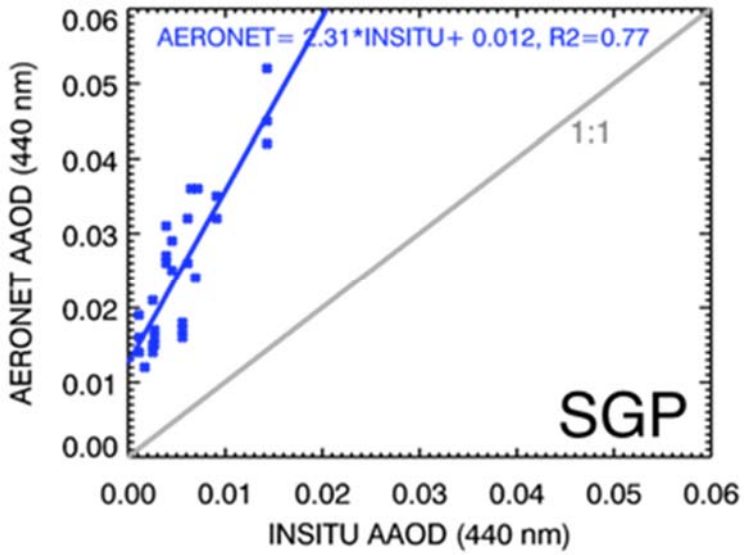


Figure 4. Comparison of aerosol absorption optical depth over Oklahoma from *in-situ* vs. remote sensing

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Clouds and aerosols at Cape Grim observed with lidar

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Abstract

The Bureau of Meteorology's UV Raman lidar with polarization capability was located at Cape Grim, Tasmania from May 2013 – May 2014. The data permit characterisation of the seasonal cycle of clouds at the northern extreme of the Southern Ocean. The Southern Ocean has large sea surface temperature biases in climate models, which are believed to be due to incorrect cloud representations in the models which allow an incorrect amount of shortwave radiation to reach the ocean. Surface measurements have not yet been made in this region but are required to provide basic climatological parameters in order to validate models and evaluate satellite retrievals. We will present an overview of our Cape Grim lidar cloud detection algorithm and the climatology of various key parameters including cloud base height and cloud fraction. Using the Raman backscatter channel, we determine the cloud and aerosol backscatter, extinction and optical depth and will illustrate these with reference to co-located surface short-wave and long-wave radiation observations. Lastly, we will illustrate the seasonal variability of various cloud and aerosol parameters.

Sources of cloud condensation nuclei inferred from volatility and hygroscopicity measurements over the Southern Ocean

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Abstract

Recent modelling has highlighted the importance of pristine environments to the uncertainty in aerosol radiative forcing [Carslaw *et al*., 2010]. In addition, large biases in modelled low to mid-level clouds over the Southern Ocean have been identified [Huang *et al*., 2014; Bodas-Salcedo *et al*., 2012]. Uncertainty in aerosol cloud interactions is likely to contribute to the cloud biases and an enhanced understanding of cloud condensation nuclei (CCN) is required.

Measurements of remote marine aerosol composition and CCN concentrations are relatively scarce, particularly over the Southern Ocean [Cravigan *et al*., 2015]. In this presentation the results from aerosol volatility, hygroscopicity and CCN concentration measurements over the Southern Ocean will be discussed. These measurements were taken in January and February 2015 during the Cold Water Trials of the RV-Investigator (CSIRO, Hobart).

Non-sea salt (nss) sulfates are formed from the atmospheric processing of dimethyl sulfide (DMS) and consistently dominate remote marine aerosol concentrations at peak CCN sizes (<200 nm). This work highlights the importance of nss sulfate formation and atmospheric processing to remote marine CCN concentrations. Sub-200 nm sea- spray aerosols (SSA) are more transient than nss sulfates, yet provide significant enhancement in CCN concentrations [Cravigan *et al*., 2015]. The observed SSA flux and size dependant organic enrichment over the Southern Ocean will be compared to that reported in the North Atlantic [Ovadnevaite *et al*., 2014]. These observations, and further like it, are key to refining model representation of CCN and cloud formation in the Southern Ocean.

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Atmospheric aerosol formation over East Antarctic sea ice – possible Hg catalysed nucleation?

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Abstract

Aerosol observations above the Southern Ocean and Antarctic sea ice are scarce. Measurements of aerosols and atmospheric composition were made in East Antarctic pack ice on-board the Australian icebreaker *Aurora Australis* during the spring of 2012. One particle formation event was observed during the 32 days of observations. This event occurred on the only day to exhibit extended periods of global irradiance in excess of 600 W m^{-2}. Within the single air-mass influencing the measurements, number concentrations of particles larger than 3 nm (CN_3) reached almost 7700 cm^{-3} within a few hours of clouds clearing, and grew at rates of 5.6 nm h^{-1}. Formation rates of 3 nm particles were in the range of those measured at other Antarctic locations at 0.2–1.1 ± 0.1 cm^{-3} s^{-1}. Our investigations into the nucleation chemistry found that there were insufficient precursor concentrations for known halogen or organic chemistry to explain the nucleation event. Modelling studies utilising known sulfuric acid nucleation schemes could not simultaneously reproduce both particle formation or growth rates. Surprising correlations with Total Gaseous Mercury (TGM) were found that, together with other data, suggest a mercury driven photochemical nucleation mechanism may be responsible for aerosol nucleation. Given the very low vapour pressures of the mercury species involved, this nucleation chemistry is likely only possible where pre-existing aerosol concentrations are low and both TGM concentrations and solar radiation levels are relatively high ($\sim$ 1.5 ng m^{-3} and $\geq$ 600 W m^{-2}, respectively), such as those observed in the Antarctic sea ice boundary layer in this study or in the global free-troposphere, particularly in the Northern Hemisphere.

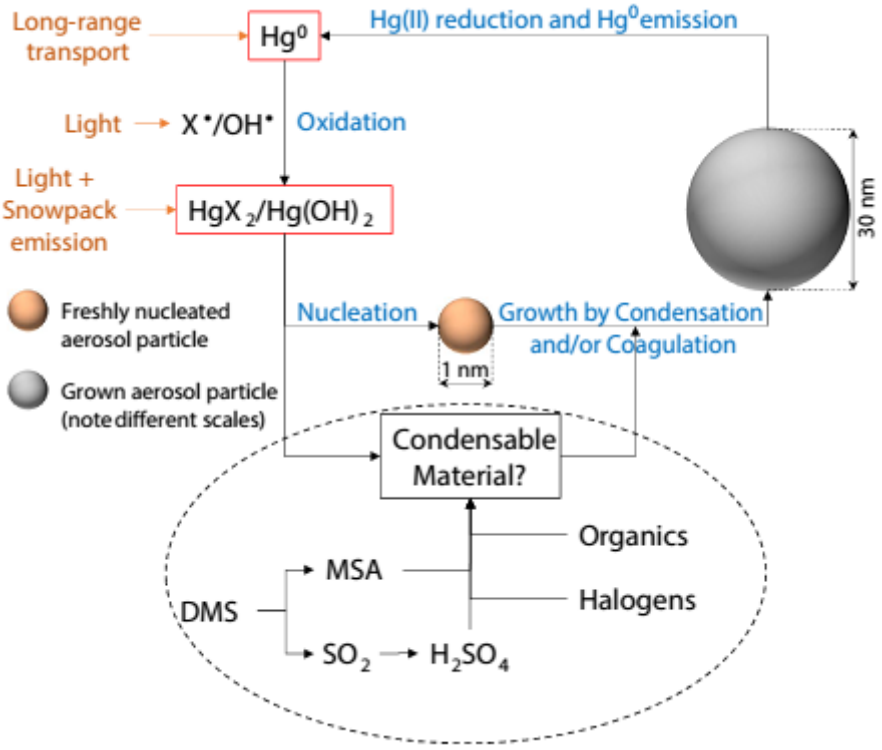


Figure 5. A suggested nucleation and growth mechanism driven by atmospheric mercury present from long-range transport.

Characterisation of atmospheric fine particles using QEMSCAN and isotopic carbon measurements

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Abstract

Atmospheric fine particles play a crucial role in the human health impacts of air pollutants and other atmospheric processes. In this presentation preliminary characterisation of particles using QEMSCAN and isotopic carbon measurements will be described.

Estimations in the radiative forcing of atmospheric aerosols or fine particles are responsible for large uncertainties in the estimation of the Earth's overall energy budget, and hence the impact on climate change and variability. This forcing can arise directly and/or through interactions of aerosols with clouds. Radiative transfer models (RTMs) have been developed to calculate the aerosol radiative forcing but these models are usually based on simplistic descriptions of particle properties. Mineral dust is one contributor to aerosol or particle derived forcing. The mineral component of airborne dust is a mixture of many minerals (eg, iron oxides, quartz, feldspar, illite, kaolinite, smectite, carbonates and gypsum) each of which has discrete scattering behavior. In addition the direct radiative effects are dependent on: the size distribution of advected dust particles; dust composition or mineralogy; and particle shape. Current models usually assume spherical particle shape, a poor representation of the shape of particles generated by mechanical processes. Composition is also crucially important: at the shorter wavelengths responsible for extensive scattering, the absorption by haematite is up to three orders of magnitude greater than the other minerals. Thus, dust radiative forcing is highly dependent on the presence and abundance of iron oxides, particularly 'free iron' (ie, iron oxides occurring as discrete individual particles).

The figure shows the results of a measurement using the scanning electron microscopic technique, QEMSCAN, originally developed by CSIRO for quantitative analysis of minerals. QEMSCAN has the capability to provide size, shape and composition data on large numbers of particles and hence to improve the input data for radiative transport models, but does not adequately address the mixed composition of particles of size around 1 μm. Possible enhancements to this technique will be discussed.

Further characterisation of fine particles by isotopic carbon measurements will also be discussed.

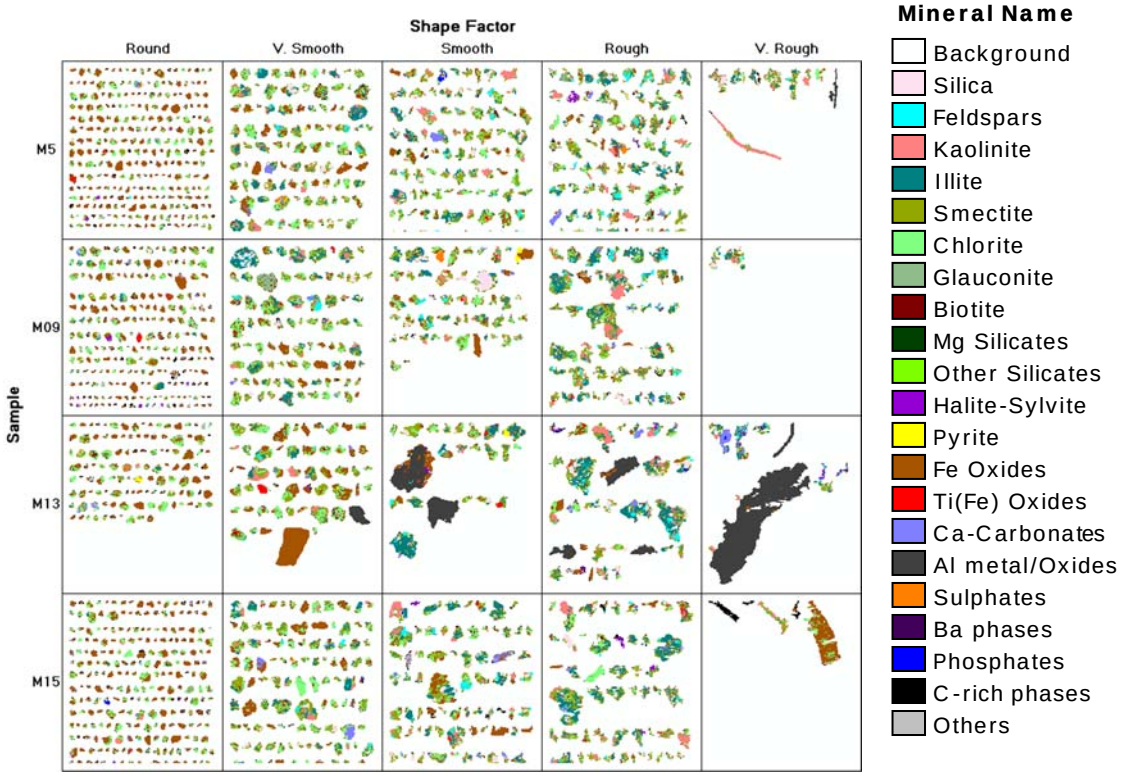


Figure 6. QEMSCAN analysis of atmospheric fine particles

Measurement of dissolved greenhouse gases (CO_2, CH_4, N_2O & CO) and their water-atmosphere exchange in inland waters

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Abstract

Global greenhouse gas (CO_2, CH_4, N_2O and CO) emissions from inland waters are significant yet estimates remain highly varied and are quoted with large uncertainty [Regnier *et al*., 2013; Raymond *et al*., 2013]. Recent CO_2 estimates range from 0.75 - 3.3 Pg C yr^{-1}, which is comparable in magnitude to the global land or ocean anthropogenic CO_2 sink [Regnier *et al*., 2013; Raymond *et al*., 2013; Richey, 2004; Travnik *et al*., 2009; Cole *et al*., 2007; Battin, *et al*., 2009; Aufdenkampe, *et al*., 2011; Butman and Raymond, 2011]. However, these estimates are not adequately constrained by small scale measurement data, particularly for CH_4, N_2O and CO, which have received far less attention than CO2 [Bastviken *et al*., 2011; Beaulieu *et al*., 2011]. Here we investigate and present *in situ* measurements of inland water-atmosphere greenhouse gas exchange examined on rivers, lakes and reservoirs within Europe and Australia. Gas analysis was conducted using a Fourier-Transform InfraRed (FTIR) Trace Gas Analyser, which allowed simultaneous and continuous measurement of CO_2, CH_4, N_2O, CO and $\delta^{13}C$ in CO_2. Coupling the analyser to an equilibrator and a floating chamber facilitated either continuous measurement of gas partial pressures within the waters and the overlying atmosphere or the direct measurement of water-atmosphere gas exchange. Where these measurements coincided, gas transfer velocities were derived and compared to those modelled from water and/or air turbulence parameters. Overall, we provide an overview of the employed measurement techniques and their capabilities as well as a selection of the results from various field campaigns.

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Constraining the carbon cycle with carbon 13 observations

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Abstract

Carbon 13 is used as a constraint on global carbon fluxes, in particular to partition carbon flux between the ocean and land. Carbon 13 is also a proxy for water stress in ecosystems. Using an atmospheric transport model along with a Bayesian synthesis analysis we can calculate the statistically best estimate of the flux.

Why Carbon 13:

The land and ocean discriminate against atmospheric carbon 13 by different amounts. Plants discriminate against carbon 13 when carbon dioxide is diffusing through the stomata (the site of air-sea exchange in leaves) and when carbon is carboxylated by the Ribisco enzyme. This photosynthetic discrimination is lacking in the ocean and it is this difference between land and ocean which we aim to detect.

Motivation:

Previous efforts to include carbon 13 measurements in global inversions have had great success at constraining IAV of carbon flux [Rayner 08]. The success of previous efforts motivates a re-examination of assumptions used about land air disequilibrium flux (the flux that comes from the biosphere and atmosphere not having equilibrated their ratio of C^{13} to C^{12}**)**

The improvement:

In this study we include a more sophisticated fractionation model to link CO_2 flux with $^{13}CO_2$ measurements. This fractionation is statistically calculated from a Land Biosphere model (LPJ) [Scholze *et al*., 2003]. A statistical algorithm is used to see the improvement that this fractionation achieves [Michalak *et al*., 2005]. We will present an updated estimate of recent interannual variability based on these improvements.

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Effect of fuel loading on greenhouse gases emissions from fires in the CSIRO Pyrotron

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Abstract

In February & March 2014 a measurement campaign took place at the CSIRO Pyrotron, a wind tunnel designed to study fires, to measure the emissions of trace gases from eucalypt fires. The fuel was collected from the Wombat State Forest in Victoria, as part of the DEPI Smoke Emissions and Transport Project.

The fires were designed to mimic conditions typical of hazard reduction burning in terms of 'Byram fireline Intensity'. Fuel moisture, fuel load and wind speed were carefully selected to achieve a Byram fireline intensity of around 500 kW/m. Fuel contiguity is also an important factor in enabling a fire to spread, so the fuels used were sieved to remove fragmented material. The campaign originally aimed to determine the dependence of both the coarse fuel load and the mode of fire spread (heading or backing) on the resulting emission factors. Unfortunately, there were problems with backing fires failing to propagate well, and so the campaign concentrated on a detailed study of whether the emission factors (primarily for heading fires) were sensitive to the fraction of coarse fuel in the total fuel burned.

Greenhouse and trace gases, mercury, volatile organic compounds and particulates were monitored during each fire. This presentation will present results from open-path FTIR and off-axis ICOS measurements for CO_2, CO, CH_4 and N_2O.

Particles in Western Sydney: Model-observation verification

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Abstract

Airborne particulate pollution is of concern to NSW communities and is a significant health risk. Air quality modelling is an important tool for understanding particulate pollution, but is limited by uncertainties. This project, addresses uncertainties in particle modelling in Sydney using data collected during the Sydney Particle Study [Cope *et al*., 2013]. The project objectives are to:

1. understand and quantify the uncertainties associated with the measurement and modelling of airborne particulate matter in the NSW Greater Metropolitan Region
2. develop uncertainty quantification techniques for this and more general application in air quality studies
3. provide information about uncertainties of airborne particulate matter that will aid the assessment of modelling studies of regulatory scenarios to improve air quality in the Sydney GMR.

The Sydney Particle Study showed that organic material makes up around one half of PM2.5 mass in the NSW Greater Metropolitan Region, GMR. That study combined observations with chemical transport modelling based on emissions inventories, meteorological processes and atmospheric chemical reactions. This demonstrated the importance of the chemical reactions of volatile organic compounds (VOCs) in contributing to the formation of secondary organic aerosol (SOA) found in the organic fraction of PM2.5. The study also showed that there were significant model-observation differences for the Sydney Airshed. The observations and modelling of the Sydney Particle Study provided the starting material for this work. Two examples of the uncertainty work will be presented.

The project commenced in May 2015 and is finishing in June 2016, supported by the NSW Environment Trust.

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Tropospheric Ozone Assessment Report: Global metrics for climate change, human health and crop/ecosystem research – a new global collaboration

I. E. Galbally[1*], R. W. Gillett[1], S. B. Molloy[1] and participants in the TOAR Oceania and Antarctica Working Group

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Abstract

The Tropospheric Ozone Assessment Report (TOAR), is a new Activity of the International Global Atmospheric Chemistry Project (IGAC), (see http://www.igacproject.org/TOAR).
The mission of TOAR is to provide the research community with an up-to-date scientific assessment of tropospheric ozone's global distribution and trends from the surface to the tropopause.

Tropospheric ozone is a greenhouse gas and pollutant detrimental to human health and crop and ecosystem productivity. Since 1990 a large portion of the anthropogenic emissions that react in the atmosphere to produce ozone have shifted from North America and Europe to Asia. This rapid shift, coupled with limited ozone monitoring in developing nations, has left scientists unable to answer the most basic questions: Which regions of the world have the greatest human and plant exposure to ozone pollution? Is ozone continuing to decline in nations with strong emission controls? To what extent is ozone increasing in the developing world? How can the atmospheric sciences community facilitate access to the ozone metrics necessary for quantifying ozone's impact on human health and crop/ecosystem productivity?

TOAR is designed to answer these questions through the development of an assessment report based on expert opinion and analysis, and the generation of a range of ozone metrics (i.e., exposure and dose indices) at hundreds of sites around the world.

TOAR has formed regional working groups to gather ozone data for these metrics analyses including a Working Group for Oceania which includes Indonesia, Australia, Papua New Guinea, New Zealand, the Pacific islands and Antarctica. More than 70 stations over Oceania and Antarctica have committed to providing surface ozone data. This will provide an overview of surface ozone for the first time over what is probably the least well monitored quarter of the Earth's surface.

The plan is for the TOAR reports to be released in late 2016.

Further information

http://www.igacproject.org/TOAR

The CAPRICORN Project – investigating cloud-aerosol interactions over the Southern Ocean

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Abstract

The Southern Ocean is one of the cloudiest and most remote locations on earth. The pristine nature of the atmosphere in this region makes it an ideal testbed for the investigation of aerosol-cloud interactions. Current state-of-the-art climate models significantly underestimate both aerosol and cloud loading in the Southern Ocean, resulting in a large bias in the shortwave radiative balance in this region (Figure 1), representative of too much shortwave radiation being absorbed at the surface [Mason *et al*., 2014; Shindell *et al*., 2013].

The Clouds, Aerosols, Precipitation and atmospheric Composition Over the southeRN ocean (CAPRICORN) project is the first of a series of projects designed to remove this bias in models by increasing the number of measurements in this region and developing our understanding of aerosol and cloud processes, and importantly, the interactions between them. A major experimental campaign will occur in March-April, 2016 and will utilise the recently commissioned RV Investigator as a platform to investigate the Southern Ocean atmosphere. This poster will outline the scientific objectives and plan, the instrumentation utilised in experimental campaigns, and give an overview of the data collected so far from test voyages.

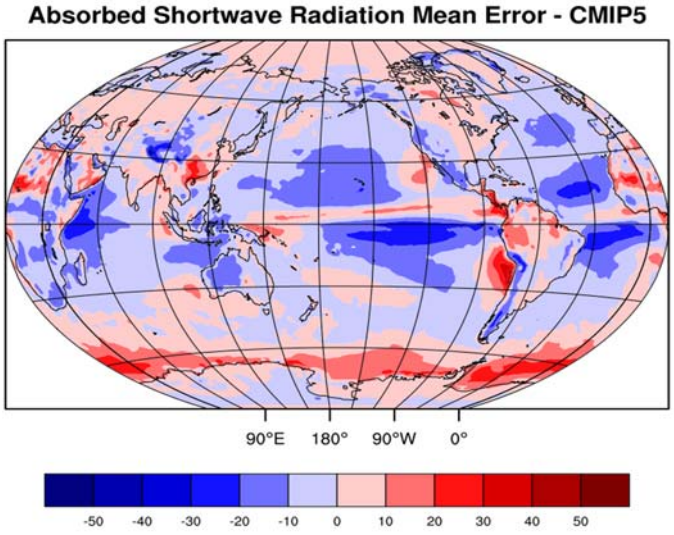


Figure 7. CMIP5 model clouds do not reflect enough sunlight. Ensemble mean error for CMIP5 models in shortwave radiation absorbed by the Earth System. Positive values indicate too much shortwave radiation absorbed by the surface. Source: Marchand *et al*., 2014.

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Using atmospheric radiocarbon to estimate fossil fuel sources: A test case with a known source

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Abstract

Atmospheric radiocarbon is a promising tracer for estimating the contribution of fossil fuel sources to the changes in atmospheric CO_2. Using atmospheric transport models and inverse techniques we can hope to estimate fossil fuel sources from radiocarbon measurements. In this study, we test this method using a known source. We use the Weather Research and Forecasting model (WRF-Chem) to investigate the $FFCO_2$ emission of a point source on 24th and 25th August 2013. The data consists of 20 samples of atmospheric CO_2 dissolved in weak NaOH solution. We use four-nested model domains with horizontal resolution of 9, 3, 1 and 0.33km, centered on Kogan Creek Power Station, which is a coal-fired power station located in the western Darling Downs in Queensland. We use the observed meteorology data from the Bureau of Meteorology to verify our model. The C-14 integrating air samples are used to examine the skill at modeling the small scale $FFCO_2$ and to test whether we can estimate the emissions.

The comparisons between simulated and observed values of wind speed and wind direction show that our model is reasonably reliable, with correlation coefficients of 0.67 and 0.63 respectively. We use three methods to extract the data of modeled $FFCO_2$ concentration: 1. Extract data from the closest location to the observation, 2. Extract data from a 3x3 square of grid cells centered on the observation then calculate the mean and maximum value, 3. Extend method 2 to include the bottom two layers of the model.

The model simulates well the overall structure of the results (correlation of 0.71) but underestimates the magnitude of spatial variations. This suggests either an underestimate of the emissions or that the model is diluting the influence of the power station.

Trends in CCl_4 from a network of total column measurements

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Abstract

Carbon tetrachloride (CCl_4) is an important trace gas species that is relevant to both Kyoto and Montreal protocols. It is a potent greenhouse gas with a warming potential of 1730 relative to CO_2 on a 100 year timescale, while is contributes 10% to the stratospheric chlorine budget and is responsible for about 10% of stratospheric O_3 depletion. While sources (industrial processes) of CCl_4 are almost all anthropogenic, sinks (ocean, soil and atmosphere) have large associated uncertainties [WMO, 2014].

The Network for the Detection of Atmospheric Composition Change (NDACC), that includes instrumentation at the University of Wollongong, is a long term effort of many institutions worldwide to measure a number of atmospheric gases that have important roles in both tropospheric and stratospheric chemistry. While gases like O_3 in the stratosphere and CO in the troposphere have been primary targets of this network, advances in analysis techniques have meant that species like CCl_4, which has a number of spectroscopic challenges, have renewed efforts to quantify their long term abundances.

The dataset from Wollongong, from a high resolution Fourier Transform Spectrometer, includes spectra covering the 12.5 micron region that has a relatively weak absorption complex of CCl_4 that requires state of the art radiative transfer calculations to include effects due to linemixing in the spectrally interfering species CO_2, as well as significant interference from water vapour. These data will be compared with other northern hemisphere results [Rinsland *et al*., 2012] to gauge the progress on an NDACC wide effort to derive a trend estimate of the CCl_4 total column.

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Phototautomerization: A new pathway to formation of organic acids

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Abstract

Every year, about 1.6 billion tonnes of non-methane volatile organic compounds (NM-VOCs) are released to the troposphere, mainly due to biogenic sources. Organic acids are significant products of atmospheric processing of these NM-VOCs, with 60 to 120 megatonnes per year found in the atmosphere. These organic acids are the key factor in formation of acidic rains, highly oxidized organic aerosols and secondary organic aerosols. Until recently atmospheric models were unable to explain the observed volume of these acids. In 2012, our group hypothesized that keto-enol photo-tautomerization of atmospheric carbonyls could be a new pathway for formation of organic acids [Andrews *et al*., 2012]. Subsequently, we successfully measured the formation of vinyl alcohol from irradiation of acetaldehyde under atmospheric conditions [Clubb *et al*., 2012].

The focus of our project is to extend the work on phototautomerization to a variety of larger carbonyls which have not been investigated before. Using FTIR (Fourier Transform Infrared) spectroscopy we aim to i) measure the spectra of 1-propenol and 2-propenol using the Norrish Type II reaction and ii) study the phototautomerization of acetone and propanal to form these two enols. We have recently been able to identify 1-propenol from the photochemistry of neat 2-methylbutanal molecules.

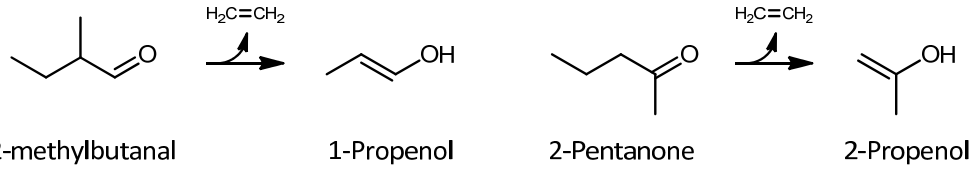


Figure 8. Photodissociation of 2-methylbutanal to 1-propenol and 2-pentanone to 2-propenol

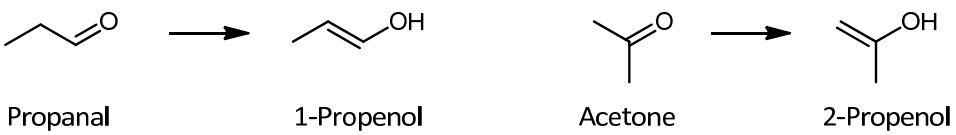


Figure 2. Phototautomerization of propanal to 1-propenol and acetone to 2-propenol.

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First data from the new Cape Grim VOC monitoring program

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Abstract

In November 2014 a new in situ VOC monitoring program was commissioned at Cape Grim. The configuration of the Cape Grim VOC instrument is based on an online instrument which has been running successfully at the Cape Verde observatory for several years. VOC measurements are made every hour via a dual channel online gas chromatograph (GC) with flame ionization detectors (FID). Two columns and two FIDs allows quantification of both light hydrocarbons (C2-C8) and a range of oxygenated VOCs such as aldehydes, ketones and alcohols.

Will provide an update about the automated processing of the chromatograms using GCWerks and discuss some quality assurance results, including cold trap breakthrough volumes for different hydrocarbons. We present one year of data for some simple hydrocarbons and provide a comparison between concentration data obtained on this system with other present (NOAA flasks, AGAGE Medusa) and past (CSIRO canister sampling) hydrocarbon measurements at Cape Grim.

We will discuss future challenges that need to be overcome including ozone removal from sample air for reliable alkene measurements, and avoidance of surface effects for oxygenated VOCs.

Identifying the potential influence of climate change on mercury air surface exchange

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Abstract

Human activities over the last few centuries has altered the earth's climate system and consequently has influenced the global mercury budget. Potential links between climate change and natural mercury emissions has not been adequately explored within current literature. In order to understand how impending climate predictions may influence future mercury emissions it is important to first understand how current climate parameters influence mercury exchange from different surfaces. This research aims to investigate the relationship between climate controls and mercury air-surface exchange and determine the potential implications of these findings with a view to approaching climate change. Mercury flux data was obtained for a number of sites across Canada and the United States and Australia, using micrometeorological methods, comprising both background and enriched substrates. The Arrhenius equation was applied to gain a better understanding of which parameters control mercury flux. The results found that climate and environmental parameters were the dominate influence for substrate-flux relationships for both background and enriched sites. Extrapolating these results with temperature it was calculated that for a 4.4°C increase in temperature there is a 62% increase in mercury flux, approximately 15% for every 1°C change in temperature.

Assessing the accuracy of WRF in simulating meteorology, NSW

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Abstract

Air quality is a basic requirement of human health and liveability. Originating from either anthropogenic, natural sources or chemically formed; air pollutants can exceed the recommended standards dependent on region and time. In order to minimise these occurrences it is crucial to identify and understand the influencing processes, e.g. their sources and sinks, chemical transformation and transport. Accurately modelling the local meteorology will help improve predictions of current and future air quality in NSW and would be of great benefit in the protection of the community and environment as well as sustaining industry.

The Weather Research and Forecast model (WRF) is the latest generation mesoscale numerical weather prediction system, superseding the mesoscale model MM5. The use of this more advanced meteorological model may further improve the ability to predict air quality impacts as well as providing advanced forecasting of meteorology for predictive and proactive dust management by industry.

In this study the WRF model will be nested over NSW and will include an investigation of input data, land use and grid resolution to better represent the region. A model evaluation framework will be employed to investigate the performance of the model against observations.

Methane, nitrous oxide and ammonia emissions from manure stockpiling by the swine and poultry industries of Australia

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Abstract

The swine and poultry (meat & layer) industries together represent ~0.27% of Australia's total greenhouse gas (GHG) emissions inventory [DoE, 2013]. Emissions from pork production make up 85% of this contribution while meat chickens 12% and layer chickens 3% and in all cases manure management is the source of these emissions. Methane (CH_4) and Nitrous oxide (N_2O) are largely responsible for total emissions from both sectors, however ammonia (NH_3) should also be considered for its indirect contribution through physical and biochemical pathways. Very few studies have been carried out to document and understand emissions of CH_4, N_2O and NH_3 from manure management by the swine and poultry sectors in Australia.

Emission measurements of CH_4, N_2O and NH_3 have been made from spent litter from a swine production facility and manure removed from a tunnel ventilated layer hen facility. Open path Fourrier Transform Infrared Spectroscopy (OP-FTIR) was used to make gaseous mixing ratio measurements and emissions rates inferred using a backward lagrangian stochastic model, WindTrax. Validation of the measurements was achieved through a controlled release experiment using N_2O.

Layer hens were confirmed to be a low emitter of GHG's however significant quantities of NH_3 were detected from the control and mitigation stockpiles. Covering layer chicken manure resulted in an 87% reduction in total direct and indirect GHG emissions dominated by reduction in NH_3. Total yearly emissions from a litter based swine production approach with litter stockpiling were found to be 56% lower than a conventional slatted floor shed flushing system with an anaerobic effluent treatment pond.

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Surface ozone measurements from Baring Head and Lauder, New Zealand

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Abstract

Tropospheric ozone is an important constituent of the atmosphere as it is a greenhouse gas, and it also plays a key role in the oxidation chemistry of the atmosphere through its role in the production of the hydroxyl radical [Galbally *et al*., 2011]. Surface ozone measurements are currently made at two sites in New Zealand: at Baring Head (41°S, 175°E) and at Lauder (45°S, 170°E). The Baring Head measurements were made with a Dasibi UV ozone monitor (Model 1003-PC) from 1991-2004, and with a TEI49i instrument from 2005 onwards. The Lauder measurements have been made with a TEI49c instrument since 2003.

The Baring Head site is in a hilly rural environment, on the coastal cliff edge at an altitude of 95 m above mean sea level. Baring Head is approximately 15 km south-east of Wellington city. In southerly winds the site frequently receives very clean air masses from the Southern Ocean which have had no contact with land for many days.

The Lauder station is located in a broad river valley. The station is surrounded by pastoral land dominated by sheep and cattle farming along with seasonal cropping. The valley is sparsely populated, and there is no major industry in the region.

Both sites exhibit a marked seasonal cycle, as shown in Figures 1 and 2, with minimum values during the summer (December - February) and maximum values in the winter/early spring (July - September). This is very similar to that seen at Cape Grim, Australia (41°S, 145°E) [Oltmans *et al*., 2006].

At both sites, strong winds are often associated with high ozone concentrations, as shown for Baring Head in Figure 3. These high concentrations result from a shift in the source/sink balance likely dominated by physical processes with enhanced source processes including vertical exchange and mixing processes, which bring ozone from aloft down to a lower level, and dominate over changes in dry deposition

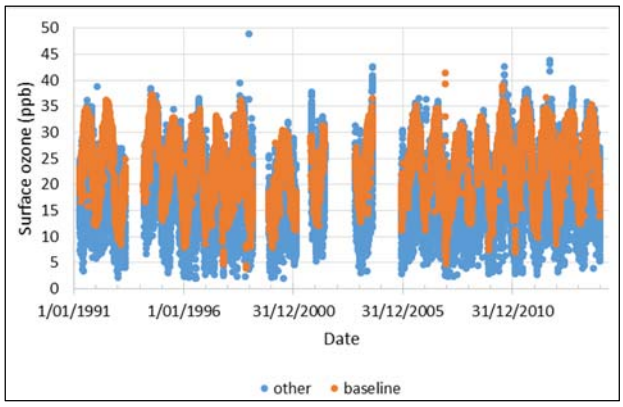


Figure 9. Baring Head hourly surface ozone (1991-2014). Baseline conditions are defined as when the wind speed is greater than 7 m/s, and the wind direction is between 90° and 350°.

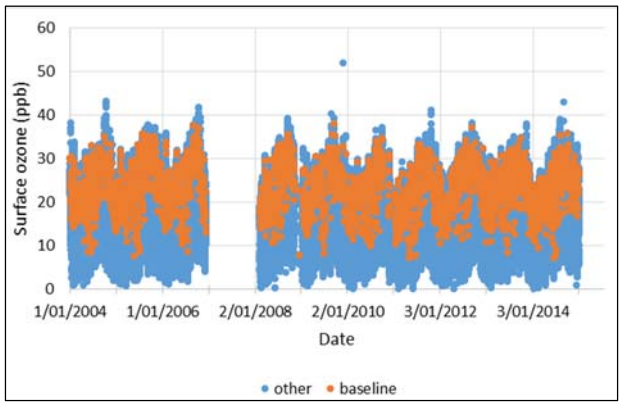


Figure 2. Lauder hourly surface ozone (2004-2014). Baseline conditions are defined as the 3pm (local time) when the wind speed is greater than 5 m/s.

At Baring Head the greatest surface ozone variability occurs with northerly winds and calm periods. This variability is caused by two effects: (1) northerly winds pass over the land surface, which is a more effective sink for ozone than the ocean [Galbally and Roy, 1980] and the source/sink balance appears much more variable in light winds, and in addition (2) the urban centres to the north of Baring Head are sources of NO_x and hydrocarbons, which are important precursors to ozone production. In contrast, at Baring Head the southerly winds have a relatively narrow range of high ozone concentrations. The southerly winds come from the ocean, with lower deposition velocities [Chang *et al*., 2004], and some of the time in descending air masses bringing ozone from aloft.

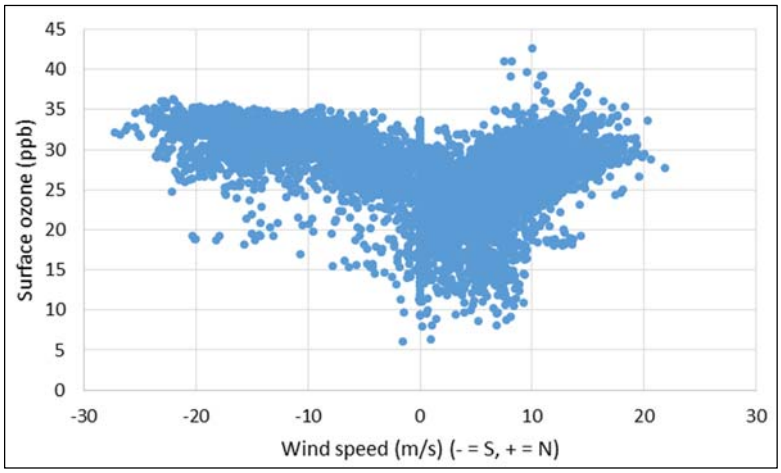


Figure 3. Baring Head hourly surface ozone vs directional wind speed for the month of August (2006-2014). Negative directional wind speeds are when the wind is from the south (90° to 270°), and positive directional wind speeds are when the wind is from the north (270° to 360°, or 0° to 90°).

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Clean air and urban landscapes – Towards a clean air plan for Western Sydney

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Abstract

The negative health impacts of airborne particulates on urban populations are now well established. Whilst the air quality in Australian cities is generally very good compared to many other parts of the world, Sydney experiences occasional poor air quality events that expose the population to heightened health risks. Health effects are also known to occur at air pollution concentrations that are within national air quality standards, meaning that health benefits can be realised through improving air quality even in regions with relatively low pollution levels. The population within the Sydney basin is predicted to grow by ~ 20% in the next decade, increasing both the local sources of pollution and the population exposed.

The Clean Air and Urban Landscapes hub has formulated a project to address this issue called the Western Air-Shed Particulate Study for Sydney (WASPSS). The project will provide the tools and evidence to develop a Clean Air Plan for Western Sydney. Research activities will be focussed around three main research aims, each with their own subproject:

1. Extend air quality measurement/monitoring capacity to support improved characterisation of air quality in Western Sydney.
2. Implement and validate state-of-the-science regional air quality modelling to assess major sources contributing to air pollution in Western Sydney and assess benefits arising from a range of possible mitigation measures.
3. Evaluate existing methods applied internationally and locally for estimating human exposure to airborne pollutants, and estimate air pollution related exposures and health effects for Western Sydney.

The project will enable policy makers to estimate the benefits of different mitigation strategies to the future air quality in Western Sydney.

Tropospheric hydrogen – an update based on measurements from Cape Grim, the CSIRO global flask network and Antarctic firn air

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Abstract

A comprehensive review of current understanding of tropospheric hydrogen (H_2) was presented by Ehhalt and Rohrer in 2009. While the broad features of the global atmospheric budget of H_2 are well established, there remains a significant uncertainty in the largest single term in this budget, namely the magnitude of the soil sink. How the Cape Grim H_2 data (both flask and *in situ*), combined with the other available data, may improve estimates of the soil sink of H_2 will be presented.

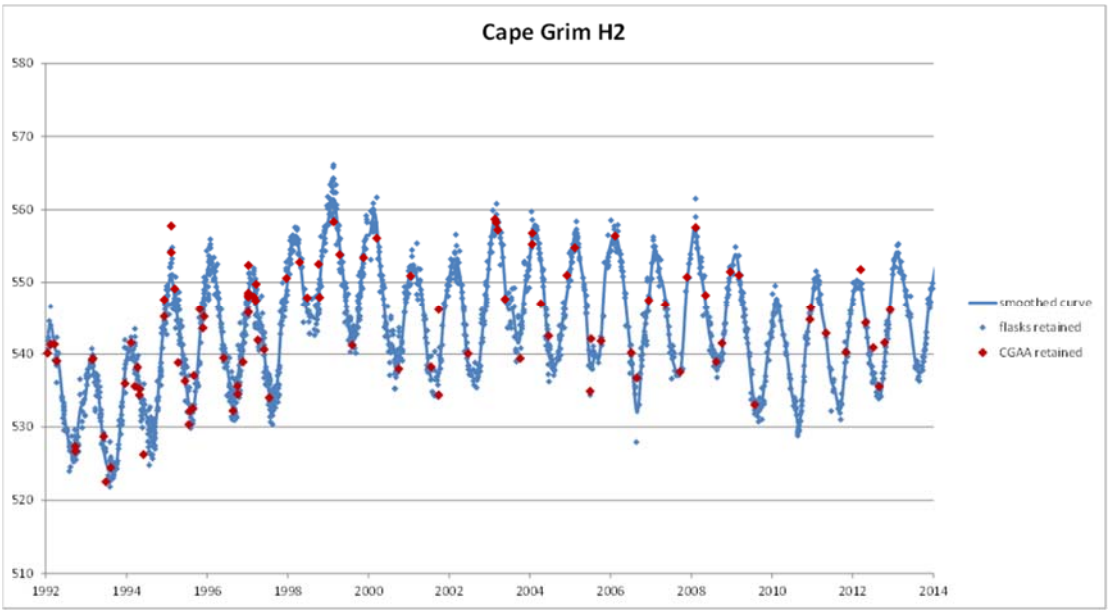


Figure 1. Atmospheric H_2 record at Cape Grim from flask air samples measured at CSIRO GASLAB, with superimposed values of H_2 measured in the Cape Grim Air Archive (CGAA). Mixing ratio units are nanomoles per mole in dry air (parts per billion, ppb).

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Atmospheric abundance and global emissions of perfluorocarbons CF_4, C_2F_6 and C_3F_8 since 1900 inferred from ice core, firn and atmospheric measurements

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Abstract

Perfluorocarbons (PFCs) are very potent and long-lived greenhouse gases in the atmosphere, released predominantly during aluminium production and semiconductor manufacture. Here we present the first continuous records of the atmospheric abundance and global emissions of three perfluorocarbons (CF_4, C_2F_6 and C_3F_8) from 1900 to the present. The records are derived from a multi-site inversion of high precision measurements of PFCs in air from two polar ice cores, four polar firn sites and air archive tanks and atmospheric air sampled from both hemispheres.

We show that the background (preindustrial) level of CF_4 was 34.1 ± 0.3 ppt attributed to a natural source from rocks, and zero (below detection) for C_2F_6 and C_3F_8, followed by large increases due to the aluminium industry. We find a significant peak in the CF_4 and C_2F_6 emissions during World War II, presumably due to the high demand for aluminium for construction of aircraft. The PFC emissions per kilogram of aluminium produced at the time of WWII were significantly higher than today. Since WWII, the desire for increased efficiency and reduced electricity consumption has led to improvements and better control of the smelting process, and in turn lower emissions of PFCs per kilogram of aluminium. More recently, both the aluminium and semiconductor industries have worked successfully to reduce PFC emissions even further, leading to decreases in emissions and slowing growth in atmospheric abundance despite continuing increases in aluminium production and semiconductor manufacture. We see a dip of about 15% in both CF_4 and C_2F_6 emissions in 2009, most likely associated with the impact of the global financial crisis on global aluminium and semiconductor production.

Particulate characterisation study of Western Sydney using WRF-Chem

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Abstract

Recently, there have been increasing concerns of particulate exposure to the population in the Sydney region. The newly established Clean Air and Urban Landscapes (CAUL) hub, one of the National Environment Science Programs (NESP) run by the Department of the Environment, has been tasked with conducting a latest characterisation study of particulate pollution in Western Sydney. Previous CSIRO-led observational studies such as the Sydney Particulate Studies 1 and 2 [Cope *et al*., 2014] (conducted in summer and autumn respectively) have shown that sea salt (34%) and organic matter (34%) were significant components of PM2.5 for summer where as in the autumn study, organic matter (57%) was found to be a significant contributor to PM2.5 (with sea salt only contributing 5%). Since then there has been a number of measurement and modeling studies such as the 16th and 17th October bush fires, the MUMBA campaign (21 December – 15 February 2013) and the Lower Hunter monitoring campaign from 15-29 May 2014. These studies have provided a wealth of measurement data needed for model validation and interpretation.

Here we will present results from a particulate modeling study using the Weather Research and Forecasting Chemistry (WRF-Chem) model and observational data that was measured during one of the field campaigns above.

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Developments in the CSIRO Australian Greenhouse Gas Observation Network (AGGON)

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Abstract

The Cape Grim Baseline Air Pollution Station (CGBAPS) is the central reference observation site in the Australian regional Greenhouse Gas Observation Network (AGGON). Recent developments in the greenhouse (GHG) program at CGBAPS include new in-situ analysers for N_2O/CO and $^{13}CO_2/^{12}CO_2$ using Quantum Cascading Lasers (QCL) (Aerodyne, QC-TILDAS). Recently, two additional observation sites were added to this network ('Burncluith' and 'Ironbark'), associated with the atmospheric monitoring of fugitive emissions from Coal Seam Gas (CSG) extraction projects, being developed in the Australian state of Queensland. Currently each site is limited to a single Cavity Ring Down Spectrometer (CRDS) (Picarro, G2300 & G2400).

In addition, a new Australian Marine National Facility blue water research vessel RV Investigator was recently commissioned with dedicated atmospheric observation capability on-board. This includes in-situ N_2O/CO (Aerodyne, QC-TILDAS) and CO_2/CH_4 (CRDS) (Picarro, G2300) analysers in the GHG program.

A key research application of AGGON is to monitor changes in the efficiency of the Southern Ocean CO_2 sink using a well inter-calibrated, high precision, Southern Ocean atmospheric observation sub-network. The atmospheric data from this network is dominated by regional ocean-atmosphere exchange, making this an important top-down complement to ocean-based Southern Ocean carbon observation and modelling research. Recent analysis of this data has revealed small but consistent diurnal and seasonal variations that will improve our understanding of Southern Ocean CO_2 exchange such as that related to biological production.

In addition to an expansion of the network, the research programs at other network sites have also been developing. The pilot Australian Tropical Atmospheric Research Station (ATARS) established at Gunn Point, near Darwin in Australia's Northern Territory (12.249S, 131.045E, elevation 25 metres). A key research application of this site is to understand the impact on the atmosphere from the regular (mostly controlled) seasonal biomass burning events that occur over the large expanse of tropical savannah in this region. The GHG program consists of in-situ CO_2/CH_4 and $^{13}CO_2/^{12}CO_2$ CRDS analysers (Picarro, G1300 & G2100i) and a flask air samples collection program. In addition, there are research programs for reactive gases, aerosols, radon (ANSTO), gaseous mercury (Macquarie University) and short lived biogenic halocarbons (University of Cambridge).

The status of these new sites will be presented here, including a selection of data and results from recent network developments.

Understanding the primary oxidation of terpenes

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Abstract

Within our biosphere, well more than half of the natural release of (non-methane) volatile organic compounds (VOCs) can be attributed to isoprene and the family of terpenes [Whalley *et al*., 2014]. Successive oxidation of isoprene, chiefly initiated by reaction with the hydroxyl radical (OH), accounts for more than half of the global formation of biogenic secondary organic aerosols (SOAs) [Ghosh *et al*., 2010]. These aerosols have long been known to impact local and global climate through radiative forcing and are involved in cloud nucleation.

Presently, atmospheric chemistry models fall short in their ability to predict the concentration of OH, in regions of high isoprene concentration, often by more than an order of magnitude [Whalley *et al*., 2014]. We are investigating this shortfall in atmospheric models by starting with the first radical in the mechanism – the hydroxyisoprenyl, the spectroscopy and structure of which has not been reported.

Two of the hydroxyisoprenyl isomers have an allylic chromophore, which makes their spectra amenable to study. Therefore, our studies are proceeding towards these unknown radicals via a study of similar sized systems involving the allylic chromophore. We conduct modified resonance enhanced multiphoton ionisation (REMPI) spectroscopy experiments in order to gain mass and isomer specific information about the vibrational and electronic structure of these isolated radicals. Currently, we have remeasured the higher excited states of the allyl and 2-methylallyl radicals and will hope to present data on the multiple isomers of the prenyl and hydroxyisoprenyl systems, corresponding to the first measurements of the H and OH addition to isoprene.

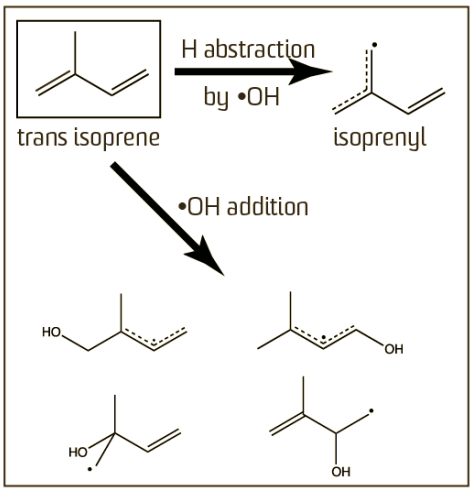


Figure 10. Hydroxyl initiated oxidation of isoprene

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Water in the visible: Retrieving water vapour column amounts from sun photometry

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Abstract

Water vapour is well recognized as the most significant greenhouse gas, but one that is driven primarily by climate. As a result there are numerous methods, both ground- and satellite-based that have been developed to measure atmospheric water vapour [Schneider *et al.*, 2010], including the microwave measurements carried out at Cape Grim in 1993 – 1995 [Boers, 1996].

Since 2001 sunphotometers with a filter measuring at 812 nm have been deployed at Cape Grim, as part of national network of sunphotometers run by the Bureau of Meteorology. This wavelength has been chosen as solar radiation is attenuated by water vapour.

The difficulty with this measurement is how to reliably calibrate it - a presumption of 'Beer-Lambert law' linearity is fundamentally flawed, given the variation in absorption line strength within the band-pass of the filter (Figure 1) and the variability of water vapour during the day. A number of methods have been proposed to cope with these issues, such as the methods outlined by Schmid *et al*. [2001]. The method chosen for this analysis is to use Wollongong measurements where water vapour column amounts retrieved from FTIR are used to derive a calibration function for co-located sunphotometers. This calibration has then been used to derive an estimate of water vapour column amounts at Cape Grim.

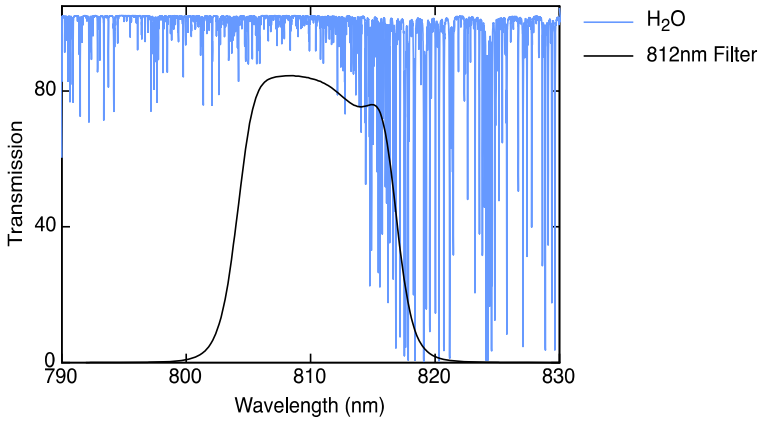


Figure 11. Transmission of a 812 nm bandpass filter (black line) and water vapour (blue line) as a function of wavelength.

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A simple method for combustion of methane using CuO

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Abstract

Conversion of sample C into CO_2 is an important step in preparing radiocarbon targets for accelerator mass spectrometry (AMS). We present a simple method for the complete oxidation of methane (CH_4) to CO_2 in a sealed system using copper oxide (CuO) as the source of oxygen. Results shows that CH_4 can be completely converted to CO_2 in two hours in the presence of CuO at temperature at 800°C or higher inside a quartz tube.

Experiments were performed using a miniaturised graphitisation furnace of 'conventional' design (the 'MCF') [Yang *et al*., 2015; Yang and Smith, 2015]. It is comprised of the reactor body, a horizontal hot finger (6 mm OD quartz tube, 120 mm long) and a vertical cold finger (6 mm OD Pyrex® tube, 120 mm long). The total internal volume is 3.8 mL. The reactor body has three integrated valves for connection to the vacuum manifold, to the sample port and for isolation of the reactor. We developed a small electrically-heated furnace which can raise the temperature of the hot finger (T_{HF}) to 1100°C. The cold finger temperature (T_{CF}) is controlled by a cooling system we designed earlier [Yang et al., 2013] over the range -170°C to -50°C.

Initially, we evaluated the evolved O_2 pressure as a function of temperature (T_{HF}) for pure CuO by heating a known amount of CuO in the hot finger. The reactor pressure, P_R, was recorded as T_{HF} was smoothly increased from room temperature (RT) to 1000°C and then gradually decreased back to RT. Results show that i) during heating, P_R began to noticeably increase from 2.2 mbar at T_{HF} = 750°C, rising exponentially to 210 mbar as the temperature increased to 968°C, ii) during cooling, P_R behaved similarly for a given T_{HF}, iii) P_R was independent of the mass of CuO, over the range of 50 mg to 500 mg that we tested.

Combustion of CH_4 has been previously reported [Pack *et al*., 2015]. We trialled a new approach, loading the reactor with about 300 mg of CuO, evacuating it then filling with CH_4 at atmospheric pressure from a gas sample bag. With T_{CF} = -120°C to trap H_2O and CO_2, the hot finger was heated and P_R began dropping at T_{HF} = 800°C. With T_{HF} = 910°C, P_R dropped constantly and reached a minimum value of 68 mbar after two hours, corresponding to the expected O_2 pressure at that temperature. The yield of CO_2, determined by raising T_{CF} = -65°C to keep H_2O trapped, showed that 99.9% of the CH_4 had been converted. It important to mention that the cold finger temperature of -120°C was chosen for combustion of CH_4, rather than the -170°C commonly used by us during graphitisation, to prevent partial trapping of CH_4, and yet to efficiently trap CO_2. In addition, we have also completely combusted CH_4 within two hours with T_{HF} = 800°C and T_{CF} = RT. This indicates that trapping CO_2 and H_2O during is not necessary during the combustion.

This combustion method was also tested on a gas mixture of 18% CH_4 and 82% Ar, with a final CO_2 yield of 99.3%. The MCF is also capable of separating and combusting CH_4 in environmental samples that contain CO_2, CH_4 and other gases. This is accomplished by using an additional cold finger on a spare port of the MCF, permitting separation of CO_2, H_2O and other condensable gases from the remainder which is then isolated in the reactor and combusted.

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Mercury in the Southern Hemisphere and the Cape Grim mercury measurement program

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Abstract

The UNEP Minamata Convention on Mercury, is a global treaty, promulgated in 2013, signed by 128 countries, including Australia with the mission to protect human health and the environment from the adverse effects of mercury. Since 2011 Cape Grim station has undertaken continuous measurements of atmospheric levels of total gaseous mercury (TGM). As the atmosphere represents the dominant pathway for distribution of mercury globally the Cape Grim mercury atmospheric composition measurements will play an increasingly important role in the assessment of the impact of the Minimatta treaty as well as contributing to improving the understanding of the global mercury cycle. The Cape Grim mercury measurements have already made a significant contribution to the understanding of background levels of TGM in the Southern Hemisphere [Slemr *et al*., 2015] where it is shown that these levels are significantly lower than previously thought. This finding has significant implications to global mercury modelling and inter-hemispheric transport of atmospheric mercury. Recently we have implemented new technology developed at the University of Nevada-Reno at Cape Grim to measure the reactive component of atmospheric mercury; total reactive mercury (TRM) and speciation of TRM. The complete suite of atmospheric mercury data now collected at Cape Grim is critical to improving our understanding of mercury biogeochemical cycling.

Reference

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A symphony of atmospheric mercury across the Australian continent

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Abstract

The Minamata Convention on Mercury, signed by Australia in 2013, is aimed at developing global policy designed to reduce the environmental and human health impacts of this potent neurotoxin [Kessler, 2013]. As the atmosphere represents the dominant pathway of environmental mercury [Driscoll *et al.*, 2013], development and evaluation of such policy is reliant on long-term monitoring capabilities undertaken at effective spatial resolutions [Cinnirella *et al.*, 2014]. Recently, data collected at Cape Grim were used in conjunction with those from other international sites to show that atmospheric mercury concentrations in the Southern Hemisphere are up to 30% lower than previously believed – between 0.85 and 1.05 ng m^{-3} [Slemr *et al.*, 2015]. Since then, the monitor at Cape Grim has been joined by others at Gunn Point and in the Hunter Valley, providing a glimpse at the latitudinal gradient of atmospheric mercury across Australia, as well as one of the world's few tropical mercury monitoring datasets. Here we aim to present data from all three sites for the years 2014/15 and highlight an apparent decrease in mercury concentration with increasing latitude. Exploration into daily and seasonal variation at each of the three sites will be included, as well as an outline of the context for the global significance of an effective Australian atmospheric mercury monitoring programme.

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New developments in measuring reactive mercury in the atmosphere

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Abstract

Mercury (Hg) is a ubiquitous environmental contaminant with both natural and anthropogenic sources contributing to atmospheric loading and subsequent transport and deposition on a global scale. Recognizing the pervasive toxicological effects of Hg in biological food webs and ultimately humans, signatories to the United Nations Environment Program Minimata Convention on Mercury committed to continued reductions and ongoing monitoring of Hg in all spheres of the environment. Currently, monitoring networks rely on a single commercially available system developed by Tekran Instruments® for measurement of all atmospheric Hg species. The Tekran® speciation system delivers the advantages of automation and relative high time resolution, using a multistage sample path that selectively collects and pre-concentrates, in the following order, gaseous oxidized mercury (GOM), particulate bound mercury (PBM), and gaseous elemental mercury (GEM). Each Hg fraction is thermally reduced, in turn, to elemental Hg0 for quantification by cold vapor atomic fluorescence spectroscopy (CVAFS), an accurate and robust analytical methodology that is directly calibrated to known Hg0 vapor concentrations. However, reactive mercury species (RM = GOM + PBM) cannot be directly measured and there is no robust in-field calibration process for RM. Published studies indicate the KCl coated denuders used in the Tekran® system have variable GOM collection efficiencies depending on atmospheric chemistry. Water vapor and ozone in particular have been shown to cause losses in GOM retention. In response, alternate methods for quantifying GOM have recently been investigated. Among these newer methods is a filter-based sampler system that uses a cation exchange membrane (CEM) composed of polyethersulfone to selectively remove GOM from an air sample stream. Laboratory experiments and field deployments of the CEM filter system have demonstrated consistently higher GOM recoveries relative to GOM concentrations reported by co-located Tekran® speciation systems. This difference suggests the CEM material is less susceptible to interferences relative to the KCl denuder and therefore better suited to quantifying total atmospheric GOM concentrations, as well as presenting significant reductions in both capital investment and ongoing operating costs. We are currently establishing a CEM filter system at the Cape Grimm Baseline Air Monitoring Station, Tasmania, Australia, and hope to maintain additional CEM filter systems in Sydney, NSW, and potentially Darwin, NWT, Australia.

Time variation patterns of CH_2O and NO_2 monitored by MAX-DOAS, PTRMS and NO-NO_2-NO_x instruments during Measurement of Urban, Marine and Biogenic Air (MUMBA) Campaign

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Abstract

This study focuses on the time variation of CH2O and NO2 monitored by Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS), Proton Transfer Reaction Mass Spectroscopy (PTRMS) and NO-NO2-NOx instruments during the Measurement of Urban, Marine and Biogenic Air (MUMBA) Campaign. This campaign took place in the seaside city of Wollongong, located in the Illawara region of New South Wales, Australia, approximately 80 km South of Sydney. Two months (21 December 2012 - 15 February 2013) of measurements of CH2O and NO2 were made. This study compares the diurnal variations of CH2O and NO2 produced by these three different monitoring instruments. While the instruments were located close together, the data from MAX-DOAS are integrated amounts across the slant column path, whereas the other two instruments are measuring at a single location. There are significant similarities in the measurements made by the differing instruments. The diurnal behaviour of both NO2 and CH2O can be understood in terms of the variations in sources and photochemical oxidation.

Evidence builds for a biogenic field campaign in Australia

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Abstract

The Model of Emissions of Gases and Aerosols from Nature (MEGAN) is used all over the world to calculate the biogenic contribution of volatile organic compounds. Measurements from four different field campaigns have been modelled using MEGAN, one in spring (Tumbarumba 2006), two in summer (Sydney 2011 and Wollongong 2013) and one in autumn (Sydney 2012). This research has demonstrated that the predicted concentrations of isoprene are up to a factor of 10 too high when compared to measurements [Emmerson *et al*., 2015, Paton-Walsh *et al*., 2015]. One reason for this is that eucalypt trees emit the highest concentrations of isoprene than any other plant types, however there are many different species which have not been tested. Global models assume South East Australia has a high percentage of eucalypts which leads to the overestimation.

This talk will lay out the drivers behind project KOALA – Characterising the Organics and Aerosol Loading of Australia.

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Characterizing emissions and chemical evolution from aircraft

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Abstract

Observations of atmospheric composition from aircraft over the past decade have greatly increased our understanding of anthropogenic and natural emissions of volatile organic compounds (VOCs) and other precursors of ozone and aerosols. Furthermore, the airborne observations allow for sampling air over a range of photochemical ages, allowing quantification of chemical processing. Results from several experiments using the NSF/NCAR C-130 aircraft will be presented, highlighting the value of this platform as a tool to test and improve our understanding of the complex interplay of chemical constituents over a regional domain. The MILAGRO/MIRAGE-Mex experiment characterized the chemical evolution of the pollution plume from Mexico City in March 2006. Observations over the northeast Pacific Ocean were made during the INTEX-B experiment in April-May 2006. In June-July 2013 the NOMADSS/SOAS experiment sampled biogenic emissions and their products over the southeast U.S., a heavily forested region with urban areas. The FRAPPE experiment in July-August 2014 sampled the varied environment of Colorado, with urban, forest, agriculture and oil/gas exploration emissions, over complex terrain. The results from these experiments will be placed in the context of possibly using the NCAR C-130 for an experiment in Australia.

Organic nitrate chemistry and its implications for nitrogen budgets: Insights from aircraft and ground-based observations in the southeast US

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Abstract

Nitrogen oxide radicals ($NO_X \equiv NO + NO_2$) are critical in controlling tropospheric ozone production and influencing aerosol formation, with indirect impacts on atmospheric oxidation capacity, air quality, climate forcing, and ecosystem health. In continental regions, a dominant loss pathway for NO_X is reaction with biogenic volatile organic compounds (BVOCs, mainly isoprene and monoterpenes) to form organic nitrates (Browne and Cohen, 2012). Although organic nitrates play a central role in the NO_X budget, their chemistry remains the subject of debate, with key uncertainties surrounding the organic nitrate yield from BVOC oxidation, the recycling of NO_X from organic nitrate degradation, and the role of organic nitrates in secondary organic aerosol formation (Perring et al., 2013). Two campaigns in the Southeast US in summer 2013 provided datasets of unprecedented chemical detail for addressing these uncertainties: the airborne NASA SEAC^{4}RS (Studies of Emissions and Atmospheric Composition, Clouds, and Climate Coupling by Regional Surveys) and the ground-based SOAS (Southern Oxidants and Aerosols Study). In this talk we will use simulations with a high-resolution 3-D chemical transport model (GEOS-Chem) to interpret organic nitrate observations from both campaigns, with focus on their impacts on atmospheric nitrogen budgets. We will also discuss the relevance of our results to atmospheric chemistry in Southeast Australia—and the need for further observational constraints in this high-BVOC, low-NO_X region.

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Decdal-scale trends and variability in atmospheric composition over Wollongong, Australia

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Abstract

The ground-based solar Fourier Transform Infrared Spectrometer (FTIR) at the University of Wollongong provides a long-term record of atmospheric composition above Wollongong, NSW. The FTIR has been measuring infrared spectra since May 1996, from which the total column of a variety of absorbing trace gases can be retrieved. Measurements include those of carbon monoxide (CO), hydrogen cyanide (HCN), formaldehyde (HCHO), ethane (C_2H_6) and methanol (CH_3OH).

In this presentation we will present long-term trends of these priority trace gases, interpreted using these decadal-scale records in combination with simulations from the global atmospheric chemical transport model GEOS-Chem.

Modelling tropospheric composition in the Southern Hemisphere

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Abstract

Global models are useful tools for interpreting trends and variability of trace gases, especially in the Southern Hemisphere (SH) where observations are sparse. Comparatively small direct emissions in the SH mean that composition in the remote SH is mainly determined by intercontinental and inter-hemispheric transport of trace gases and their oxidation products from the source regions, which are mostly in the tropics, associated with biomass burning and biogenic emissions, and industrial sources in the Northern Hemisphere (NH). In this talk I will present results from a few modelling studies, assessing how changes in anthropogenic and biogenic emissions impact SH composition. In particular, a global chemistry-climate model was used to interpret observed long-term trends in carbon monoxide (CO), ethane (C_2H_6), and HCN measured at Lauder, New Zealand, and Arrival Heights, Antarctica. Negative trends in all three species have been observed at both locations, and are analysed using a set of model simulations to attribute the observed trends in these species [Zeng *et al*., 2012]. I will also summarise a recent multi-model study on investigating the impact of tropical biogenic emissions of isoprene and monoterpenes, which have large uncertainties in their emission strength, on SH CO and HCHO using four different global models [Fisher *et al*., 2015; Zeng *et al*., 2015]. The models are evaluated against CO and HCHO columns measured using ground-based Fourier-Transform Infrared (FTIR) spectroscopy, in situ surface CO, aircraft CO profiles, and satellite CO columns. The study identifies inter-model differences in modelling SH CO and HCHO, in particular due to differences in chemical mechanisms between the models, and the importance of developing more accurate global biogenic emission inventories. We also suggest that large missing sources of HCHO in the remote SH would be required to close the HCHO budget; such large emissions would be inconsistent with our present understanding of organic emissions in the SH. More comprehensive observations are needed to resolve this problem.

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Modelling 20th century atmospheric composition

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Abstract

In situ measurements of atmospheric composition exist for only the last few decades. We know that anthropogenic sources of climatically relevant gases and aerosols were changing many decades prior to that. Measurements derived from air trapped in snow and ice reach much further back in time than in situ observations. These long-term records allow analysis of trends spanning both hemispheres for multiple atmospheric components relevant to climate. Firn and ice core records therefore provide an important record that predates modern in situ observations. Ice and firn records, together with in situ observations, are invaluable for evaluating models of past atmospheric composition and climate.

ACCESS-UKCA is a state-of-the-art global composition-climate model with detailed representations of tropospheric and stratospheric chemistry and aerosol, and their impact on climate. We have developed an emissions dataset that drives the model which includes anthropogenic, biomass-burning, and natural sources of climatically-relevant atmospheric constituents.

In the work presented here, we evaluate the ACCESS-UKCA model by comparing to multi-decadal records of aerosol (e.g. black carbon, mineral dust) and gas-phase atmospheric constituents (e.g. carbon monoxide) from 1920 to the present day. We further explore trends in these constituents in both hemispheres. Variations in modelled seasonal and diurnal cycles over this time period are investigated. In the aerosol phase, black carbon and mineral dust can be considered as sporadic and poorly quantified vectors for nutrient supply to the remote oceans. Long-term records, combined with a model capable of simulating these quantities, provide an excellent tool for probing the effects of changing atmospheric composition on the climate system.

Atmospheric trace gas inversion with spatial statistical models

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Abstract

Atmospheric trace-gas inversion is a method for assessing the spatial distribution of gas emissions, or flux, from (i) mole fraction measurements and (ii) atmospheric simulations from deterministic computer models. Spatial statistics is a field of research devoted to the characterisation and uncertainty quantification of processes that are only partially observed in space and time. In this talk I will informally show how the problem of atmospheric trace-gas (specifically, methane) inversion can be first described, and then tackled, using spatio-temporal stochastic models and computationally efficient estimation methods from spatial statistics. The proposed framework offers new possibilities for atmospheric trace gas inversion, one of which is a reduced reliance on flux inventories that are frequently used as 'priors' for flux estimation. The approach is illustrated on a case study of methane (CH_4) emissions in Great Britain [Zammit-Mangion *et al*., 2015].

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What can we learn from comparing the Cape Grim and Casey Picarro records of atmospheric CH_4 and CO_2?

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Abstract

In this presentation, we will explore for the first time what we can learn from having continuous, high precision *in situ* measurements of CO_2 and CH_4 at both Cape Grim, Tasmania, and Casey, Antarctica.

Historically, we have only had access to relatively sparse flask data (typically weekly) from Casey (and the other Antarctic stations). With the advent of in situ measurements on the Antarctic mainland, a great deal of rich information has become available to us. For instance, we can now see a clear phase difference in the seasonal cycle of CH_4 between Casey and Cape Grim. (Figure 1).

Additionally, by comparing the two *in situ* traces, it has become apparent that during summer, the Cape Grim CH_4 record periodically drops below baseline. (Figure 1.) In this presentation, we consider the possible mechanisms for these excursions, by examining the meteorology and other trace species such as radon, ozone and a selection of species measured by the AGAGE instruments.

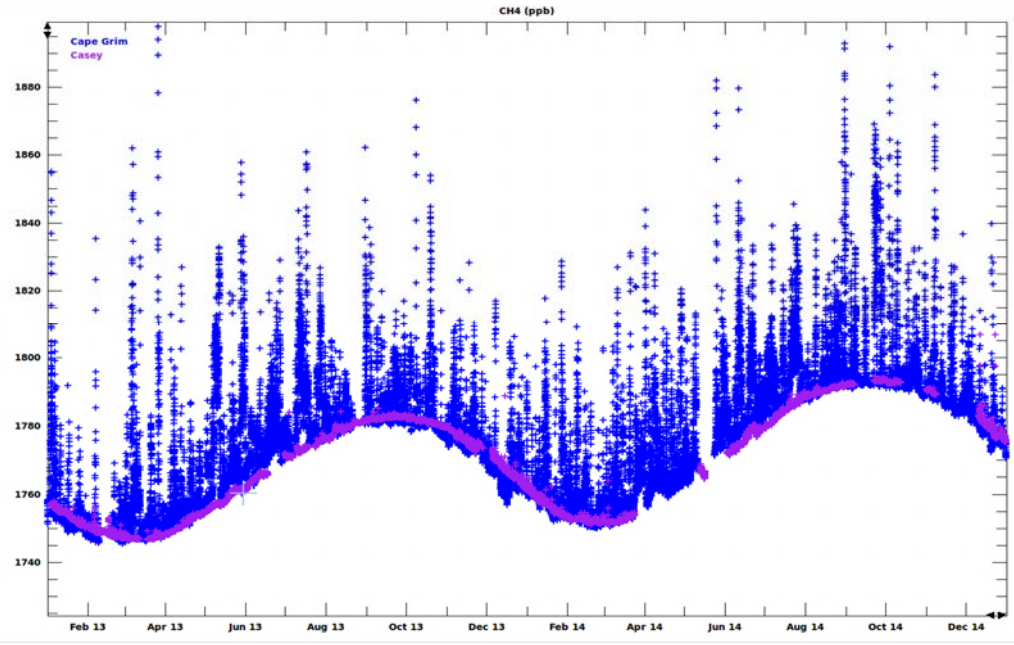


Figure 12. Hourly mean methane mixing ratios at Casey, Antarctica and Cape Grim, Tasmania for the period 2013 to 2014.

Total depletion of methane in cave atmospheres

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Abstract

High concentrations of CO_2 up to 20,000 ppm are reported for air in many limestone caves. Regular spot sampling and analysis of cave atmospheres reveals [Spötl *et al*., 2005] seasonal and diurnal CO_2 concentration and $\delta^{13}C\text{-}CO_2$ variation. To account for the relative contributions of different potential sources of CO_2 in caves to speleothem growth, in 2009 we conducted a 2 week pilot study at Jenolan Caves [Waring *et al*., 2009]. This study used an FTIR spectrometer and provided the first continuous cave record of $\delta^{13}C\text{-}CO_2$ and trace gas atmospheric composition showing a strong diurnal pattern. We discovered extreme carbon monoxide and methane depletion with a diurnal antithetic relationship to CO_2 and positive correlation with $\delta^{13}C\text{-}CO_2$, and hypothesised a microbiological sink for CH_4. A longer-term study was required to fully decipher the cave atmosphere and the cause of methane depletion.

Here we report the outcome of a continuous 3 year investigation of *in situ* CO_2, $\delta^{13}C\text{-}CO_2$ and CH_4 cave atmospheric composition using a Picarro G1101i isotopic CO_2 and CH_4 instrument. Difference between external and cave temperatures drives a convective bi-directional air flow through the cave system. In summer, convective air-flow driven by cooler cave air provides a slight cave suction to draw in soil gas. The converse winter convective air-flow is expels relatively warm cave air upwards through major cave openings and also through small fissures and overlying soil. The seasonal bias in cave convection accounts for strong seasonally biased cave CO_2, $\delta^{13}C\text{-}CO_2$ and CH_4 records. Total methane depletion to < 10 ppb in Chifley Cave in summer is caused by a two-step process of soil then cave methanotrophic bacterial CH_4 consumption.

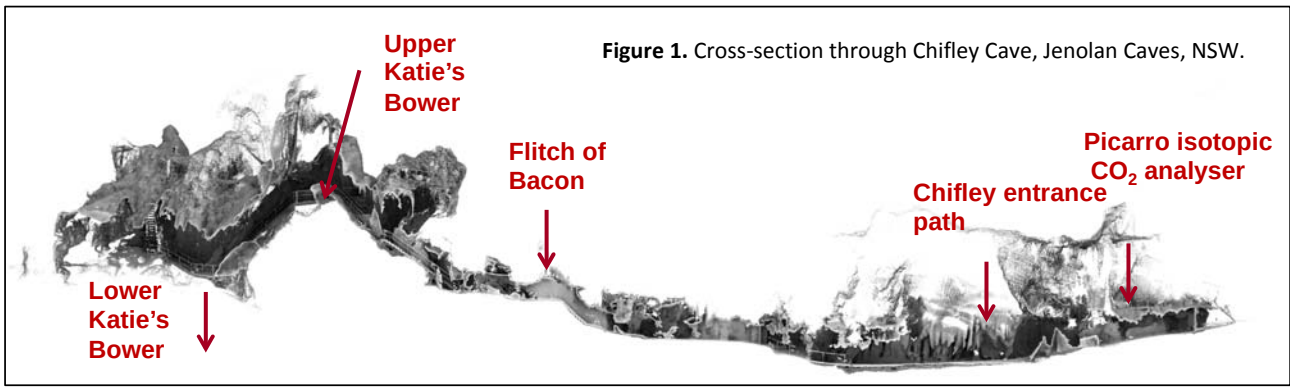


Figure 1. Cross-section through Chifley Cave, Jenolan Caves, NSW.

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An AirCore system for measuring vertical profiles and ground-based sources of greenhouse gases in Australia.

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Abstract

The idea of an AirCore [Karion *et al*., 2010] was first developed at the US National Oceanic and Atmospheric Administration in 2005. Inspired by an ice core, the AirCore method involves capturing a sample of a concentration profile and preserving the spatial variation for analysis at a later time. In order to minimise diffusion within the sample, a tube with diameter 0.25" or 0.125" and length around 100 m and has been widely used. After *in situ* collection of the sample, the AirCore is then analysed using a Picarro™ cavity ring-down spectrometer. Typically, CO_2, CH_4 and CO are analysed, though the method could be applied to other gases if suitable analysers are available.

The AirCore method is particularly effective for measuring vertical profiles. For this purpose, the AirCore is launched on a weather balloon, to altitudes of up to 30km. The AirCore is closed at one end, and due to the pressure difference between the tube and the atmosphere, largely evacuates at low pressures in the upper atmosphere. The AirCore then re-fills with increasing pressure upon descent. After recovery, the sample can be analysed on the ground, typically within a timeframe of a few hours. This has been used for the purpose of monitoring stratospheric circulation [Moore *et al*., 2014]. We have observed and assisted with campaigns in 2015 in Sodankylä, Finland, and Lauder, New Zealand to validate total column measurements from the Total Carbon Column Observing Network (TCCON).

The AirCore principle can also be applied to horizontal profiling for measurements of spatial or temporal variability of ground-level concentrations. In this case, air is pumped through an AirCore at constant mass flow rate. The flow can be halted at any time to preserve the sample held within the tubing. Previous work has used this technique for mapping plumes of gas leaks [Jackson *et al*., 2014] in order to locate and quantify these leaks.

In this presentation, we present results from the campaigns at Sodankylä and Lauder. In addition, we show the results of initial tests of a horizontal AirCore at a CSG leak simulation site, and comparisons with open-path FTIR data. We also discuss progress towards deployment of future profiling in Australia.

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Initial results from an AirCore campaign at the Lauder TCCON site

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Abstract

We will present an overview of, and initial results from, a series of AirCore [Karion *et al*., 2010] flights co-located with NIWA's Lauder atmospheric research station (45.034° S, 169.68° E, 370 m above sea level) in September 2015.

It is expected that three double AirCore flights will be carried out between 1st and 15th September 2015 at, or proximate to, the Lauder atmospheric research station. These flights will take in-situ measurements of CO_2 and CH_4 between the surface and up to 30 km.

These measurements can be compared with ground based measurements of CO_2 and CH_4 made using an in-situ Fourier transform spectrometer and flask samples as well as CO_2 using a Licor-7000 analyser.

The results will also be compared with Total Carbon Column Observing Network (TCCON) *[Wunch et al*., 2011] retrievals of the column averaged dry air mole fractions of CO_2 and CH_4 (XCO_2 and XCH_4) from solar absorption spectra measured at Lauder using two high resolution Fourier transform infrared (FTIR) spectrometers. In order to meaningfully compare these measurements a smoothing function must be applied following the method of [Rodgers and Connor, 2003]. These measurements can then be used to further validate and increase the robustness of the network wide calibrations factors that are applied to Xgas retrievals across the TCCON.

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Australian CO_2 'landscape' from TCCON and Lagrangian transport modelling

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Abstract

The Total Carbon Column Observing Network (TCCON) is a network dedicated to the accurate and precise measurements of two main anthropogenic greenhouse gases: Carbon dioxide (CO_2) and Methane (CH_4). TCCON also provides highly precise measurements of other atmospheric constituents including N_2O, HF, CO, H_2O, and HDO. The Wollongong TCCON site has been operational since 2008 and delivers publicly available data to CDIAC [ftp://tccon.ornl.gov/2014Public/wollongong01/, Griffith *et al*., 2014]. In this study, we present a method that exploits the precision of total column data from TCCON combined with the Stochastic Time-Inverted Lagrangian Transport Model (STILT), which leads to a 'picture' of the Australian CO_2 emissions, showing possible emission source regions that have the most influence on our measurements. We also show state-to-state contributions and differences.

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Response of terrestrial carbon cycle to climate variability and atmospheric CO_2: Numerical sensitivity experiments using the land-surface model CABLE v2

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Abstract

The inter-annual variation of the global carbon cycle is dominated by the terrestrial biosphere, therefore a better understanding of the major drivers and response mechanisms of the inter-annual variation terrestrial carbon cycle is important for improving the prediction of future evolution of global carbon cycle and therefore climate change. Using the Australian community land surface model (CABLE), we performed a number of numerical simulations to analyze the response of the terrestrial carbon cycle to the inter-annual variation of physical climate variables and surface CO_2 concentration. Our results show that increased CO_2 concentration has the largest positive effect on the trend of the land sink over the last 60 years, and the effect is strongest in Amazonian and African rainforest. Inter-annual variations of precipitation and surface air temperature have dominant effects on the inter-annual variation of the land carbon sink. The carbon sink of the regions that are most sensitive to precipitation on net ecosystem productivity (NEP) variability are ENSO-affected regions, such as semi-arid areas. We built a simple box model to help diagnose CABLE's behavior. Results show that changes in NPP have a much larger effect on observed variations in NEP than changes in soil turn-over rate. Furthermore, residence time, a quantity related to the capacity of carbon storage decreases over time. This results from the responses of soil respiration to the increased air temperature and atmospheric CO_2 concentration.

Designing optimal greenhouse gas observing networks for Australia

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Abstract

Atmospheric transport inversion is commonly used to infer greenhouse gas (GHG) flux estimates from concentration measurements. The optimal location of ground based observing stations that supply these measurements can be determined by network design. Here, we use a Lagrangian particle dispersion model (LPDM) in reverse mode together with a Bayesian inverse modelling framework to derive optimal GHG observing networks for Australia. This extends the network design for carbon dioxide (CO_2) performed by Ziehn *et al*. [2014] to also minimize the uncertainty on the flux estimates for methane (CH_4) and nitrous oxide (N_2O), both individually and in a combined network using multiple objectives. Optimal networks are generated by adding up to 5 new stations to the base network, which is defined as two existing stations, Cape Grim and Gunn Point, in southern and northern Australia respectively. The individual networks for CO_2, CH_4 and N_2O and the combined observing network show large similarities because the flux uncertainties for each GHG are dominated by regions of biologically productive land. There is little penalty, in terms of flux uncertainty reduction, for the combined network compared to individually designed networks. The location of the stations in the combined network is sensitive to variations in the assumed data uncertainty across locations. A simple assessment of economic costs has been included in our network design approach, considering both establishment and maintenance costs. Our results suggest that while site logistics change the optimal network, there is only a small impact on the flux uncertainty reductions achieved with increasing network size.

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