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incorporating the

Cape Grim Annual Science Meeting 2018

Abstracts

4-6 December 2018

hosted by

CSIRO Oceans and Atmosphere, Climate Science Centre

Priestley Lecture Theatre
Aspendale, Victoria, Australia



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

Citation

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Day 1: Tuesday, 4 December 2018

09:00	**Convenors**	**Welcome & general information on arrangements etc**
Chair	**Matt Woodhouse**	**Session 1 – Oral Presentations**
09:10	Scott Chambers	Radon-222 based method for evaluating chemical transport models under contrasting atmospheric mixing conditions
09:30	Alastair Williams	Long-term trends in atmospheric radon at Cape Point vs Cape Grim: a preliminary investigation
09:50	Paul Krummel	The 2018 Antarctic ozone hole
10:10	Matthew Tully	Trends in ozone hole metrics 2001-2018
10:30	**Morning Tea**	**Canteen**
Chair	**Alastair Williams**	**Session 2 – Oral Presentations**
11:00	Ashok Luhar	Top-down modelling of methane emissions in the Surat Basin (Queensland), a region of coal seam gas production
11:20	Maximilien Desservettaz	Aerosols composition and sources from a remote rural site in Queensland
11:40	Kathryn Emmerson	Modelling pollen source terms for Victoria
12:00	Jeremy Silver	The state of grass pollen modelling for thunderstorm asthma risk forecasting
12:20	**Lunch**	**Canteen**
Chair	**Kathryn Emmerson**	**Session 3 – Oral Presentations**
13:40	David Etheridge	Reconstructing Carbon-14 of carbon monoxide using Law Dome Ice to constrain long-term atmospheric hydroxyl variability
14:00	Robert Ryan	High daytime HONO mixing ratios retrieved from MAX-DOAS observations at Broadmeadows, Melbourne
14:20	Scott Kable	Atmospheric photochemistry: the forgotten role of the ground state
14:40	Paul Fraser	Chlorofluorocarbon (CFC-11, CFC-12, CFC-113) emissions in Australia: 1962-2017
15:00	**Afternoon Tea**	**Canteen**
Chair	**Max Desservettaz**	**Session 4 – Oral Presentations**
15:20	Rachel Law	Current status of the ACCESS-ESM1.5 submission to the Coupled Model Intercomparison Project 6 (CMIP6)
15:40	Tilo Ziehn	Assessment of land based carbon cycle reversibility with ACCESS-ESM
16:00	Ashok Luhar	Investigating tropospheric ozone bias in ACCESS-UKCA
16:20	Ian Galbally	The reconstruction of the historic record (1896-present) of tropospheric ozone
16:40	**End of Day 1**	

Day 2: Wednesday, 5 December 2018

Chair	**David Griffith**	**Session 5 – Oral Presentations**
09:00	Ann Stavert	The Macquarie Island [LoFlo2G] high-precision continuous atmospheric carbon dioxide record
09:20	Bradley Hall	One-step preparation of gravimetric CO_2-in-air standards
09:40	Nicholas Deutscher	An atmospheric assurance system for the near-shore Gippsland basin
10:00	Ian Enting	Climatic influence on 20th century CO_2
10:20	Peter Rayner	Testing estimates of terrestrial productivity using carbonyl sulfide
10:40	**Morning Tea**	**Canteen**
Chair	**Scott Chambers**	**Session 6 – Oral Presentations**
11:10	Paul Krummel *et al*.,	The Cape Grim GG-ODS sub-program review
11:50	Stephen Wilson	N_2O emission estimates from South Eastern Australia 1993 - 2016
12:10	Paul Krummel	Cape Grim CO_2-e passes 500 ppm – or has it?
12:30	Zoë Loh	Causes of short-term variability in the methane mixing ratio under baseline conditions at Cape Grim
12:50	Hinrich Schaefer	The role of ENSO in recent trends of growth rates in atmospheric methane
13:10	**Lunch**	**Canteen**

Chair	Robert Ryan	Session 7 – Oral Presentations
14:10	Meg Turner	Identifying methane hot spots in southeast Melbourne
14:30	Wenwen Huo	Sampling atmospheric C-14 and other atmospheric components on two different sites in Melbourne
14:50	Beata Bukosa	Simultaneous shipborne measurements of CO_2, CH_4 and CO and their application to improving greenhouse gas flux estimates in Australia
15:10	Christopher Caldow	Water-atmosphere greenhouse gas (CO_2, CH_4 and N_2O) exchange in two of the world's major rivers: the Elbe and the Murray
15:30	Nicholas Jones	Measurements of greenhouse gases in the Arctic from novel ground-based remote sensing instruments
Chair	**Paul Krummel**	**Session 8 – Poster Session**
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Rachel Corran		Atmospheric $\Delta^{14}CO_2$ Southern Hemisphere latitudinal gradient over recent decades
Maggie Corrigan		Hot ground state photochemistry of aldehydes in the atmosphere
Max Desservettaz		Evaluating global biomass burning emission inventories for CO in Australasia
Sonya Fiddes		What happens to the climate when coral reefs go extinct?
Roger Francey		The potential of consistent co-monitored CO_2 differences between primary baseline sites to better constrain the global carbon budget
Maheshinderjeet Garg		Air Toxic emissions estimation from coal and gas electricity generators using Australian energy distribution data
Jesse Greenslade		Top-down estimates of isoprene emissions in Australia inferred from OMI satellite data
Alan Griffiths		The implications of detector response time for radon observations at Cape Grim
Elise-Andrée Guérette		Towards a more comprehensive characterisation of biogenic volatile organic compounds in the greater Sydney region
Ruhi Humphries		Southern Ocean aerosols – a seasonal perspective from Macquarie Island
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Neil Page		Ship-based constraints on the Southern Ocean mercury cycle
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Hinrich Schaefer		Where is the missing CO_2? A regional multi-species approach to trace the fate of atmospheric CO_2 in Fiordland National Park, New Zealand
Hinrich Schaefer		Developing a high-precision measurement technique for nitrous oxide isotopomers in air
Jeremy Silver		Modelling CO_2 over south east Australia and comparison with Cape Grim data
Jack Simmons		Aerosol properties across the southern polar front in summer
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Cathy Trudinger		Model-data fusion framework to constrain Australia's terrestrial carbon and water budgets
Yohanna Villabos Cortes		Regional inverse modelling for the estimation of CO_2 fluxes in Australia using satellite observations from the Orbiting Carbon Observatory-2 (OCO-2)
Imogen Wadlow		Evaluation of aerosol representation by ACCESS-UKCA in the Southern Ocean
Blair Welsh		Vibrationally excited products of roaming reactions in the atmosphere as a novel source of hydroxyl radicals
Matthew Woodhouse		Increasing hydrogen use: effects on global atmospheric chemistry
18:00		**End Day 2**
18:30	**Dinner**	**MordyHQ (McNaughton Room) – 528 Main Street, Mordialloc**

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09:20	Sean Hartery	Measurements of sea spray aerosol in the Southern Ocean
09:40	John Ivey	Detecting non-sea salt, biogenic/ anthropogenic atmospheric aerosol contributions and mixing above the Great Barrier Reef, using optical laser particle sizing
10:00	Steven Utembe	Cloud brightening studies over the Great Barrier Reef using WRF-Chem
10:20	**Morning Tea**	**Canteen**
Chair	**Christopher Caldow**	**Session 10 – Oral Presentations**
10:50	Hilton Swan	Identifying coral reef-derived atmospheric dimethylsulfide
11:10	Sarah Lawson	Atmospheric DMS, methanethiol and acetone over the South West Pacific during the SOAP voyage
11:30	Clare Paton-Walsh	COALA-JOEYS – Characterising Organic Aerosol Loading in Australia – Joint Organic Emissions Year-long Study
11:50	Fabienne Reisen	Performance and deployment of low cost sensor SMOG units
12:10	John Monash Science School students	Using Cape Grim data in a Year 11 Programming Course
13:10	**Lunch**	**Canteen – End of meeting, safe travels, we hope you enjoyed Aspendale**

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Radon-222 based method for evaluating chemical transport models under contrasting atmospheric mixing conditions

S. D. Chambers[1*], E.-A. Guérette[2], K. Monk[3], A. D. Griffiths[1], Y. Zhang[4], H. Duc[3], M. E. Cope[5], K. M. Emmerson[5], L. T. Chang[3], J. D. Silver[6], S. R. Utembe[6], J. Crawford[1] and A. G. Williams[1]

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Abstract

We introduce a novel technique to derive statistically-robust benchmarking data for the evaluation of chemical transport models (CTMs) in urban regions under contrasting atmospheric mixing conditions. The technique employs atmospheric class-typing, using near-surface radon measurements to estimate the mean nocturnal mixing state from which mixing conditions of the following day are inferred based on an assumption of short-term atmospheric persistence [Chambers *et al*., 2018]. Grouping of the 24-hour mixing class-types can be adjusted based on the length of the available dataset (i.e., the required number of days per category), or the desired range of in-class variability. Calculating hourly distributions of benchmarking observations across diurnal mixing class composites helps to: (i) bridge the gap between scales of simulation and observation, (ii) clearly represent the variability resulting from spatial and temporal heterogeneity of sources and meteorology rather than being confused by it, and (iii) provide a means by which to group results over whole diurnal cycles that separates 'natural complicating factors' (e.g., synoptic non-stationarity, rainfall, mesoscale motions, periods of extreme stability, etc.) from parameterisation problems, or model-to-model differences. Seven models are evaluated over a 1-month period in autumn 2012 at Westmead, NSW, as part of the Sydney Particle Study II. For all models, meteorological model skill varied both across the diurnal cycle and with changing atmospheric mixing class. Model skill regarding the simulated magnitude and duration of 'rush hour' peak primary pollution events (e.g., carbon monoxide (CO); Figure 1) varied strongly as a function of atmospheric mixing class. Overall, the mean bias and its standard deviation of simulated primary pollutant concentrations (e.g., nitric oxide (NO), CO; Figure 2) were the most sensitive to changes in atmospheric mixing class. Typically, model skill was the poorest at times when public exposure was the highest, which has important implications for using chemical transport models to assess potential health risks in new and rapidly evolving urban regions, and also for prioritizing areas of model improvement for future applications.

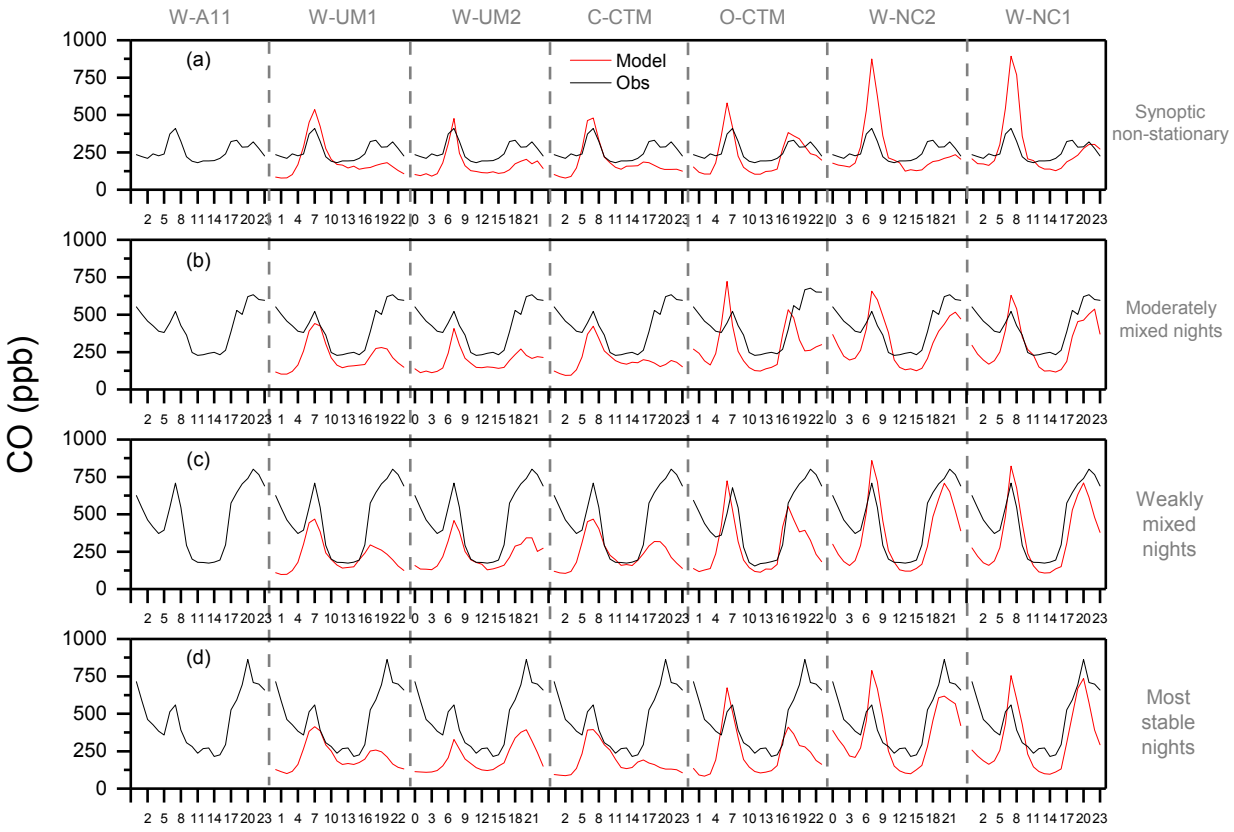


Figure 1. Diurnal composite simulated and observed 5 m agl., CO concentration for each of the seven models and four radon-based atmospheric mixing categories at Westmead during SPS-II.

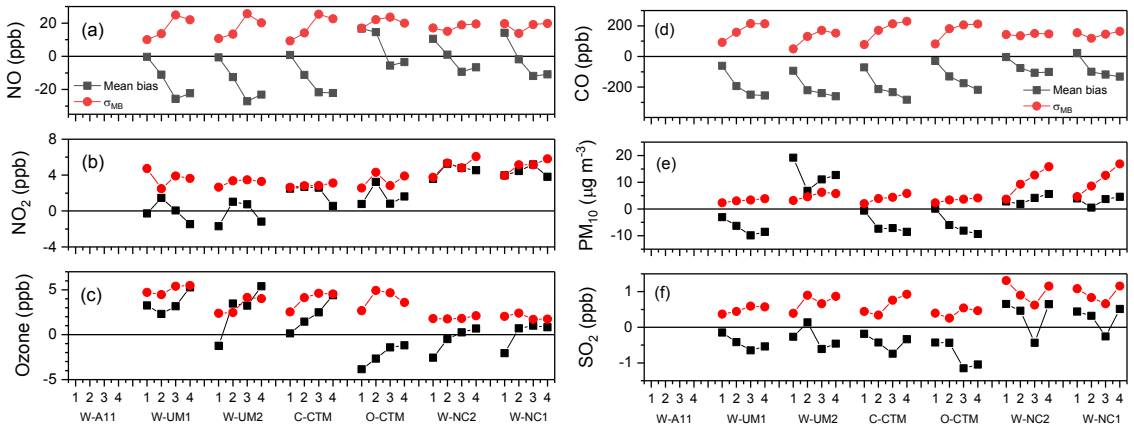


Figure 2. Mean bias and its standard deviation for all seven models and four atmospheric mixing states for (a) NO, (b) NO_2, (c) O_3, (d) CO, (e) PM_{10}, and (f) SO_2.

References

Chambers, S. D., A. Podstawczyńska, W. Pawlak, K. Fortuniak, A. G. Williams and A. D. Griffiths, Characterising the state of the urban surface layer using Radon-222*, J. Geophys. Res. – Atmos., in press, December 2018*.

Long-term trends in atmospheric radon at Cape Point vs Cape Grim: a preliminary investigation

R. Botha[1], A. G. Williams[2*], C. Labuschagne[3], S. D. Chambers[2], J. Crawford[2] and S. K. Nolan[4]

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Abstract

A recent study of fifteen years (1999 to 2013) of continuous hourly atmospheric radon observations at Cape Point Station in South Africa [Botha *et al*., 2018] revealed a strong seasonal cycle, with maxima during the winter months when air masses arriving at Cape Point from over the African continental surface are more frequently observed, and minima during the summer months when an oceanic fetch is predominant. Furthermore, a slow decline in the higher radon percentiles (75^{th} and 95^{th}) for the winter and spring seasons was found over the 15-year period, with most of the change occurring in the first nine years (1999-2007). This observed inter-annual decline appears to be associated with changes in the frequency of air masses having originated from over the African continental surfaces, and no significant trend was found in the lower radon percentiles associated with oceanic air masses. It was suggested that the general decrease of atmospheric radon associated with continental air-masses at Cape Point could be attributed to changing meteorological conditions or soil moisture availability, possibly driven by climate change.

Cape Grim is in a similar geographical position to Cape Point, with the Southern Ocean directly to the south and a large semi-arid land mass to the north. As such, trace gas observations at both stations are sensitive to long-term changes in hemispheric flow patterns and the availability of terrestrial soil moisture. In this presentation, the results of Botha *et al*. [2018] will be summarised and then compared with a preliminary analysis of atmospheric radon concentrations covering the same period at Cape Grim.

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The 2018 Antarctic ozone hole

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Abstract

The 2018 ozone hole developed around mid-August and rose sharply to reach a peak size in mid-September. The 2018 season has been characterised by very stable and cold stratospheric conditions which have resulted in a persistent Antarctic ozone hole which remained large in areal extent and low ozone minima from September through to the second week of November when the first major warming event for this year occurred. In terms of the metrics used to gauge the severity of any particular ozone hole, this year's hole ranks between 12-14th out of 39 years of available satellite data for most of the metrics.

The development and recovery of the 2018 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 2018 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 11% since their peak around 2000, or have fallen by approximately 21% 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.

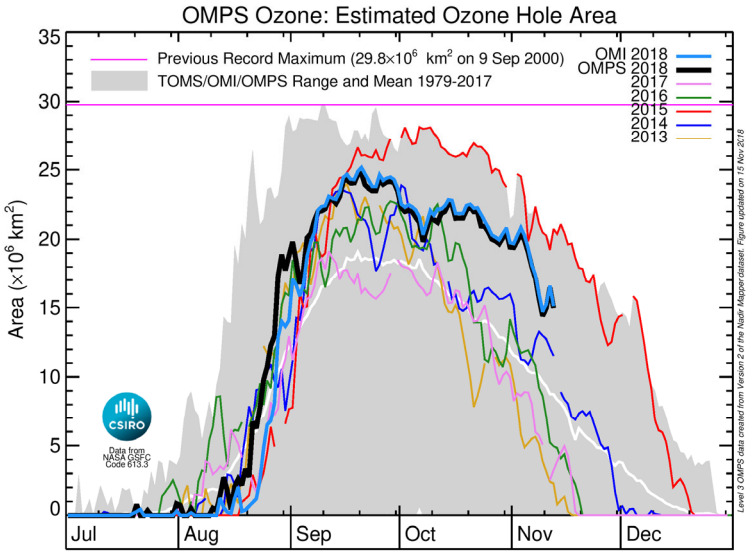


Figure 1. The Antarctic ozone hole area as of 12 November 2018, showing the relatively large areal extent and persistence of the ozone hole this year.

Trends in ozone hole metrics 2001-2018

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Abstract

We report the linear trends over the years 2001-2018 of a number of standard metrics used to describe the severity of the Antarctic Ozone Hole, both with and without a simple adjustment to account for meteorological variability. The trends are compared to those from the years 1979-2001. All metrics considered showed a trend over the period 2001-2017 towards reduced ozone depletion, at significance levels ranging from 2.4 to 3.9 standard errors of the trend after the adjustment has been performed. The adjustment for meteorological variability has little effect on the values of the trends but does substantially reduce the scatter and therefore the uncertainty of the trends. Updated results extended to include the 2018 Antarctic Ozone Hole will also be presented.

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Top-down modelling of methane emissions in the Surat Basin (Queensland), a region of coal seam gas production

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Abstract

A multi-year study of monitoring of methane (CH_4) within the Surat Basin, Queensland, was undertaken as part of CSIRO's Gas Industry Social and Environmental Research Alliance (GISERA, https://gisera.csiro.au). The Surat Basin, with a selected domain size of 350 km x 350 km, is a significant region of coal seam gas (CSG), agricultural and coal mining activities. The primary aim of the study was to quantify CH_4 emissions across the region using 'top-down' or inverse modelling through the use of *in situ* observations of atmospheric CH_4 concentrations from two monitoring stations.

The monitoring stations, Ironbark and Burncluith, were established 80 km apart on either side of existing and future-projected CSG activity in locations where predictive modelling suggested would optimise the size and frequency of the regional CSG methane emission signals. Continuous measurements of CH_4 and carbon dioxide (and carbon monoxide at Burncluith), together with meteorology, were made at the two sites for about 3 years with an overlapping period of 1.5 years.

A gridded 'bottom-up' methane emission inventory for the region was compiled. When used in CSIRO's regional transport model TAPM, it yielded a lower frequency and magnitude of concentration peaks than measured. Possible reasons include weaker/missing sources in the inventory, particularly near the monitors, and errors in the modelled transport.

A novel and efficient inverse methodology was devised and applied to estimate regional CH_4 emission distribution in the Surat Basin. It combines a Bayesian inference approach, a high-resolution backward-in-time formulation of the regional transport model TAPM, and a posterior probability density function sampling scheme. It uses hourly CH_4 concentration timeseries from multiple stations and options for prior (or initial) emission distribution across the domain with specified uncertainties. The inverse modelling results for the Surat Basin indicate that even without an informative prior, the measured concentrations are able to constrain the methane emissions realistically. The use of the bottom-up emission inventory as a prior leads to the best emission estimates (as judged from their ability to describe the CH_4 concentration data) and gives a total emission for the full domain that is slightly lower than the inventory total. The inferred emissions in a smaller subdomain covering areas around the two stations are 30% higher than the inventory emissions. These areas are dominated by CSG and agricultural emissions. There are potentially other sources active in this sub-domain that are not accounted for in the inventory. It is also apparent that having only two monitoring stations across the large domain that contains many methane sources is a limitation for some parts of the domain.

The work presented here is the first application in Australia of a state-of-the-art inverse technique for the estimation of methane emissions at regional scale using hourly mean data and hourly modelled (backward) transport. It is capable of incorporating model and measurement uncertainties, as well as non-Gaussian distributions of the prior and uncertainties. The results suggest that overall our inverse methodology works well in providing an independent measurement-based estimate of the emissions from multiple, concurrent sources.

Aerosols composition and sources from a remote rural site in Queensland

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Abstract

From August to October 2017, an intensive study of atmospheric composition was undertaken at a rural site in Queensland as part of the GISERA study of air Quality and Hydraulic Fracturing in the Surat Basin. A component of this study included the measurement of aerosol concentration and composition using two methods: 1) on-line measurements using a Palas FIDAS 200s aerosol spectrometer, and 2) Sampling of PM_{10} onto filters by Low Volume Sampler-Gravimetric Method with subsequent analysis of elemental composition, major soluble ions and anhydrous sugars such as levoglucosan. Source apportionment analysis using the composition data via Positive Matrix Factorisation determined that eight factors contributed to PM10 aerosol during the study: Soil, secondary ammonium sulfates, secondary nitrate aged sea salt, non-wood biomass burning, fresh sea salt, wood smoke, glucose, and primary bioaerosols. While the glucose, soil and bioaerosol factors were attributed to local sources such as road dust and biological activity, other factors were related to more regional sources combined with atmospheric transformation and transport. Early results from the analysis of aerosols composition and sources, and characterisation of transport processes using back trajectory analysis will be presented providing important information on the factors influencing aerosols in the background atmosphere for a rural Australian region.

Modelling pollen source terms for Victoria

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Abstract

The Victorian Department of Health and Human Services have commissioned a pollen forecasting system in response to the Thunderstorm Asthma event of November 2016 that killed 10 people. In little over a year, we have developed a pollen emissions module for the CSIRO Chemical Transport Model (C-CTM) the results of which are being tested against eight pollen observation sites in Victoria.

This talk will highlight how the C-CTM has been adapted to carry pollen particles, and the ensemble of pollen emissions methodologies we have developed and tested. These methodologies include different descriptors for the pollen season, from a simple Gaussian representation, to using satellite data to infer flowering times inferred by the level of 'greenness' observed.

The best pollen emission methodology is being installed at the Bureau of Meteorology to be run in forecast mode.

The state of grass pollen modelling for thunderstorm asthma risk forecasting

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Abstract

In response to the thunderstorm asthma episode of November 2016, the Victorian Department of Health and Human Services commissioned the Bureau of Meteorology (in collaboration with the CSIRO and university partners) to develop and roll out forecasting tools to predict the risk of such events in future. Allergic asthma in south-eastern Australia is, for a large fraction of those affected, triggered by grass pollen, and it is thought that epidemic asthma in this region is associated with elevated grass pollen concentrations.

In 2017, a statistical model for daily grass pollen counts was developed and run for real-time forecasts. This model was trained with pollen counts from Parkville, Melbourne, and incorporated weather data (temperature, humidity, wind direction), land-use and satellite-derived land-surface indices. This model showed adequate skill compared with measurements at six of the eight pollen counting sites. In 2018, this model has been updated using measurements from 2017, representing a dramatic increase in spatial coverage.

In parallel with this, the CSIRO chemical transport model (C-CTM) has been adapted to emit and transport grass pollen particles. The 2017 grass measurements have been used to select from an ensemble of grass pollen emission schemes, all of which account for variation in space and time but vary in their assumptions. The pollen C-CTM is running routinely at the Bureau of Meteorology for grass pollen forecasting.

In this talk, we will present further details about development, and summarise the pre-season evaluation as well as mid-season real-time results.

Reconstructing carbon-14 of carbon monoxide using Law Dome ice to constrain long-term atmospheric hydroxyl variability

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Abstract

The changes in atmospheric composition over the Anthropocene are quantified mainly from measurements of air inclusions in polar ice. The unique glaciological characteristics of Law Dome in the Australian Antarctic Territory have been key to this research, providing continuous, highly resolved and precise concentrations of all the main greenhouse gases and ozone depleting gases and some of their isotopic ratios. The natural and anthropogenic emissions inferred from these records guide model future predictions and inform policy decisions. However, the past rate of removal from the atmosphere for many gases has been mainly assumed, which limits the knowledge of past emissions and our ability to predict future climate change or stratospheric ozone levels under a given emissions scenario.

This ambitious project plans to further explore Law Dome's treasure of atmospheric trace gas information by quantifying changes in the oxidising capacity of the atmosphere over the industrial period. We will measure the carbon-14 isotope of carbon monoxide (^{14}CO), an integrating proxy of the concentrations of the hydroxyl radical, the main atmospheric oxidant. Significant scientific and technical challenges will be addressed by using novel ice drilling, air extraction and analytical techniques developed by Australian and US collaborators over the past two decades. The in situ production of ^{14}CO will be minimised by the enormous snow accumulation rate at DE08 on the east side of Law Dome and by extracting air as soon as the ice cores are brought to the surface. Even with ultra-small sample analysis by accelerator mass spectrometry, hundreds of kg of ice will still be required for each ^{14}CO measurement.

A team of about ten people from two nations and six research groups will converge on DE08 over the 2018-19 summer. The OH record inferred from the ^{14}CO measurements will be used with atmospheric model simulations to reveal how OH is affected by emissions and environmental changes such as warming.

High daytime HONO mixing ratios retrieved from MAX-DOAS observations at Broadmeadows, Melbourne

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Abstract

The atmosphere's self-cleansing capability is chiefly determined by the hydroxyl radical (OH), which reacts rapidly with gaseous emissions from the Earth's surface. Through rapid daytime photolysis, nitrous acid (HONO) is a potentially significant source of OH. However, the extent of the significance is highly uncertain because several observation campaigns around the world have revealed the presence of a strong daytime HONO source which cannot be reconciled with the known photochemical mechanisms. Using the multi-axis differential optical absorption spectroscopy (MAX-DOAS) method, we have measured vertical distributions of HONO, along with other UV-vis absorbers such as nitrogen dioxide and formaldehyde, from December 2016 to June 2018 at the Bureau of Meteorology site in Broadmeadows, northern Melbourne. High daytime HONO mixing ratios up to 400 ppt were observed especially in summer and autumn, which implied a midday-maximum HONO production rate 1 $ppb.h^{-1}$ above the expected photostationary state. Furthermore, the average midday HONO mixing ratio implied a local OH source up to four times stronger than from ozone photolysis alone. The strong vertical gradient observed, with HONO present predominantly close to the ground, combined with a dependence of HONO mixing ratio on modelled soil-moisture suggests that reactive soil nitrogen emissions may be contributing to the observed HONO.

Atmospheric photochemistry: the forgotten role of the ground state

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Abstract

Absorption of sunlight and subsequent photochemistry of molecules in the atmosphere drives the entire atmospheric oxidation pathway. Consequently, atmospheric photochemical products, pathways and quantum yields have been investigated, experimentally and theoretically, for more than half a century.

A scan of the literature and databases of atmospheric photochemistry reveals that almost all mechanisms are attributed to reaction on an excited singlet or triplet state of a molecule. However, notable exceptions exist where reactions proceed after the molecule returns to the ground electronic state, e. g. HCHO produces H_2 + CO on the ground state following excitation in the near-ultraviolet.

Experimental studies often implicate the involvement of both singlet and triplet states. Typically, the singlet character is attributed to reaction on the lowest excited singlet state, S_1. Recent experiments in our labs instead determine that the relevant singlet state is frequently the ground state, S_0. The S_0 potential energy surface, at energies relevant to photolysis, is complex. A large number of chemical pathways are available, including radical production, formation of closed shell molecular photofragments, and isomerisation into other chemical species.

In this talk, I will show experimental evidence of multiple competing pathways on the ground state of selected carbonyl compounds containing two to five carbon atoms. In addition to the well-known Norrish Types I and II reactions, we have identified the following active pathways:

- Concerted triple fragmentation into CO, H_2 plus an alkene;
- Production of H_2 from all carbonyls;
- Dissociation into ketenoids (ketene, methylketene, dimethylketene, etc);
- Photoisomerisation to ketenoids;
- Photoisomerisation to enols;
- Production of alkyne and allene products.

The results include experiments performed in a bulb, up to 1 atm pressure, and in a jet-cooled molecular beam. The bulb experiments are used to identify final, stable products and to determine quantitative wavelength- and pressure-dependent quantum yields. These are complemented by molecular beam experiments that provide insight into the reaction mechanisms if they are controversial or ambiguous. The beam ensures a collision-free environment and provides a guarantee of only unimolecular processes. Interpretation of the beam results can also be used to determine the mechanism when there are completing chemical pathways to the same products.

Our conclusion is that carbonyl photochemistry is a rich source of atmospheric organic compounds, many of which are not present in current models. It remains to be seen whether these new pathways have a significant impact in our understanding of various aspects of tropospheric chemistry.

Chlorofluorocarbon (CFC-11, CFC-12, CFC-113) emissions in Australia: 1962-2017

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Abstract

Chlorofluorocarbons (CFCs) have been used over the past 70 years as refrigerants, aerosol propellants, foam blowing agents and solvents. CFCs used in aerosol cans and as solvents are released to the atmosphere within a few years of production, while CFCs in refrigeration and air conditioning equipment and in foams (collectively called 'banks') are released over longer time scales, up to decades. CFCs released to the atmosphere since the mid-20th century are responsible for about 40% of stratospheric ozone depletion and nearly 10% of climate change driven by long-lived greenhouse gases [Molina and Rowland, 1974; Ramanathan, 1975; Carpenter and Reimann, 2014; Myhre and Schindell, 2014].

The global production and consumption of chlorofluorocarbons (CFCs), which currently supply 60% of ozone depleting chlorine transported from the troposphere to the stratosphere [Rigby *et al*., 2014], were phased-out under the international obligations of the Montreal Protocol in 2010 (UNEP, 2012). Under the same Protocol, manufacture and importation of CFCs in and into Australia were effectively banned at the end of 1995 (95% phase-out), well ahead of the requirements of the Montreal Protocol for developed countries at that time (50% phase-out by 2000; Environment Australia, 2001).

Global emissions of CFCs peaked in 1987-1988 at nearly 1100 Gg (k tonnes) per year, declining to about 100 Gg per year in 2016 [Rigby *et al*., 2014; Engel and Rigby, 2018]. Emissions of CFC-12 (CCl_2F_2) have declined approximately monotonically, as expected under the Montreal Protocol, whereas emissions of CFC-11 (CCl_3F) and CFC-113 (CCl_2FCClF_2) stopped declining by the early 2000s [Rigby *et al*., 2014] and there has been an unexpected and persistent increase in the global CFC-11 emissions since about 2010, due largely to unreported new production from East Asia [Montzka *et al*., 2018; Engel and Rigby, 2018]. If this increase in global CFC-11 emissions were to continue, it could delay recovery of Antarctic ozone depletion by up to 20 years [WMO, 2018].

This finding has encouraged a new focus on the status of current CFC-11 emissions, and also the other CFCs, at global and national levels, in both developed and developing countries.

Observed trends in atmospheric abundances and past production estimates of CFCs have been used to gain 'top down' insights into CFC bank sizes and their roles as global emission sources for the CFCs [Daniel *et al*., 2007]. In this paper we derive total Australian emissions of CFCs from 1962 to 2017, using atmospheric observations made at Cape Grim, Tasmania (1976-2018), and Australian CFC consumption from production, import and export data, compiled by the Australian government and industry. Comparison of total emissions and consumption data enable estimates of CFC 'banks' in Australia and current emissions are discussed in terms of these legacy 'banks' of CFCs.

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Current status of the ACCESS-ESM1.5 submission to the Coupled Model Intercomparison Project 6 (CMIP6)

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Abstract

CSIRO and collaborators are preparing two submissions for CMIP6 using different versions of the Australian Community Climate and Earth System Simulator (ACCESS). Here we focus on one of those submissions, namely ACCESS-ESM1.5, which will be the first Australian submission to include an interactive carbon cycle. ACCESS-ESM1.5 is an updated version of ACCESS-ESM1 (Law et al., 2017), with updates including both code and parameter changes. These will be described and the impact of the changes on a control simulation will be demonstrated. CMIP6 comprises core experiments that all models are expected to perform, and more than twenty optional model intercomparison projects (MIPs) that build on the core experiments and focus on different science questions. The ACCESS-ESM1.5 submission will target three MIPs initially: ScenarioMIP which includes simulations to 2100 under different forcing scenarios; C4MIP which looks at climate-carbon cycle feedback questions; and CDRMIP which explores some idealised experiments addressing carbon dioxide removal. We will discuss a selection of the proposed experiments and our progress towards running them.

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Assessment of land based carbon cycle reversibility with ACCESS-ESM

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Abstract

Future levels of climate change depend not only on carbon emissions but also on carbon uptake by the land and the ocean. Here we are using the Earth System Model (ESM1) version of the Australian Community Climate and Earth System Simulator (ACCESS) to explore the potential and impact of removing CO_2 from the atmosphere through the climate and carbon cycle reversibility experiment. This experiment builds on the standard Coupled Model Intercomparison Project (CMIP) experiment, increasing CO_2 at 1% per year until $4xCO_2$ is reached. The atmospheric CO_2 levels are then decreased at the same rate which brings the CO_2 back to pre-industrial levels. We then continue to run the model with constant CO_2 for another 350 years. Our analysis focuses on the response of the land carbon cycle. We find that carbon stores are largely reversible at the global scale over the time scale of changing CO_2. However, carbon stores continue to decrease after CO_2 returns to its initial value, and the land loses another 60 PgC with the largest change in the tropics (overshoot). It takes about 300 years beyond the period of changing CO_2 for the carbon stores to recover. Interestingly, we saw strong regional variations in the strength of the land response to changing CO_2. Australia showed the largest increase/decrease in biomass carbon (about 40%) and the largest variability in productivity which was strongly correlated with rainfall. Assessing the large differences in the regional response are crucial for better understanding the impacts on, for example, ecosystem services.

Investigating tropospheric ozone bias in ACCESS-UKCA

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Abstract

The UK chemistry and aerosol model [UKCA; Abraham *et al*., 2012; O'Connor *et al*., 2014; http://www.ukca.ac.uk) is the atmospheric composition component of the Australian ACCESS global climate model [Bi *et al*., 2013; https://www.csiro.au/en/Research/OandA/Areas/Assessing-our-climate/CAWCR/ACCESS]. It includes both tropospheric and stratospheric chemistry and is used for computing the radiative feedbacks of ozone and methane within the coupled climate system and for other modelling purposes. Here we use ACCESS-UKCA (at UMvn8.4) in atmosphere-only mode with sea-surface temperatures prescribed (Woodhouse et al., 2015). The model simulations are conducted at 1.875 degrees x 1.25 degrees resolution, with 85 vertical levels extending to 85 km in height. The model uses monthly-varying anthropogenic and natural emissions, including aircraft and lightening NOx emissions and biogenic emissions of isoprene. We run ACCESS-UKCA in nudged mode by assimilating ECMWF's ERA-Interim reanalyses. We investigate the ability of the model to simulate tropospheric ozone observations from global in-situ and ozone-sonde measurements, and the various factors and processes responsible for any biases in the modelled ozone compared to the data.

Comparison of the modelled tropospheric ozone with measurements shows that ACCESS-UKCA significantly underestimates the observed ozone, particularly in the mid to high latitudes over the Southern Hemisphere. In order to investigate the reasons for this bias, we examine the various terms in the tropospheric ozone budget in the model, namely the chemical production and loss, dry deposition to the surface which includes a new scheme for deposition to the ocean (Luhar et al., 2018), stratosphere-to-troposphere exchange (STE), and emissions of ozone precursors, particularly oxides of nitrogen (NO_x) due to lightning. We analyse the response of the simulated tropospheric ozone and other species (e.g. carbon monoxide and methane) to variations in the above budget terms, and examine their impact on the ozone bias, and its burden and budget. Finally, we comment on the relative importance of the main factors causing the ozone bias.

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The reconstruction of the historic record (1896-present) of tropospheric ozone

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Abstract

The Tropospheric Ozone Assessment Report (TOAR), is an Activity of the International Global Atmospheric Chemistry Project (IGAC), (see http://www.igacproject.org/TOAR) that commenced in February 2015 and will complete in early 2019. 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. Key basic questions are: 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?

The assessment report is being published as a series of papers in the peer-reviewed journal, *Elementa – Science of the Anthropocene*. Papers published so far are available through a Special Feature of *Elementa*, see references. Other papers are in the pipeline.

As a reactive gas ozone does not, or is highly unlikely to, persist in bubbles in ice cores or in cylinders. Hence no current measurements of past concentrations are possible, and the historic record can only be constructed from historic measurements which have substantial uncertainties due to both bias and imprecision. The historic surface ozone record 1896-1975 and tropospheric ozone record 1933-present have been constructed from measurements that pass the four criteria: (a) instrumentation whose ozone response can be traced to modern tropospheric ozone measurement standards, (b) samples taken when there is low probability of chemical interference (c) sampling locations, heights and times when atmospheric mixing minimises vertical gradients of ozone in the planetary boundary layer above and around the measurement location and (d) the laugh test.

Two of the commonly used early data sets do not pass all four criteria. These are the early measurements (a) with the Schönbein filter paper technique and (b) the potassium iodide-arsenite technique used at Montsouris for 1876-1910 The use of these data sets for trend analyses is not recommended.

In total, 60 acceptable sets of surface ozone measurements are currently identified, commencing in Europe in 1896, Greenland in 1932 and globally by the late 1950's all measured under conditions likely to give ozone mole fractions similar to those in the planetary boundary layer. Similarly there are 7 sets of observations of ozone in the free troposphere that cover 1933-1955.

These time series are matched with modern measurements from the Tropospheric Ozone Assessment Report (TOAR) Ozone Database and used to examine changes between the historic and modern observations. These historic ozone levels are higher than previously accepted for surface ozone in the late 19th early 20th Century. This historic surface ozone analysis provides a new test for historical reconstructions by Climate-Chemistry models.

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TOAR Database of Surface Ozone Metrics

TOAR has produced a relational database of global surface ozone observations, and generated a comprehensive suite of ozone metrics products including standard statistics, health and vegetation impact metrics, and trend information. The metrics are made available through a common data portal and a web interface as described by Schultz *et al*. [2017] in the TOAR Special Feature described above. Pre-compiled surface ozone metrics data sets can be downloaded from PANGAEA.

The Macquarie Island [LoFlo2G] high-precision continuous atmospheric carbon dioxide record

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Abstract

The Southern Ocean (south of 30°S) is a key global scale sink of carbon dioxide (CO_2). However, the isolated and inhospitable nature of this environment has restricted the number of oceanic and atmospheric CO_2 measurements in this region. This has limited the scientific community's ability to investigate trends and seasonal variability of the sink. Compared to regions further north, the near-absence of terrestrial CO_2 exchange and strong large-scale zonal mixing demands unusual inter-site measurement precision to help distinguish the presence of mid-to-high latitude ocean exchange from large CO_2 fluxes transported southwards in the atmosphere.

Here we describe a continuous, *in situ*, ultra-high-precision, Southern Ocean region CO_2 record, which ran at Macquarie Island (54° 37' S, 158° 52' E) from 2005–2016 using a 'LoFlo2' instrument, along with its calibration strategy, uncertainty analysis and baseline filtering procedures. Uncertainty estimates calculated for minute and hourly frequency data range from 0.01 to 0.05 μmol mol^{-1} depending on averaging period and application. Higher precisions are applicable when comparing MQA LoFlo measurements to those of similar instruments on the same internal laboratory calibration scale and more uncertain values are applicable when comparing to other networks.

Baseline selection is designed to remove measurements that are influenced by local, Macquarie Island, CO_2 sources, with effective removal achieved using a within-minute CO_2 standard deviation metric. Additionally, measurements that are influenced by CO_2 fluxes from Australia or other Southern Hemisphere land masses are effectively removed using model-simulated radon concentration. A comparison with flask records of atmospheric CO_2 at Macquarie Island highlights the limitation of the flask record (due to corrections for storage time and limited temporal coverage) when compared to the new high-precision, continuous record; the new record shows much less noisy seasonal variations than the flask record. As such this new record is ideal for improving our understanding of the spatial and temporal variability of the Southern Ocean CO_2 flux particularly when combined with data from similar instruments at other Southern Hemispheric locations.

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One-step preparation of gravimetric CO_2-in-air standards

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Abstract

The NOAA Global Monitoring Division maintains the mole fraction scale for CO_2 used by the WMO Global Atmosphere Watch program. That scale is defined by 15 primary standards (modified natural air) value-assigned using the NOAA CO_2 manometer. We have recently identified a potential bias in the manometric measurement. In order to better understand this bias and move towards a scale revision, we have prepared CO_2 standards using an independent method. Recent advances in our understanding of the behaviour of CO_2 in aluminum cylinders (drift) and experiments to characterize the adsorption of pure CO_2 to stainless steel surfaces enable the preparation of gravimetric CO_2-in-air standards with relatively low uncertainty. This work supports our efforts to maintain the WMO CO_2 scale.

An atmospheric assurance system for the near-shore Gippsland basin

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Abstract

Carbon Capture and Storage (CCS) has been suggested as a means of storing greenhouse gases that would otherwise be destined to be in the atmosphere. Given that the ultimate goal is to stop these gases from being present in the atmosphere, where they would contribute to the enhanced greenhouse effect and subsequent climate change, we need to ensure that they remain in storage. This requires atmospheric measurement, monitoring and verification (MMV).

In Australia, a previous demonstration project occurred in the Otway basin. A second CCS demonstration project is planned, using the near-shore Gippsland basin. CO_2 injection is planned within regions off the coast of Gippsland, presenting challenges for atmospheric MMV.

In this project, we are designing and deploying a range of techniques to establish a measurement and modelling network to provide atmospheric MMV as part of the Gipnet project, which will additionally provide seismic and marine MMV. The atmospheric assurance system includes a network of atmospheric sensors: an in situ FTIR, several Picarro cavity ringdown spectrometers, and a horizontal open-path FTIR. These instruments are complemented by a detailed local-to-regional scale (inverse) model.

This presentation will provide an update on the progress of the atmospheric monitoring network within the Gipnet project. In particular, we will focus on developments and field testing of the open-path FTIR, which has been deployed at the University of Wollongong and at Elizabeth Macarthur Agricultural Institute (EMAI), and is now capable of measurement-to-measurement repeatability of better than 1 ppm for CO_2 over pathlengths of 3 km. Activities to attempt to calibrate the open-path measurements using mobile Picarro and horizontal Aircore techniques will also be introduced, in addition to updates on measurements and modelling already occurring within the Gippsland region.

Climatic influence on 20th Century CO_2

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Abstract

The effect of climate change on atmospheric carbon dioxide (CO_2) is of concern because it completes a feedback loop between CO_2 and climate. The amplification from such positive feedback has been an important contribution to the oscillation between glacial and interglacial conditions. The extent to which such feedback will operate over the 21st century remains poorly quantified. A number of studies have looked at changes over the last one or two millennia of pre-industrial changes, seeking to quantify feedback in terms of the parameter Γ defined by Friedlingstein *et al*. [2003]. A recent analysis by Rubino *et al*. [2016] incorporated the appreciation that the Γ and β used in the Friedlingstein analysis are not constants, but need to include a dependence on timescale.

Studies of changes over the 20th century have proved inconclusive [e.g. Rafelski *et al*., 2009; Bastos *et al*., 2016]. The parallel increases in temperature and CO_2 determine $\Gamma/(1+\beta_O+\beta_L)$ rather than distinguish the effects. The main distinguishing information comes from changes on smaller scales, most notably the so-called 1940s dip. We have previously [Enting and Clisby, 2017] applied the formalism with time dependent Γ to various records. We found that the paleo record of northern hemisphere temperatures from Moberg *et al*. [2005] could, with a single Γ, match much of the preindustrial change and the 20th century change. The puzzling aspect of this result was that the features in the Moberg reconstruction that gave this agreement do not appear in northern hemisphere averages of direct observations.

We see this as reflecting the combination of two effects:

1. that Γ needs to include spatial dependence
2. that the Moberg reconstruction is derived from a very sparse network.

We are continuing to explore what this result is telling us.

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Testing estimates of terrestrial productivity using carbonyl sulfide

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Abstract

Carbonyl sulfide (COS) is assimilated by plants as a by-product of photosynthesis but is not respired. Thus, its flux is a proxy for gross primary productivity (GPP). This is, however, by no means the only source, so attribution requires careful treatment of other sources and their uncertainties. In this talk we will present a preliminary test of various estimates of GPP by comparing predicted and observed seasonal cycles of COS arising from several estimated distributions of GPP. The global GPP estimates vary by 60% so the differences in simulated COS cycles are large. By comparing these differences with the uncertainties engendered by other components of the COS cycle, we will assess whether COS can distinguish between the various GPP products and, if so, which of them is supported by the COS observations.

Cape Grim GG-ODS sub-program review: 2010-2018

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Abstract

The Cape Grim Baseline Air Pollution Station has been producing long-term high-quality data and research outputs on the composition and chemistry of the remote marine boundary layer of the Southern Hemisphere for more than 40 years. Regular reviews of the science sub-programs undertaken at Cape Grim are intrinsic to sustaining a culture of science excellence. The Cape Grim Greenhouse Gases related sub-programs were last reviewed together in 2010, and they were also reviewed as part of the 2016 Cape Grim 40th Anniverary Science Program review. One of the recommendations from the 2016 review was that the existing three greenhouse gas sub-programs – carbon dioxide (CO_2) and CO_2 isotopes ($^{13}CO_2$, $C^{18}OO$); non-CO_2 greenhouse and ozone-depleting gases (methane – CH_4, nitrous oxide – N_2O, halocarbons, other trace species and reactive gases, as well as carbon monoxide – CO, and hydrogen – H_2) which is part of the international Advanced Global Atmospheric Gases Experiment (AGAGE) program; and the Cape Grim Air Archive – be combined into one large sub-program. The GG-ODS (Greenhouse Gases & Ozone Depleting Substances) sub-program was born out of this.

The overarching goals of the GG-ODS program are:

- to continue the long-term, highest-quality observations of all the important, long-lived trace gases that drive climate change and ozone depletion, using both in situ measurements and flask samples;
- the maintenance of accurate, stable, internationally-accepted calibration standards and procedures;
- the collection, analysis and storage of Cape Grim air archive samples;
- to ensure regular submission of the Cape Grim GG-ODS data to the relevant national and international data archives;
- to enhance the measurement science at Cape Grim through the introduction of state-of-the-art measurement capability;
- to sustain collaboration with international laboratories and programs;
- to use the Cape Grim data, through national and international partnerships, to derive, by inverse and other modelling techniques, global and regional sources (emissions) and sinks for these important trace gas species;
- to inform 'bottom-up' national and global emissions inventories with 'top-down' estimates based on Cape Grim and other global observational data;
- to participate fully in all the national and international assessments of climate change and ozone depletion to ensure that Cape Grim data receive the widest possible global recognition and application; and
- to ensure that Cape Grim retains its status as a premier Baseline Station in the GAW hierarchy.
- Here we will present an overview of the GG-ODS sub-program covering the achievements from 2010 through to 2018 and the future directions of the program.

N_2O emission estimates from south eastern Australia 1993 - 2016

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Abstract

N_2O has been measured at Cape Grim as part of the ALE/ GAGE/ AGAGE network for over 40 years [Prinn *et al*., 2018]. There is also a long record of radon measurements at the site. The ratio of enhancements of N_2O and radon when air travelled from south-eastern Australia was used to infer N_2O emission rates from an early part of this record some 20 years ago [Wilson *et al*., 1997]. Since then, there have been significant improvements in the measurement precision and accuracy of both radon and N_2O, and so this analysis has been repeated including the use of a much more detailed understanding of the spatial and temporal distribution of radon emissions [Griffiths *et al*., 2010], and the use of atmospheric back trajectories to define the emission locations.

The magnitude of the emissions calculated for this 23 year period is consistent with the earlier analysis. With this extended data set it is evident that the emissions from the mainland of Australia have steadily increased, in line with the increased use of nitrogenous fertilizer and with little evidence of a decrease in emissions during the period of the 'millennium' drought. This indicates that at the larger spatial and temporal scale the emissions of N_2O are not heavily rainfall dependent.

The annual cycle of N_2O emissions shows two peaks in emission – in September and March (and so minima in January and June/July). This can be understood in terms of variations in temperature, moisture and fertilizer usage.

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Cape Grim CO_2-e exceeds 500 ppm … or has it?

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Abstract

Using Cape Grim carbon dioxide (CO_2) and non-CO_2 greenhouse gas data (GHGs: methane - CH_4, nitrous oxide - N_2O, chlorocarbons – e.g. carbon tetrachloride - CCl_4, chlorofluorocarbons - CFCs, hydrochlorofluoro-carbons - HCFCs, hydrofluorocarbons - HFCs, perfluorocarbons - PFCs, sulfur hexafluoride - SF_6, and others) we are able to derive key Kyoto and Montreal Protocol policy-relevant parameters for Cape Grim such as CO_2 levels, equivalent-CO_2 (CO_2-e) levels and Effective Equivalent Stratospheric Chlorine (EESC). We are also able to do this globally using data from the CSIRO and AGAGE (Advanced Global Atmospheric Gases Experiment) global networks.

Global CO_2 levels exceeded 400 ppm in 2015 and Southern Hemispheric CO_2 in March 2016, and have remained above 400 ppm ever since. Just as global 400 ppm CO_2 was a significant psychological milestone that resonated in the public and policy domains, it is likely that this will also be the case for 500 ppm CO_2-e. When will this occur? We had originally predicted that global CO_2-e would occur around 2020, with Cape Grim likely to follow within a year of the global value exceeding 500 ppm.

So what has changed? The amount of heat each type of GHG can trap depends on its spectroscopy – which wavelengths of the electromagnetic spectrum it can absorb and how strongly it does so. Despite being the simplest hydrocarbon, there is still much to learn about the fundamental spectroscopy of methane. A 2016 update of radiative forcing formulas [Etminan *et al*., 2016] suggested that inclusion of shortwave absorption would have a significant effect on the radiative forcing of methane. New research, published recently in *Science* [Collins *et al*., 2018], which draws on the 2016 work of Etminan *et al*., reveals that inclusion of the shortwave component of methane's absorption spectrum requires an upward revision of methane's radiative forcing, by 15%. By applying the new formulas outlined in Etminan *et al*. [2016] for CO_2, CH_4 and N_2O for radiative forcing, we have found that Cape Grim has already passed the anticipated milestone in July 2018, and that the Global CO_2-e reached this milestone in 2017. We will show the CO_2-e results based on these new formulations and compare them to those outlined in IPCC [2001], along with the effects of which minor non-CO_2 greenhouse gases are included in the calculations.

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Causes of short-term variability in the methane mixing ratio under baseline conditions at Cape Grim

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Abstract

Baseline conditions at Cape Grim are rigorously defined. Under such conditions we expect the mixing ratios of the well-mixed, long-lived greenhouse gases, which include CO_2, CH_4 and N_2O, along with the suite of synthetic greenhouse gases, to show essentially little or no variability beyond measurement precision over timescales of hours to days.

With the benefit of multi-annual records of continuous, high precision (< 1 ppb) *in situ* measurements of CH_4 at Cape Grim, Tasmania, we see clear evidence that under classic baseline conditions, mole fractions of CH_4 can periodically vary by up to 10 ppb over short timescales, typically becoming depressed below the baseline curve fit.

In this presentation, we explore some of these episodes of depressed CH_4 mole fraction, investigating the meteorology associated with such events along with other trace gases such as radon, ozone and a number of species measured in the Advanced Global Atmospheric Gases Experiment (AGAGE) program.

The role of ENSO in recent trends of growth rates in atmospheric methane

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Abstract

The El Niño – Southern Oscillation (ENSO) has been suggested as a strong forcing in the methane cycle and as a driver of recent trends in global atmospheric methane levels. Such a sensitivity of the global CH_4 budget to climate events would have important repercussions for climate change mitigation strategies and the accuracy of projections for future greenhouse forcing. Here, we test the impact of ENSO on the CH_4 cycle in a correlation analysis. We use local and global records of methane mixing ratio [CH_4], as well as stable carbon isotopic records of atmospheric CH_4 ($\delta^{13}CH_4$), which are particularly sensitive to the combined ENSO effects on CH_4 production from wetlands and biomass burning. We use a variety of nominal, smoothed and detrended time series including growth rate records. We find that at most 36% of the variability in [CH_4] and $\delta^{13}CH_4$ is attributable to ENSO, but only for detrended records in the Southern tropics. Trend-bearing records from the Southern tropics, as well as all studied hemispheric and global records show a minor impact of ENSO, i.e. <28% of variability explained. Additional analyses using hydrogen cyanide (HCN) records show a detectable ENSO influence on biomass burning (up to 51%-55%), suggesting that it is wetland CH_4 production that responds less to ENSO than previously suggested. Dynamics of the removal by hydroxyl likely counteract the variation in emissions. It is possible that other processes obscure the ENSO signal, which itself indicates a minor influence of the latter on CH_4 emissions. Trends like the recent rise in atmospheric [CH_4] can therefore not be attributed to ENSO. This leaves anthropogenic methane sources as the likely driver, which must be mitigated to reduce anthropogenic climate change.

Identifying methane hot spots in southeast Melbourne

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Abstract

In order to meet the aspirations of the Paris Agreement of 2016, to keep global warming well below 2°C above the pre-industrial climate, rapid cuts in greenhouse gas (GHG) emissions are needed [Lopez *et al*., 2017]. The high radiative forcing potential and relatively short lifetime (approximately 12 years) of CH_4 means that reductions in CH_4 emissions will provide more immediate relief to radiative forcing of the climate than reductions in other gases such as CO_2 [Kirschke *et al*., 2013]. Cities contribute approximately 35% of anthropogenic methane emissions [Kirschke *et al*., 2013; Marcotullio *et al*., 2013]. A number of sources contribute to anthropogenic CH_4 fluxes in urban areas, yet little is known about their relative contribution to CH_4 concentrations in Australian cities.

This study is an initial investigation into methane sources in southeast Melbourne. Methane concentrations were measured via cavity ring-down spectrometers (Picarro, Inc.) at CSIRO's Aspendale site in south-eastern Melbourne for approximately one year. The Cape Grim baseline fit for methane was used to remove the seasonality and underlying growth rate from the Aspendale methane mixing ratios. The residuals were then used to produce pollution roses to relate CH_4 concentrations to wind direction and wind speed, giving an indication of the likely locations of methane hotspots. Meteorological data were taken from the Bureau of Meteorology's Moorabbin Airport site.

The most significant CH_4 sources appear to be located between the north and east of the Aspendale CSIRO site. Methane concentrations from these directions were predominantly within the range of the upper two quartiles of the overall distribution. High CH_4 concentrations emanating from the north are suspected to be related to the large number of landfills and waste transfer stations north of Aspendale. There were also significant concentrations of CH_4 occurring from the east, likely related to a gas storage facility in this direction. To the southeast of the site, wetlands and water treatment plants are suspected to also be contributing large amounts of urban CH_4. The qualitative analysis in this study suggests the most significant source of CH_4 may be natural gas and landfill sources. To validate these theories, a second stage of this study will include mobile measurements made around the areas identified as likely contributors in this study. Isotopic analysis of $^{13}C/^{12}C$ may also be used to further identify the origins of CH_4 in southeast Melbourne.

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Sampling atmospheric C-14 and other atmospheric Components on two different sites in Melbourne

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Abstract

The increase of greenhouse gas concentration, especially CO_2, is the main driving cause of climate change. Fossil fuel burning is the major emission source of CO_2 and this is concentrated in urban environments. In order to estimate the contribution of fossil fuel sources, atmospheric radiocarbon is used as a promising tracer in atmospheric studies. Since April 2018, flask sampling of radiocarbon, as well as the concentration of greenhouse gases (CO_2, CO, CH_4 and N_2O), was measured weekly at two sampling sites in Melbourne. One is set in CSIRO, Aspendale (ASA) and another is in the McCoy building, University of Melbourne (UoM).

The results show that the two measurement series have good consistency in CO_2 and CH_4 concentration. For the Delta ^{14}C content, however, the air sample from UoM is lower than at ASA. CO and N_2O concentrations, like other fossil fuel tracers, have similar results as Delta ^{14}C. This suggests that the air in central Melbourne is more polluted then the suburbs. According to the Delta ^{14}C calculation, the fossil fuel CO_2 values around Melbourne are between 3 and 14 ppm. Alongside these weekly samples there is a continuous record of CO_2, CH_4 and CO from a Picarro 2401 analyser at UoM. We will use this record to assess the representativeness of the flask samples and the temporal behavior of the various tracers.

Simultaneous shipborne measurements of CO_2, CH_4 and CO and their application to improving greenhouse gas flux estimates in Australia

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Abstract

Quantifying and understanding the sources and sinks of greenhouse gases is essential to understand and predict climate variability and to better interpret and represent different greenhouse gas-climate feedback processes in chemical transport models. Here, shipborne Fourier Transform Spectrometer (FTS) measurements, and a global chemical transport model, GEOS-Chem, are used to identify and quantify the sources of carbon dioxide (CO_2), methane (CH_4) and carbon monoxide (CO) around Australia. Based on the measurements, we provide an updated distribution of the studied gases. We investigate the impact of different sources and sinks that drive their variability, by identifying a series of events when we observed simultaneous enhancements in at least two of the three gases. We use these enhancements and their co-variation to identify the dominant processes driving carbon gas variability and to identify the sources of enhancements that were not captured by the model.

Additionally, we are developing a joint carbon gas simulation in the GEOS-Chem model that couples the three carbon gases studied here. This new simulation will include the chemistry between CO_2, CH_4 and CO calculated online as opposed to from archived fields as used currently in GEOS-Chem. We aim to use this new simulation to further investigate the co-variations between these gases. For example, co-variations of CO and CO_2 occur because both are emitted during combustion processes. Similarly, CO and CH_4 have a common sink from the atmosphere due to reaction with the hydroxyl radical. The implementation of the new simulation will lead to a better understanding of the interactions between these gases and a better evaluation of the accuracy of existing emission estimates. We will provide an update on progress in the development and implementation of this joint simulation.

Water-atmosphere greenhouse gas (CO_2, CH_4 and N_2O) exchange in two of the world's major rivers: the Elbe and the Murray

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Abstract

Global greenhouse gas emissions from inland waters are significant yet estimates remain highly varied and are quoted with large uncertainty. For example, carbon dioxide (CO_2) emission estimates have increased by a factor of five (0.75 Pg C yr^{-1} to 3.8 Pg C yr^{-1}) over the last decade and are comparable in magnitude to the global net uptake of CO_2 by either the land or ocean sinks [Cole *et al*. 2007; Tranvik *et al*. 2009; Raymond *et al*. 2013; Drake *et al*. 2017]. However, these global estimates are not adequately constrained by measurements, particularly for CH_4 and N_2O, which have received far less attention than CO_2.

Here we present *in situ* measurements of inland water-atmosphere greenhouse gas exchange obtained over several hundred kilometres on the Elbe (Germany/Czech Republic) and Murray (Australia) Rivers. Greenhouse gas partial pressures (pCO_2, pCH_4 and pN_2O) were measured continuously at high spatiotemporal resolution using an equilibrator coupled to a Fourier-Transform InfraRed (FTIR) Trace Gas Analyser. Water-atmosphere greenhouse gas exchange was measured directly using floating chambers coupled to the FTIR. Gas transfer velocities were derived from greenhouse gas partial pressure and water-atmosphere exchange measurements and were also modelled based on wind speed and hydrology using an ensemble of nine commonly applied parameterisations. A suite of biogeochemical parameters (e.g. pH, DO, DOC and DIN) were also measured to gain further insight into the broader mechanisms driving greenhouse gas exchange.

This presentation will reveal the high spatiotemporal variability of water-atmosphere greenhouse gas exchange observed on both river systems. Significant drivers of variability will be discussed, including diurnal cycling, wetland connectivity, water regulation and industrial discharge. Finally, this research will provide the first estimates of inland water-atmosphere greenhouse gas exchange from two globally significant inland water systems, highlighting the magnitude of this exchange compared to other regionally significant greenhouse gas fluxes.

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Measurements of greenhouse gases in the Arctic from novel ground-based remote sensing instruments

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Abstract

The Centre for Atmospheric Chemistry at the University of Wollongong (UoW) has been involved in a European Space Agency funded project to assess the ability of several low cost portable spectrometers to measure the greenhouse gases CO_2 and CH_4. This campaign, the Fiducial Reference Measurement Ground-Based Infrared Greenhouse Gas Observations (FRM4GHG) is one of several ESA led projects within the framework of GEO/CEOS to provide a suite of independent, fully characterized, and traceable ground measurements.

For the last two years, UoW has operated a Bruker IRCube FTIR at the Sodankylä (Finland) Total Column Carbon Observing Network (TCCON) site as part of the FRM4GHG project. The IRCube was installed in a container very close to the TCCON instrument (a high resolution Bruker FTIR), with measurements performed more or less simultaneously whenever there was sunlight. Over the period from March 2017 to October 2018, over 80,000 spectra were recorded, covering the near infrared region. The standard TCCON processing analysis software was used to give CO_2 and CH_4 products in the form of column averaged abundances. This significant dataset (including equivalent spectra recorded with other onsite instruments) is being used to improve the performance of each individual instrument, satellite validation activities, and model comparisons. These datasets will provide important comparative validation with respect to the standard TCCON spectrometer for precision and stability, while giving insight into the use of small low cost potable spectrometers as a supporting network for TCCON.

This presentation will give an overview of the FRM4GHG project and report results from 2017 and preliminary data from 2018.

Hydroperoxyalkyl radicals (QOOH) in the atmosphere

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Abstract

In atmospheric models, QOOH radicals (carbon-centred hydroperoxyalkyl radicals) are thought to be important intermediates in oxidation chemistry leading to highly oxygenated aerosol precursors [Savee *et al*., 2015]. Models such as the Leuven Isoprene Mechanism postulate hydroperoxy aldehydes (HPALDs) as important in increasing HO_x abundances to better match measurements [Peeters *et al*., 2014] and these HPALDs, along with HO_x, may be produced by QOOH oxidation [Praske *et al*., 2018]. Because HO_x are important to chemical processing in the atmosphere and models now rely on HPALDs to more accurately predict HO_x abundances, it is important to understand the spectroscopy, reaction mechanisms and kinetics of these molecules.

Atmospheric models of HPALD chemistry use theoretically determined rate constants and quantum yields as well as UV-vis absorption spectra inferred from other aldehydes. These have been shown to overestimate OH production [Peeters *et al*., 2014]. Experimental measurements of HPALD chemistry are scant. To the best of our knowledge, there are no published spectra for any HPALD. Additionally, very few QOOH radicals have been directly observed, and none that are atmospherically relevant [Savee *et al*., 2015].

In my PhD project, I propose to experimentally produce and observe an atmospherically-relevant QOOH radical, formed from an isoprene-type HPALD. Velocity map imaging (VMI) experiments will be used to verify the formation of the QOOH radical. Then experiments using photoionization mass spectrometry (PIMS) at the Berkeley Advanced Light Source will be performed to determine reaction rates and energetics for both HPALD and QOOH. The aim is to incorporate the rates into atmospheric chemical models, such as the Master Chemical Mechanism and GEOS-Chem, to better understand HO_x chemistry and aerosol formation in the atmosphere.

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Atmospheric $\Delta^{14}CO_2$ Southern Hemisphere latitudinal gradient over recent decades

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Abstract

^{14}C-free fossil fuel CO_2 emissions have dominated the globally decreasing trend of atmospheric radiocarbon ($^{14}CO_2$) over recent decades. Whilst fossil fuel emissions are predominantly generated in the Northern Hemisphere, $^{14}CO_2$ in the Southern Hemisphere is also sensitive to the upwelling of 'old' deep waters in the Southern Ocean. These intermediate and deep water masses remain isolated from the atmosphere for centuries, due to the slow nature of ocean circulation, thereby possessing significantly reduced ^{14}C content.

During the 'bomb period' the disequilibrium of ^{14}C at the air-sea interface controlled atmospheric $^{14}CO_2$ in the Southern Ocean region. This disequilibrium is now much smaller, such that outgassing of CO_2 from these upwelling 'old' carbon-rich (DIC) deep waters can be identified in the $^{14}CO_2$ of the overlying atmosphere.

The net carbon uptake of the Southern Ocean is characterised by the combination of outgassing of CO_2 from these 'old' deep waters and sequestration of anthropogenic carbon. Since atmospheric $^{14}CO_2$ in the overlying atmosphere is controlled by the same mechanism controlling the outgassing of CO_2, we can use $^{14}CO_2$ as a tracer of the upwelling observed to isolate the outgassing carbon component.

We provide critical new atmospheric $\Delta^{14}CO_2$ measurements from tree rings across a latitudinal range of the Southern Ocean region (New Zealand and Chile). These allow us to reconstruct the atmospheric $\Delta^{14}CO_2$ Southern Hemisphere latitudinal gradient over recent decades and investigate the temporal and spatial variability of atmospheric $\Delta^{14}CO_2$ data in the Southern Ocean region. Further to this we also explore the use of $^{14}CO_2$ in elucidating the upwelling and carbon outgassing in the Southern Ocean.

Hot ground state photochemistry of aldehydes in the atmosphere

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Abstract

Atmospheric chemistry modelling has often neglected electronic ground state photochemistry, assuming excited state reactivity dominates. This is an incorrect assumption for the relatively very abundant aldehydes, formaldehyde and acetaldehyde. Following photoexcitation of formaldehyde or acetaldehyde by a UV photon in the troposphere, efficient crossing back to the ground state produces a highly vibrationally excited ('hot') molecule [Corrigan and Jordan, *in prep*.] subsequent available ground state reactions include dissociation via roaming [Townsend *et al*., 2004] and phototautomerisation [Clubb *et al*., 2012]. We know the phototautomerisation product of acetaldehyde reacts to produce formic acid [Archibald *et al*., 2007]. But what do the hot roaming products will do? Is the hot ground state itself reactive?

My investigations centre on bimolecular reactions, whereby these hot species react with O_2 gas - a known atmospheric radical scavenger, and by far the most abundant reactive collision partner available. I will present theoretical evidence for the reaction of hot ground state aldehydes and hot roaming products with O_2 gas as a new mechanism for HO_2 radical formation in the atmosphere.

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Evaluating global biomass burning emission inventories for CO in Australasia

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Abstract

Knowledge about Australasian biomass burning emissions is under-represented in emission inventories. There was, therefore, a need to evaluate whether some of the mainstream global biomass burning emission inventories are suitable for the Australasian region. GEOS-Chem v10-01 was run, from 2008 to 2010, with three biomass burning emission inventories: FINN1.5, QFED2.4 and GFED4s; and an ACCESS-UKCA simulation with GFED4s was used as a comparison to also evaluate model variability. These four simulations were compared to a range of observations including surface mixing ratios, ground-based FTS total columns and satellite-based MOPITT total columns at five sites in Australasia: Cape Grim, Cape Ferguson, Lauder, Wollongong and Darwin. A previously documented high bias in CO levels was also found in both models, although it is slightly higher in GEOS-Chem. The three inventories were found to have up to an order of magnitude difference in their estimates of Australian biomass burning CO emissions, with FINN lowest and QFED highest. Bias aside, GEOS-Chem with GFED and QFED led to better correlation against measurements than either GEOS-Chem with FINN or ACCESS-UKCA with GFED. This poster demonstrates that GFED performs the best over the Australasian region and should, therefore, be used for this region. This study also highlighted that the FINN inventory requires improvements in its estimates of Australian savanna CO emissions.

What happens to the climate when coral reefs go extinct?

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Abstract

Marine organisms contribute approximately one fifth of the global sulfur budget via the production of dimethyl sulfide (DMS), an important precursor gas for aerosol formation. In recent years, coral reefs have been found to produce a significant amount of DMS, of similar magnitude to oceanic high primary productivity regions. This coral source of DMS is currently unaccounted for in climate modelling and has gained substantial attention in the Australian community due to its hypothesized ability to cool the local environment. With new estimates indicating that at 1.5 degrees of warming, 70-90% of coral reefs are likely to be extinct, further research into the influence of corals on climate is necessary. In this work, a coral reef source of DMS, constrained by observations, is added to the current global DMS climatology for the first time. We compare this new 'coral' climatology to the current 'no coral' climatology using the Australian Community Climate and Earth System (ACCESS) - United Kingdom Chemistry and Aerosol (UKCA) global climate-chemistry model. With this approach, we are able to determine if coral reef derived DMS has an influence on climate, and what the effects may be in the event of mass coral extinction. For each experiment, three free-running simulations were performed over ten years (2000-2009), each initialised with different atmospheric conditions. We find that the removal of coral-sourced DMS has the largest impact in the Maritime Continent, Coral Sea and Australian region, where significant differences in the small aerosol modes are found. Differences in larger aerosol modes, cloud condensation nuclei and cloud droplet number are small and are distant from the coral source. Similarly, small, differences are found in cloud fraction, precipitation and radiation budgets. We hypothesize that some of these differences, such as in precipitation and convective cloud fraction, are due to differences in large-scale atmospheric circulation, in particular the Australian Monsoon and South Pacific Convergence Zone, rather than direct and indirect aerosol effects. These results show that while on a global scale loss of coral DMS has little impact, on a regional scale such loss of coral reefs may have further implications that we currently realise.

The potential of consistent co-monitored CO_2 differences between primary baseline sites to better constrain the global carbon budget

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Abstract

Co-monitored baseline CO_2 over 25 years at Mauna Loa (mlo:19.5°N, 155.6°W, 3379m), Cape Grim (cgo, 40.7°S, 144.7°E, 94m) and South Pole (spo, 90°S, 2810 m) yield ensemble averaged monthly spatial differences with typical standard deviations of 0.17 mmol mol^{-1} for cgo-spo and 0.22 mmol mol^{-1} for mlo-(cgo or spo).

These surface sites are distinguished by their ready access to air with extremely large spatial representation. The measurement of CO_2 spatial differences between the sites benefits from flask sampling with analysis in a central laboratory using the same instrumentation and against the same internal reference and calibration standards. We use spatial differences with high time resolution (2-3 months) compared to typical growth rate studies that remove seasonality by harmonic analysis and 1.8 year smoothing. In a composite record inevitable variations in quality in any one network are smoothed.

Interannual variability (IAV) in the composite interhemispheric (IH) CO_2 differences are compared with IAV due to transport in simplified model simulations, and with IH transport informed by independent wind indices, namely upper-troposphere cross-equatorial eddy exchange in the boreal winter and mean Hadley exchange in the boreal summer. Short-term variation in wind indices contribute to Northern Hemisphere CO_2 growth rate variations (that could be attributed to terrestrial exchange if CO_2 transport models inadequately capture IH exchange).

Air Toxic emissions estimation from coal and gas electricity generators using Australian energy distribution data

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Abstract

Electricity in Australia is primarily produced from fossil fuels including coal and gas. Electricity generators are responsible for major NO_x and SO_2 emissions into the atmosphere in Australia. Accurate estimation of air toxic emissions with good temporal and spatial resolution is required to understand the regional or global impacts. Existing emission inventories of Australia do not provide the details of emissions varying spatially and temporally from the power plants. Global emission inventories provide estimated emissions for Australia using total fossil fuel consumption data from various databases lacking the technology details and characterization. In this study, Air toxic emissions from electricity generator's stacks due to combustion of coal and gas are estimated accessing the time series electricity generation data provided by National Electricity Market (NEM) (accessed through AEMO-Australian Energy Market Operator). NEM data provides the data from electricity generators in New South Wales, Victoria, Queensland, South Australia, Tasmania region using renewable (solar, wind, Hydro and biomass) and non-renewable (coal, gas and oil) sources of energy at a time resolution of 5 minutes. Emissions from electricity generators are estimated using the emission factor methodology adopted from the National Pollution Inventory (NPI) methodology document [DSEWPC, 2012]. Facility-specific information relating to fuel type, fuel characteristics, air pollution controlling devices and operating conditions are used to calculate the emissions. Estimated emissions are compared with both NPI reported emissions and Emissions Database for Global Atmospheric Research (EDGAR). To further validate estimated emissions, WRF-Chem simulation over the Latrobe valley will be done.

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Top-down estimates of isoprene emissions in Australia inferred from OMI satellite data

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Abstract

Australia is a global hotspot for biogenic isoprene emission factors predicted by process-based models such as the Model of Emissions of Gases and Aerosols from Nature (MEGAN). It is also prone to increasingly frequent temperature extremes that can drive episodically high emissions. Estimates of biogenic isoprene emissions from Australia are poorly constrained, with the frequently used MEGAN model overestimating emissions by a factor of 4-6 in some areas. Evaluating MEGAN and other models in Australia is difficult due to sparse measurements of emissions and their ensuing chemical products.

In this poster, we will describe efforts to better quantify biogenic Australian isoprene emissions using top-down estimates based on formaldehyde (HCHO) observations from the OMI satellite instrument, combined with modelled isoprene to HCHO yields obtained from the GEOS-Chem chemical transport model. We also examine how sensitive emissions estimates are to fire, smoke, anthropogenic, and transport filters. The OMI-based estimates are evaluated using *in situ* observations from field campaigns conducted in southeast Australia.

Preliminary results show that the top-down isoprene emissions are lower than MEGAN estimates by up to 90% in summer. The overestimates are greatest along the eastern coast, including areas surrounding Australia's major population centres in Sydney, Melbourne, and Brisbane. The coarse horizontal resolution of the model significantly affects the emissions estimates, as many biogenic emitting regions lie along narrow coastal stretches.

Our results confirm previous findings that the MEGAN biogenic emission model performs poorly for the Australian environment and suggests that chemical transport models driven by MEGAN are likely to over predict ozone and secondary organic aerosols from biogenic sources in the Australian environment. Further measurements of biogenic gases are critical to improving biogenic emissions and follow-on chemical transport modelling in this region.

The implications of detector response time for radon observations at Cape Grim

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Abstract

Radon measurements at Cape Grim are currently performed using a pair of dual-flow-loop two-filter radon detectors. These have a relatively slow response time whereby 40% of radon atoms are detected an hour or more after entering the detector. At inland sites, this affects the interpretation of radon measurements. At Cape Grim, however, the detector response has not been a limitation for typical applications and, historically, has been characterised only in general terms. In routine processing, the lag induced by the detector is taken into account but the smoothing effect is disregarded.

While the detector response time is likely to have been unimportant in the past, the applications for radon measurements have become more ambitious over time. As well, the Cape Grim detectors have been upgraded, atmospheric transport models have improved, and radon emissions have been increasingly well-characterised. At some point, it is inevitable that the response time will become an important consideration for studies using Cape Grim radon measurements. For measurements during non-baseline periods, it may be that the response time effect should already be accounted for.

A recently-developed procedure [Griffiths *et al*., 2016] lets us quantify and correct for the detector response time. The aim of this poster is twofold: first, to raise awareness of the existence of the response time issue, and the option for its correction; second, using trace gas measurements from fast-response instruments, to highlight some of the situations where the response time correction is, and is not, significant for Cape Grim radon measurements.

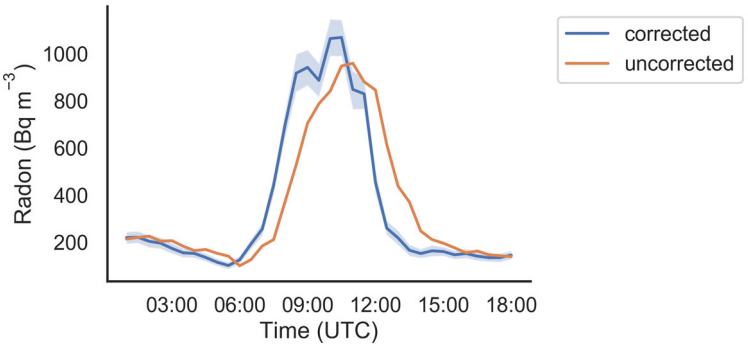


Figure 1. Cape Grim radon concentration (13 February 2015) during a non-baseline event, showing the effect of the relatively slow response time of the radon detector. The corrected radon time series has a more rapid rise and fall, a shorter apparent event duration, and accentuated peaks.

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Towards a more comprehensive characterisation of biogenic volatile organic compounds in the greater Sydney region

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Abstract

Sydney is surrounded by large swathes of eucalypt-dominated forests. Despite the importance of biogenic volatile organic compounds (BVOCs) to the airshed of the city [e.g. Cope *et al*., 2014], relatively few measurements of BVOCs have been conducted in the area. In the greater Sydney region, ambient measurements so far have mostly been made at urban or suburban sites in the context of short-term air quality campaigns [e.g. Cope *et al*., 2014; Paton-Walsh *et al*., 2017]. These campaigns provide useful snapshots but typically do not have BVOC characterisation as their focus.

Here we report on recent measurement efforts to provide a more comprehensive characterisation of BVOCs in the greater Sydney region. These include repeated spot sampling at forested sites over the 2017-2018 summer using absorption tubes followed by analysis using thermal desorption gas chromatography mass spectrometry (TD-GC-MS). The sampling program was designed to investigate differences in BVOC composition between sites and sampling periods (early vs. late summer). The results indicate that cymene and eucalyptol dominate the ambient monoterpene levels in summer.

We also describe the commissioning of a new online BVOC measurement system based on TD-GC-MS. This system will provide year-round characterisation of ambient BVOC levels at the Australian Nuclear Science and Technology Organisation campus in Lucas Heights, ~40 km southwest of the Sydney CBD and adjacent to large forested areas. This deployment is part of the COALA-JOEYS campaign (see https://www2.acom.ucar.edu/campaigns/coala) and will provide insight into the seasonal variability of ambient BVOC levels and composition.

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Southern Ocean Aerosols – a seasonal perspective from Macquarie Island

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Abstract

Being so far from anthropogenic activity, the Southern Ocean region is a unique environment that experiences the most pristine atmosphere in the world. This makes it a perfect testbed for understanding pre-industrial conditions that are so vital for reducing the uncertainties inherent in global climate and earth system models today [Carslaw *et al*., 2013]. Clouds are of particular interest in this region because of the large biases in shortwave radiation and sea surface temperatures that are present in most models. However, due to its remoteness and wild environment, the Southern Ocean is one of the most under-sampled regions of the Earth's atmosphere, making high quality observational data from the region invaluable.

The recently concluded Antarctic, Clouds and Radiation Experiment (ACRE) included a two-year intensive measurement campaign that began in March 2016 at Australia's sub-Antarctic research station at Macquarie Island (54.6°S, 158.9°E). Amongst the suite of instrumentation deployed are those for the measurements of condensation nuclei (CN_{10}) and cloud condensation nuclei (CCN) which are vital components in the formation of clouds and determining their properties. In this presentation, the first climatological analysis of the dataset is presented and compared to previous measurements in the region as well as other long-term datasets around the globe.

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Coral reefs as a source of marine biogenic aerosol and the implications for regional climate

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Abstract

Coral reefs are an important ecological, economic and social resource yet the existence of these natural wonders is being threatened by global climate change. Evidence suggests that coral reefs may play a role in local climate regulation through stress induced emissions of dimethylsulfide (DMS). Once emitted to the atmosphere, DMS oxidises to form non-sea salt sulfate aerosol and may increase local albedo over oceans through enhanced low-level cloud formation and backscattering of solar radiation, acting to cool sea surface temperature via a biological ocean feedback. Current knowledge on the strength and direction of this proposed feedback remains incomplete and constitutes a fundamental constraint on predicting the ability of coral reefs to cope with future ocean warming. We investigated the correlation between a satellite-derived coral stress metric, formulated as a function of irradiance, water clarity and tide, sea surface temperature (SST) and fine-mode aerosol optical depth (AOD) throughout the Great Barrier Reef, Australia (GBR) over an 18-year time period. AOD positively correlated with both SST and the coral stress metric [Jackson *et al*., 2018]. The influence of non-biogenic and distant aerosol sources was negligible during the study. Additionally, the correlation between AOD and coral stress improved on calm days where wind speed was low (<2 ms^{-1}), suggestive of a strong, local aerosol source above the coral reef [Cropp *et al*., 2018]. These findings support the hypothesis that the 2,300 km stretch of coral reefs can be a substantial source of biogenic aerosol and thus, potentially influence local climate. Importantly however, a tipping point in the coral stress response was also identified, whereby thermal stress reached a point that exceeds the capacity of corals to influence local atmospheric properties [Jackson *et al*., 2018]. Beyond this point, corals may become more susceptible to permanent damage with increasing stress, with potential implications for mass coral bleaching events and climate in north-eastern Australia.

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Analysing mobile methane survey data using a hidden Markov Model to delineate leak frequency in Sydney, Australia

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Abstract

Urban emissions of methane (CH_4) associated with minor gas leaks are poorly quantified and not adequately accounted for in our National Greenhouse Gas Accounts. The original gas distribution systems in Australia's major cities were installed over 100 years ago. Much of the original network has been replaced, but information on where and when is not in the public domain. Even recently installed piping can leak due to ground movements. Here we present the results of a mobile methane survey throughout the Eastern Suburbs of Sydney that aimed to assess the frequency of leaks in residential and industrial suburbs.

To determine the frequency of gas leaks in Sydney, a mobile methane survey was undertaken in July 2016, using a Los Gatos Research (LGR) greenhouse gas analyser. The air intake was mounted 2.2 m above the ground on a pole in the back of a utility vehicle. A Hemisphere GPS (model A21) was also fixed on top of the vehicle to simultaneously measure the GPS location to within 15 cm. Air from within the major plumes was collected and stored in Tedlar bags, and then analysed on a Picarro G2201-i.

Surveys were undertaken from mid-morning to late afternoon (11 am to 5 pm). Throughout the morning the boundary layer was still rising, which changes the background concentration of methane ([CH_4]) recorded in the ground level atmosphere. Variations in wind direction throughout the day can also change what is interpreted to be the background [CH_4]. Correcting for the variation in background [CH_4] is often overlooked. Many mobile methane survey studies have chosen to simply use a [CH_4] threshold above which a "plume" is defined [Gallagher *et al*., 2015; Jackson *et al*., 2014; Phillips *et al*., 2013] or to set the minimum value of the dataset as background [Hurry *et al*., 2016). We demonstrate that a better way to detect a plume associated with a leak under variable background [CH_4] conditions is to use a combination of a median filter signal analysis that is post analysed assuming a hidden Markov process and the assumption of Gaussian emissions. This output is converted into a piecewise data set to produce a map of methane plumes. Such an approach enables both short and long plumes with fluctuating [CH_4] reading to be smoothed to delineate anomalously high readings and the plume width (Figure 1).

The [CH_4] was measured in the ground level atmosphere along 230 km of roads throughout the Eastern Suburbs of Sydney. A total of 83 [CH_4] spikes, associated with 37 plumes (clusters of spikes), were detected (Figure 2). The [CH_4] measured ranged from 1.79 ppm to 18.5 ppm (associated with a plume that was mapped for 1.6 km). Plume detection frequency does not appear to be related to areas of different building construction age, or residential compared to industrial. The highest concentration plumes were all recorded on major roadways, a Keeling plot analysis of these data indicated that the CH_4 is of thermogenic origin, which suggests that the source of the CH_4 is the leaking gas from the urban gas distribution network. No major plumes were detected that could be attributed to waste, wetlands, or sewage. Future work aims to quantify the fluxes associated with typical urban infrastructure leaks.

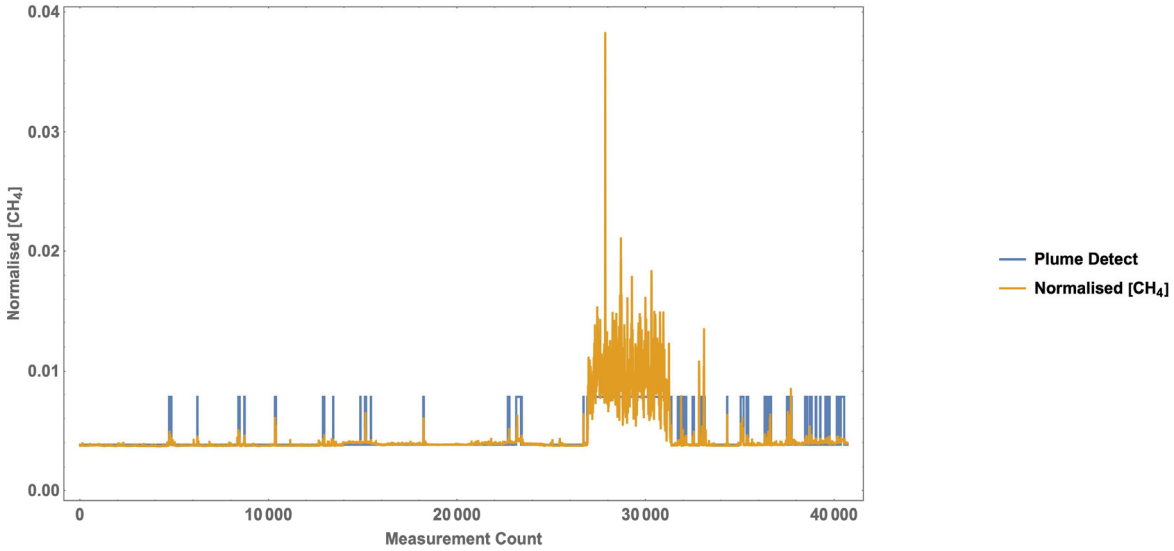


Figure 1. Normalised [CH_4] (orange) and plumes (blue) detected using a median filter and hidden Markov model.

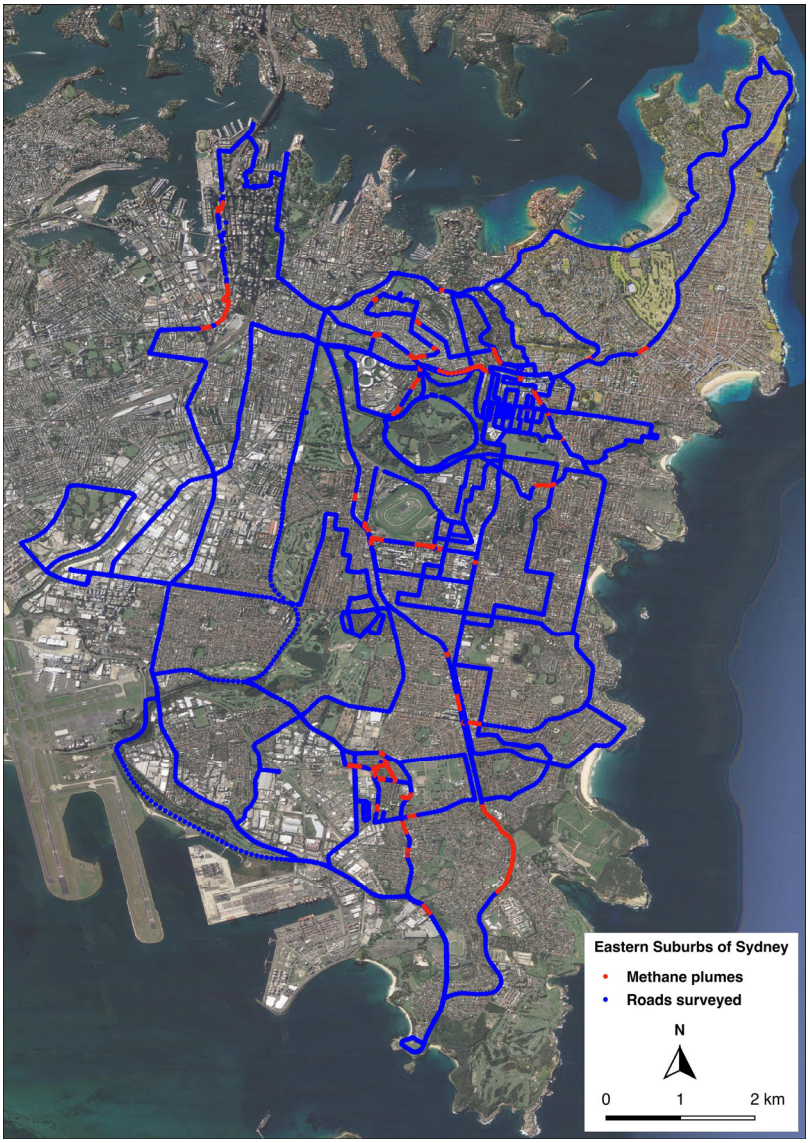


Figure 2. Mobile atmospheric methane concertation survey path (blue) throughout the Eastern Suburbs of Sydney. Methane plumes associated with gas distribution leaks are marked in red.

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Acknowledgments

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Gas Chromatography - Pulsed Discharge Helium Ionization Detector (GC-PDHID) as a Viable Replacement for the Aging GASLAB Gas Chromatographs

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Abstract

CSIRO's Global Atmospheric Sampling LABoratory (GASLAB) in Aspendale was established in the early 1990s for analysis of the major greenhouse gases and related species. Measurement programs supported by GASLAB include the CSIRO global flask air sampling network, the Icecore Extraction Laboratory (ICELAB), the Australian Greenhouse Gas Observation Network (AGGON) and the Advanced Global Atmospheric Gases Experiment (AGAGE), with 1000-3000 gas samples analysed per year.

The analytical instrumentation and techniques used for many measurements (e.g. flask, ice and some tank calibrations) are largely unchanged since GASLAB was formed. While the current techniques are still very robust, there is increasing difficulty in sourcing spare parts, and few opportunities to improve performance using newer technologies. Significant progress has been made in the last few years to develop replacements for the aging GASLAB equipment based on the Flame Ionization Detector (FID) for analysis of methane (CH_4) and carbon dioxide (CO_2), the Electron Capture Detector (ECD) for analysis of nitrous oxide (N_2O), and Reduction Gas Analyser (RGA involving mercuric oxide reduction) for analysis of carbon monoxide (CO) and hydrogen (H_2).

Pulsed Discharge Helium Ionization Detector (PDHID) is a relatively new technology, using current instrumentation (gas chromatographs). It shows good sensitivity for all analysed species (CO_2, N_2O, CH_4, H_2, Kr, Xe, Ne), offering better precision for most of the gases when compared to the existing techniques. While PDHID shows a more linear response for N_2O (compared to the ECD) and H_2 (compared to the RGA), it shows slightly less linear response for CH_4, and significantly less linear response for CO_2 when compared to the FID. However, the CO_2 non-linearity can be adequately characterized and accounted for using appropriate calibration procedures. The PDHID system under development does not yet measure CO due to a column separation issue, but we are confident this can be achieved in the near future.

PDHID has proven to be a viable alternative for the aging GASLAB techniques. It offers several benefits like carrier gas saving (it uses helium only), the same detector platform for all analysed gases (PDHID), and just one injection event for all measured species, thus saving on sample consumption. The main drawback at the moment is its inability to analyse CO. This presentation focuses on the head-to-head comparison of the GC-PDHID performance with the established techniques.

Ship-based constraints on the Southern Ocean mercury cycle

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Abstract

Antarctica and the Southern Ocean are some of the most remote regions on Earth. However, mercury (Hg) is widely distributed in the oceans as a result of long-range atmospheric transport and deposition via wet and dry processes. Previous studies have highlighted Hg contamination in the Southern Ocean and identified its biomagnification in marine food webs.

Approximately 80% of the Hg deposited into oceans is subsequently re-emitted back to the atmosphere. Most observations of Hg in the marine boundary layer have been collected in the North Atlantic and North Pacific Oceans. Geographical variations in ocean-atmosphere exchange of Hg are a major contributor to uncertainty in Hg cycling, especially in the Southern Ocean where abundant sea ice can affect both ocean Hg processing and air-sea exchange. Further uncertainty in this region can be attributed to a lack of observational constraints on the distribution of bromine oxide (BrO), the dominant atmospheric oxidant for Hg.

Two recent measurement campaigns (SIPEXII in 2012 and CAMMPCAN in 2017/18) provide new datasets of observed atmospheric Hg and BrO that can be used to better understand Hg cycling in the Southern Ocean. During both campaigns, Hg and BrO were measured on research vessel voyages that traversed the Southern Ocean from Australia to Antarctica. Additional timeseries of Hg have been measured on several land masses surrounding the Southern Ocean, including Antarctica, Argentina, Australia and South Africa. These datasets provide an opportunity to test our understanding of the Hg cycle and the redox processes over the Southern Ocean as embedded in global models.

Here, we will present an initial evaluation of the GEOS-Chem Hg model over the Southern Ocean using the new Hg and BrO observations. Our preliminary results indicate that significant uncertainties remain in simulating the southern hemisphere Hg background and air-ocean exchange processes in the Southern Ocean. Future directions for model development designed to improve model performance and enhance our understanding of atmospheric Hg cycling over the Southern Ocean will also be presented.

Calculating reaction thresholds and structure-activity relationships for carbonyl photolysis

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Abstract

Carbonyls are some of the most atmospherically abudant and photochemically active volatile organic compounds (VOCs), and the CHO chromophore allows them to undergo many different photochemical reactions across several electronic states. Since carbonyls are formed in the oxidation processes of all VOCs, and biogenic sources emit significant amounts of complex VOC structures (*e.g.* isoprene), accounting for this variety of species in atmospheric models is challenging. While well validated carbonyl experimental photolysis rates are available [Atkinson *et al*., 2006], they are often limited to small, prototypical species and do not cover all possible reaction channels under actinic flux. Atmospheric models currently circumvent this complexity by using the same photolysis parameters available for one molecule for all other molecules of that type (*e.g.* the photolysis rate for butanal is used for all larger linear aldehydes) [Jenkin *et al*., 1997]. However this does not account for how changes in molecular structure can alter photolysis rates, or even which reaction products are formed.

Computational chemistry methods provide a way to augment missing chemical data. Reaction thresholds and kinetic data can be directly compared to experiment, where available [Oruganti *et al*., 2016]. This allows for a systemic survey of the structure-activity relationships (SARs) describing the energetic trends of how alterations to molecular structure determine the reactivity of all carbonyls. Such theoretically informed SARs have already been used for other major initiation reactions (such as •OH addition) [Carl *et al*., 2007], where experimental data are not available. Additionally, theoretical SARs provide a deeper understanding of the photophysics of the carbonyl group as a whole, and allow mechanisms to be assigned based on calculated energetic thresholds.

In this work, reaction thresholds on the ground state and all accessible (singlet and triplet) excited state surfaces are calculated, and the viability of reaction channels are determined. Clear energetic trends are apparent, such as the propensity of α-bonds to break based on structural branching or conjugation. These reaction thresholds can be coupled in a master equation to provide theoretical photolysis rates which supplement missing photolysis rates, and provide a chemically rationalised framework to modify existing photolysis data to more appropriately model the diversity of carbonyls in the atmosphere.

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Where is the missing CO_2? A regional multi-species approach to trace the fate of atmospheric CO_2 in Fiordland National Park, New Zealand

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Abstract

A robust understanding of CO_2 fluxes is vital for accurate estimates of future atmospheric carbon dioxide (CO_2) levels. However, current estimation techniques show large disagreement on terrestrial CO_2 fluxes. In particular, atmospheric data suggests a larger net CO_2 sink than previously thought for New Zealand's Fiordland region, one of our largest indigenous, temperate rainforests with an area of 12,600 km^2 and a mean annual precipitation of up to 15 m.

We will test the hypothesis that Fiordland's forest is more productive than previously thought with flask samples in air parcels before and after the air has passed over Fiordland's forests. We will use a multi-tracer ensemble to determine biogeochemical trace-gas exchange on spatial scales of 50-100 km (Figure 1A). While measurements of CO_2 mole fractions indicate CO_2 level changes directly, measurements of δ^{13}C-CO_2 distinguish the forest's net CO_2 uptake due to the characteristic isotope fractionation during photosynthesis. A modified Keeling-Plot-Analysis of existing CO_2 mixing and isotope ratio data from a coastal site (Baring Head) and inland site (Lauder) suggests this approach is suitable to resolve atmospheric gradients on ~100 km scales (Figure 1B). Moreover, we will use COS (carbonyl sulfide) as an independent tracer for photosynthetic CO_2 uptake, and Δ^{14}C-CO_2 to examine ecosystem respiration and residence times. We will also analyse δ^{18}O, Δ^{17}O and clumped isotopes in CO_2 and assess the suitability of these tracers to further constrain Fiordland's CO_2 fluxes. Our measurement results will be interpreted using state-of-the-art bottom-up and top-down models.

This study will help to better understand regional CO_2 fluxes on process levels and assess the most suitable tracers for regional carbon cycle observations in comparable ecosystems.

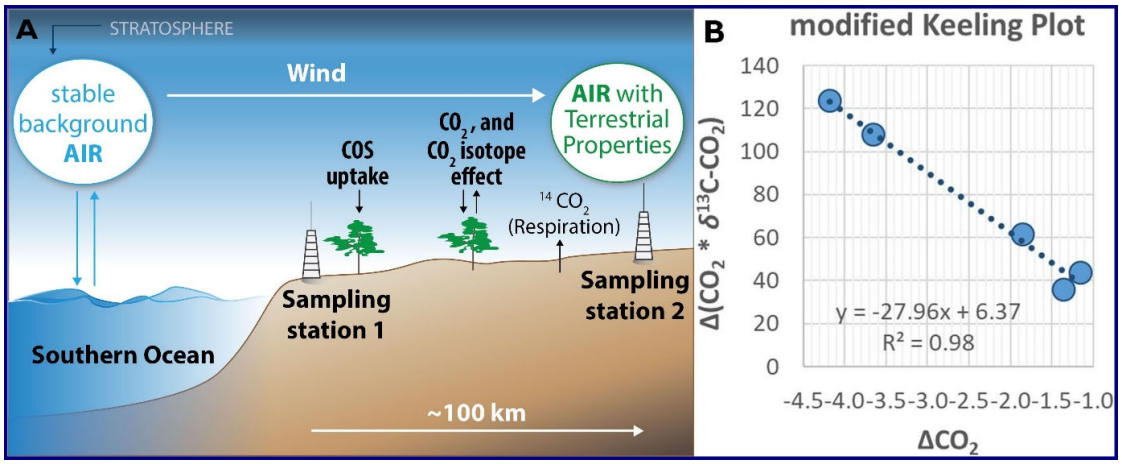


Figure 1. A) schematic of observation strategy and selected tracers, B) modified Keeling-Plot-Analysis using CO_2 mixing and isotope ratios from Baring Head and Lauder during strong Southerly events.

Developing a high-precision measurement technique for nitrous oxide isotopomers in air

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Abstract

Nitrous oxide (N_2O) is a long-lived greenhouse gas that has been accumulating in the atmosphere due to increased usage of N fertilisers in agricultural production. The current atmospheric N_2O burden is approximately 330 ppb. The main removal mechanism is chemical destruction in the stratosphere. The global budget is relatively well known but processes that control individual source contributions and the relative importance of several microbial pathways that lead to N_2O emission from soils and the oceans are poorly understood.

N_2O isotopomers provide a method to improve knowledge of N_2O formation processes. The 4 most abundant isotopic variants are $^{14}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$, $^{14}N^{15}N^{16}O(\alpha)$ and $^{15}N^{14}N^{16}O(\beta)$. The site preference variable (SP = $\delta^{15}N\alpha - \delta^{15}N\beta$) is thought to be independent of the substrate isotopic composition and depends only on the reaction(s) forming and destroying N_2O. Therefore, SP provides a possible tool to differentiate between nitrification and denitrification production pathways.

A new generation of quantum cascade laser spectrometers has potential to make rapid measurement of isotopomer variants. We modified a commercial Los Gatos Research instrument for N_2O isotopomer analysis to lock-in air samples for extended measurement time. In this static measurement mode, a precision in SP of <0.5 ‰ can be achieved in 7 minutes measurement time, when the air samples contain 3-10 ppm N_2O. Such high N_2O levels are needed to increase the signal-to-noise ratio and to improve measurement precision. We currently develop a N_2O pre-concentration system to increase N_2O in air samples to the 10-ppm range. This will enable us to resolve variations of N_2O-isotopomers in samples from soil chamber and emission experiments and will provide new insights into N_2O formation processes.

Modelling CO_2 over south east Australia and comparison with Cape Grim data

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Abstract

The CarbonNet project is planning an injection of CO_2 deep underground off the coast near Gippsland, Victoria. In connection with this, the Gippsland Monitoring Network ('GippNet') will monitor atmospheric and seismic hazards in the region. Two monitoring sites were established in October 2017 collecting in situ greenhouse gas measurements using Picarro and Ecotech Spectronus instruments. These measurements will be used for inverse modelling, as means of estimating CO_2 fluxes in the region. The aim is to monitor for atmospheric evidence of large fugitive emissions from the CO_2 sequestration site.

As a first step towards this, we have set up a system for forward simulations of CO_2 transport and dispersion. The transport model used is a modified version Community Multiscale Air Quality (CMAQ) model, from the US EPA [Byun and Schere, 2006], forced with meteorology from the Weather Research and Forecasting (WRF) numerical weather prediction model [Skamarock *et al*., 2005].

One key ingredient of these are estimating all major flux components. The Vegetation Photosynthesis and Respiration Model (VPRM, a simple terrestrial ecosystem model) is used to estimate the biosphere flux [Mahadevan *et al*., 2008]. Anthropogenic emissions are regridded from a high-resolution Fossil-Fuel Data Assimilation (FFDAS) dataset [Asefi-Najafabady *et al*., 2014]. Forest-fire emissions are based on the ECMWF's Global Fire Assimilation System (GFAS) dataset [Kaiser *et al*., 2009]. Oceanic CO_2 fluxes are estimated from the MACC/CAMS global CO_2 flux inversion [Chevallier *et al.*, 2010]; gridded concentrations from this inversion were used for initial and boundary concentration fields.

We compare simulated data with CO_2 and wind speeds measured at Cape Grim for January and July of 2014. The surface wind speed and direction were modelled very well, with correlations for the *U*- and *V*-components around 0.9. The modelled baseline CO_2 was fairly accurate, with a mean error below 1 ppm, however the model was less skilful at simulating deviations from the baseline; correlations were 0.43 in January and 0.35 in July. Departures from baseline were of greater amplitude in the measurements, and were out of phase in the the July runs.

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Aerosol properties across the southern polar front in summer

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Abstract

Aerosol measurements both north and south of the polar front in the Austral spring of 2012 show an order of magnitude step change in aerosol number concentrations across the Antarctic polar front [Humphries *et al.*, 2016], with those south of the front averaging over 1000 cm^{-3}. They postulated that this was due to the region being influenced by aerosols generated in the free troposphere that were being advected down. A return voyage to this region was made in the summer (February) of 2017 on the RV Investigator, with a more extensive range of aerosols measurements, including aerosol number concentrations and submicron size distributions. These measurements were augmented with a number of other instruments measuring trace gas species, including radon, an important tracer for atmospheric transport.

The results show interesting seasonal differences. The step change in number concentrations is virtually absent across the proposed frontal boundary, with similar aerosol number concentrations on both sides of the boundary. Despite this, there was evidence of free-tropospheric composition while crossing the atmospheric boundary. This is supported by the presence of a significantly different particle size distribution and elevated concentrations of radon-222 during the transitional period.

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Characterisation of LA-ICP-MS to measure, speciate and source apportion $PM_{2.5}$ in Garden Island, Western Australia

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Abstract

Airborne particulate matter (PM) has been observed to produce negative health impacts in humans [WMO, 2016; OECD, 2014]. However, these health impacts can vary depending on several factors, including their sources [Jalava et al., 2007; Pun *et al*., 2014]. As such, the source apportionment of PM is important to better identify the effects on health that different forms of PM produce. One approach is to determine its elemental composition, from which fingerprints of different sources can be characterised. Currently, this speciation of PM is not often conducted, partly due to analytical techniques being expensive and time-consuming.

One potentially low-cost, high-throughput alternative is Laser Ablation Inductively-Coupled Mass Spectrometry (LA-ICP-MS). This technique uses a UV laser to ablate a sample's particles to form an aerosol, which is then broken down into ions using the inductively-coupled plasma. The ions are then separated by mass/charge ratio by the mass spectrometer. As LA-ICP-MS has not been widely used to speciate PM, this project aims to identify a protocol to do so using this analytical technique. It should be noted that LA-ICP-MS requires a certified reference material (CRM) that is physically similar to the sample material to fully quantify detected elements. Given that there are currently no CRMs with similar ablation features to cellulose filter papers used for sample collection, therefore concentrations reported in this contribution are relative to the CRM glass used for calibration (NIST SRM 610).

Given that LA-ICP-MS involves scanning a small portion of the sample to approximate elemental concentrations, a key concern in employing this technique for PM speciation is that the sub-sampling may not resolve the full spatial heterogeneity of particles across a large filter paper. To better characterise these uncertainties, typical PM samples were examined under a Scanning Electron Microscope (SEM) to observe the spatial and size distributions of particles. The samples used in this experiment were of Total Suspended Particles (TSP) collected on Whatman41 cellulose filter papers using an Ecotech 3000 Hivol sampler over 20 days as part of the AIRBOX campaign in Garden Island, Western Australia between 20 April and 15 May 2018. Although the sampling regime was designed for the collection of TSP, the high proportion (> 80%) of $PM_{2.5}$ observed in the samples examined under the SEM means that the particles will be referred to in this contribution as $PM_{2.5}$.

Images taken using the SEM were analysed using a blob detection algorithm that distinguished individual particles, allowing for the determination of size and spatial distributions of particles on different sections of the filter paper. This information was then used to generate virtual samples that exhibited similar size and spatial distributions of particles to that observed on the filter paper. A simulated scanline was used to determine the amount of the virtual sample needed to be scanned to detect a representative proportion of its particles. However, this process assumes that the elemental composition of particles on the sample does not vary across particles of different sizes.

The ideal scan area derived from the virtual sample scanning was then used as the basis for sub-sampling of the physical samples using LA-ICP-MS. It was found that analysis using this technique was able to reflect atmospheric conditions of the sampling periods. For instance, high concentrations of elemental markers for smoke (e.g. K, S and Fe) were observed on a day when two bushfires occurred north-east of Perth as there were north-easterly winds. It has also been able to resolve approximate elemental concentrations, such as a near 1:1 ratio between Na and Cl that reflects the PM produced by sea spray.

Portions of these samples will also be analysed by a reference method of PM speciation, likely Digestion Inductively-Coupled Plasma Mass Spectrometry [Brown *et al*., 2010], to validate the results of the LA-ICP-MS analysis. Concentration values from LA-ICP-MS can then be applied in a factor analysis technique such as Positive Matrix Factorisation, which can identify elements in the samples that correlate strongly with each other to distinguish fingerprints for potential PM sources. This process will also be repeated for PM samples collected from an urban environment in Melbourne.

Acknowledgements

I would like to acknowledge the contribution of Joel Alroe in the collection of the Garden Island samples, as well as that of Graham Hutchinson and the TrACEES Platform in Earth Sciences at the University of Melbourne for the use of the SEM.

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Model-data fusion framework to constrain Australia's terrestrial carbon and water budgets

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Abstract

The Australian landscape is unique. It is characterised by large interannual variability in rainfall, and this drives significant variability in Australian carbon fluxes, particularly in semi-arid and savanna ecosystems. With its vast area, Australia also has significant carbon stocks. Here we constrain the CABLE terrestrial biogeochemical model for Australia at high spatial resolution (0.05°, approx. 5 km) with multiple observation types: carbon and water fluxes at OzFlux flux sites, carbon pool data, litter fall, biometric data, remotely-sensed vegetation cover, soil moisture and streamflow data. These observations are used either to constrain model parameters in a model-data fusion framework or to compare with model simulations. We generate multiple parameter sets to allow exploration of the effect on model results of parameter equifinality (whereby multiple combinations of parameters can give an equally acceptable fit to the calibration data).

CABLE used in this modelling environment is known as BIOS-3. Compared to the previous version [BIOS-2: Haverd *et al.*, 2013; Trudinger *et al.*, 2016], our model now contains a number of important enhancements, including demographic effects on biomass accumulation and turnover, and land-use and land-cover change, and is now constrained with additional observation types (biometric data and soil moisture).

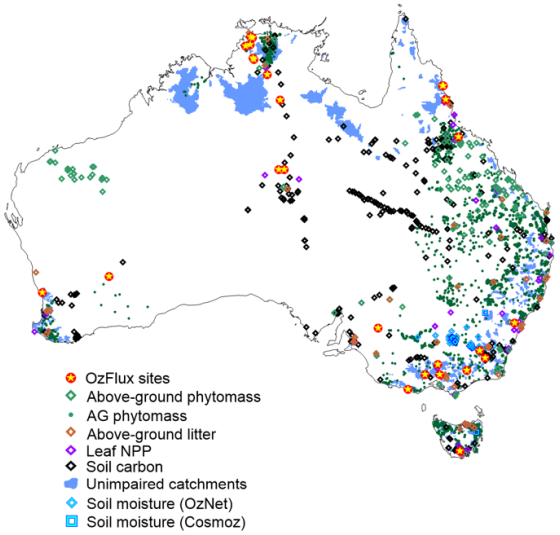


Figure 1. Observations used to constrain or compare with BIOS-3.

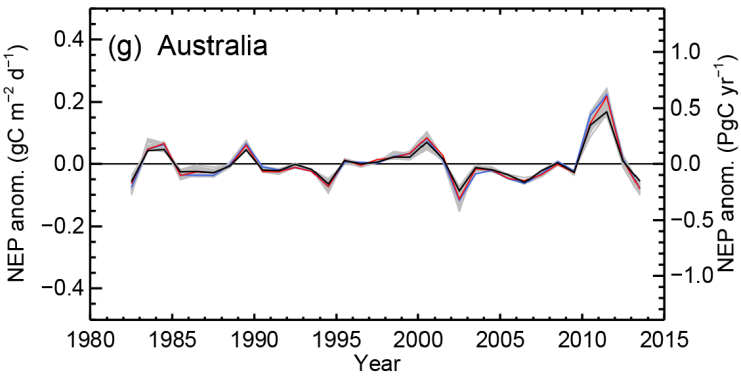


Figure 2. Annual net ecosystem production anomaly for Australia from BIOS-2 (positive values indicate uptake by the biosphere). The best case is shown in black, grey lines show results for the parameter ensemble, and blue and red show results for alternative model structural choices. A high anomaly in 2010-11 is associated with strong C uptake during exceptionally wet conditions following prolonged drought.

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Regional inverse modelling for the estimation of CO_2 fluxes in Australia using satellite observations from the Orbiting Carbon Observatory–2 (OCO-2)

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Abstract

Climate change projection depends mainly of the amount carbon dioxide in the atmosphere. Ocean and terrestrial biosphere play an important role in the climate through the carbon-cycle feedback, since they can maintain in balance the accelerating emissions caused by human activities. Therefore, understanding and Quantifying the carbon cycle fluxes is relevant for understanding the future climate change. Despite the efforts of terrestrial and ocean models to simulate CO_2 fluxes over land and ocean, there remain large uncertainties over its quantification, especially at regional scale. Inverse modelling based on atmospheric CO_2 observations has been proved to be a method that can improve the accuracy of CO_2 fluxes estimated by either biosphere or ocean models over places with high-density data. Satellite-based space observations offer an alternative to constrain CO_2 surface fluxes in places lacking ground-based measurements. In this study, we propose to use regional inverse modelling technique to quantify CO_2 surface fluxes over Australia using satellite data retrieved from the Orbiting Carbon Observatory-2 (OCO-2). The technique uses a Bayesian variational assimilation technique (4DVAR) and the application of a regional chemical transport model called CMAQ and its adjoint. We will present the information content of OCO-2 measurements for constraining hourly fluxes over Australia and a preliminary retrieval with real data. This research will allow us not only to reduce the uncertainties observed over CO_2 surface fluxes over Australian continent, but also to understand the recent anomalies that the terrestrial carbon sink has experienced in the last years in Australia.

Evaluation of aerosol representation by ACCESS-UKCA in the Southern Ocean

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Abstract

Aerosols play a significant role in the Earth's climate through interaction with radiation and cloud processes, by scattering and absorbing radiation, and altering cloud albedo. The Southern Ocean (SO) is an under-studied region of climatic significance dominated by natural aerosols. These aerosols contribute to the largest uncertainties in radiative forcing estimates. Hence, it is important to increase understanding of how effectively these are represented in Global Climate Models (GCMs).

Modelling the SO has proven difficult for GCMs due to a lack of observational data and complex atmospheric processes, resulting in significant biases in the simulated radiation budget. While consensus is yet to be reached on the sources of these biases, aerosol and clouds have been identified as playing a key role.

In this study we investigate the representation of aerosols in the Australian Community Climate and Earth System Simulator (ACCESS). A version of this model, ACCESS-UKCA, incorporates the detailed microphysical aerosol scheme GLObal Model of Aerosol Processes- mode (GLOMAP-mode), which simulates aerosol size distribution through a suite of microphysical processes including; aerosol nucleation, coagulation, cloud processing and condensation. There is limited literature in evaluating aerosol properties in ACCESS-UKCA, particularly against below-cloud measurements in the Southern Ocean.

ACCESS-UKCA was run from years 2000-2009 with meteorology nudged to ERA-Interim at 6-hourly intervals and a resolution of 1.25° latitude by 1.85° longitude [Fiddes, 2018]. The gridded monthly Aerosol Optical Depth (AOD) model output at 550nm was compared with MACC (Monitoring Atmosphere Composition and Climate) reanalysis. ACCESS-UKCA model data was compared with AOD data at Cape Grim (TAS) and Lauder (NZ), and analysed for bias and representation of sub-annual cycles. Additionally, AOD data gathered on research voyages in the Southern Ocean was compared against model AOD output. Time series AOD collected from the model and monitoring stations have been evaluated against satellite data to determine discrepancies in aerosol representation. This study indicates that whilst ACCESS-UKCA captures seasonal variability, the model exhibits an underestimation of AOD in the Southern Ocean, suggesting a lacking representation of aerosols in the area.

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Vibrationally excited products of roaming reactions in the atmosphere as a novel source of hydroxyl radicals

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Abstract

Hydroxyl (OH) and hydroperoxyl (HO_2) radicals are the most important radicals in the atmosphere. Reaction with OH is the dominant mechanism for the removal of most volatile organic compounds (VOCs) [Heard and Pilling, 2003]. Atmospheric models can both over- and under-predict the concentration of these radicals in various regions, sometimes by large margins. For example, OH production is observed to be an order of magnitude higher than modelled in region of very high isoprene [Stone *et al*., 2012]. HO_2 is found to be under-predicted in very polluted regions [Stone et al., 2012]. Discrepancies in the concentrations of these radicals, as predicted by atmospheric models, has led to unknown reactions of carbonyls being suggested as a possible missing source of these radicals [Romero *et al*., 2005].

Roaming photodissociation mechanisms such as those exhibited by formaldehyde (H_2CO) and acetaldehyde (CH_3CHO) produce H_2 and CH_4 photofragments that are exceptionally hot [Bowman and Shepler, 2011]. The amount of internal energy is sufficient to overcome the usually prohibitive 230 kJ/mol barrier to reactions with atmospheric O_2. Our hypothesis is that these hot roaming fragments will react with O_2, where they will form the hydroperoxyl (HO_2) radical, along with H-atoms or CH_3 radical co-products, both of which form further peroxy radicals

Using velocity map imaging (VMI) and continuous wave cavity ring down spectroscopy (cw-CRDS) techniques, the reactivity of these hot fragments towards O_2 are being investigated, with a particular focus on reaction energetics and rates. If this research is successful, roaming reactions may be able to account for at least some of the incongruous levels of OH and HO_2 in the atmosphere, and provide a missing mechanism of the dynamics of these radicals in these environments.

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Increasing hydrogen use: effects on global atmospheric chemistry

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Abstract

As the world comes to terms with its carbon addiction, an inevitable transition from burning of fossils fuels to other energy sources will occur. This transition will require new mechanisms to move and store energy, with one possibility being hydrogen. Increasing use of hydrogen as an energy vector will lead to additional release of hydrogen to the atmosphere due to the unintended release of hydrogen during its manufacture, transport, storage, and use. Possibilities for hydrogen use include shipping, land transport, electricity use and distribution.

The effect of increased concentrations of atmospheric H_2 (molecular hydrogen), NH_3 (ammonia) and CH_3OH (methanol) on atmospheric constituents, and subsequently climate, are not well quantified and may become significant as the hydrogen economy grows. Here, the ACCESS-UKCA global composition-climate model is used to simulate the impacts of increased fluxes (and hence increases in concentration) of NH_3 and CH_3OH on key climate-relevant atmospheric constituents such as OH (hydroxyl), and O_3 (ozone).

In ACCESS-UKCA, we find that a modest increase of emissions of NH_3 and CH_3OH results in regionally and locally significant increases in these species. The subsequent impacts on atmospheric oxidative capacity are globally negligible for the scenario tested, however there are locally significant differences. These local and regional effects may impact air quality, and merit further investigation.

One significant uncertainty is the size of the contribution that hydrogen will make to the energy mix in the future, both regionally and globally. Thus it is difficult to specify the changes in emissions that are necessary to conduct these kinds of simulations. This uncertainty is a fundamental constraint on our ability to understand the impact on atmospheric composition of a transition to a hydrogen-based economy.

The Cape Grim sea-salt record revisited

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Abstract

The Cape Grim program boasts a record of the soluble ion composition of coarse and fine particles that extends back to 1986. Samples have been collected weekly under baseline conditions and the chemical composition record and associated archive of filters house a wealth of information yet to be fully explored.

A recent assessment of the baseline sea-salt record derived from these filters concluded that due to differences in the size selective inlets on the high volume samplers used to collect these samples over time, the nearly 30-year record is comprised of three shorter records (i.e. 1978-1988; 1989-2001; 2002-present), thus rendering the dataset less than optimal for analysis of trends in sea-salt concentrations [Keywood, 2014].

This conclusion will be reassessed in this presentation. Using size-resolved soluble ion composition data collected during the summer of 2004 we are able to correct significant parts of the high volume sampler record to PM10, thus creating a continuous sea-salt record for 1990-2017. Using this record the climatology of sea-salt at Cape Grim over 27 years will be presented.

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Measurements of sea spray aerosol in the Southern Ocean

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Abstract

Due to their inherent hygroscopicity and size, wind/wave generated sea salt aerosol (SSA) act as a significant contributor to the population of cloud condensation nuclei and the aerosol optical depth in the marine boundary layer (MBL). Aerosol models, like GLOMAP-mode, calculate SSA fluxes according to the Gong-Monahan equation, which scales SSA fluxes according to the fractional coverage of sea surface white-caps [Mann *et al*., 2010]. At present, the fractional coverage of sea surface white-caps is parameterized as a function of the 10 m wind-speed, with parameters constrained from the observations of Monahan & O'Muircheartaigh, 1980. A recent satellite imagery study by Albert et al., however, has suggested that while the wind-speed dependence observed by Monahan & Ó'Muircheartaigh is accurate for calm winds (<10 m/s), it is too strong in high wind conditions and may be leading to over-predictions of SSA [Albert *et al*., 2016]. Among the windiest places on earth's surface, this could lead to a strong model bias in SSA concentrations over the Southern Ocean [Albert *et al*., 2016].

In order to elucidate a better understanding of the relationship between SSA concentrations and wind speed in the MBL, we will present concentrations of aerosol measured during a recent voyage to the Ross Sea aboard the *R/V Tangaroa*. These measurements will be compared to model calculations of SSA derived from the Gong-Monahan equation and source-receptor calculations from the Lagrangian particle dispersion model, FLEXPART-WRF. Over the course of the experiment, we found that our observations were best reproduced by a model of SSA flux which incorporated the wind-speed dependence of Albert *et al*. Our *in situ* observations also suggest that the lifetime of these aerosol is much shorter than is currently modelled within FLEXPART-WRF.

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Detecting non-sea salt, biogenic/anthropogenic atmospheric aerosol contributions and mixing above the Great Barrier Reef, using optical laser particle sizing

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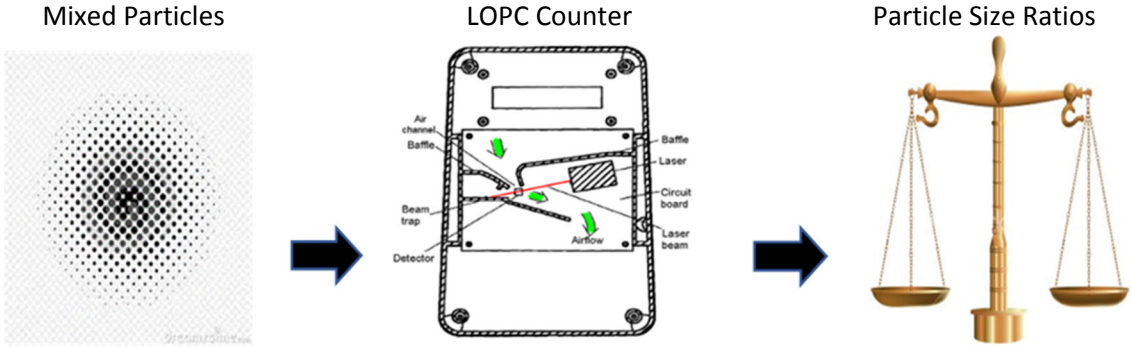
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Abstract

We have used the particle (aerosol) number ratio from inexpensive dual channel 0.5 < d_p < 2.5µm and d_p > 2.5µm (d_p – particle diameter) optical laser particle counters to detect atmospheric variations in the planetary boundary layer (PBL) and marine/terrestrial aerosol contributions at coastal sites adjacent to the Great Barrier Reef (GBR). By monitoring these two size ranges, we can resolve the sea salt contributed aerosol signal. Radon (^{222}Rn) and back trajectories were used to establish air mass histories. This provides a methodology for the measurement of non-sea salt marine and continental aerosols d_p > 0.5µm that either intrude into the lower marine boundary layer (MBL) or evolve into the d_p > 0.5µm size range increasing their contribution to the accumulation mode aerosol population. Results from both coastal and island GBR sites confirm that the ratio of small-to-large wind-generated sea salt aerosols is constant, enabling the size ratio to detect aerosol intrusions to the PBL either within the PBL or from the MBL. Potential aerosol size ratio variations within the PBL include those from shipping, natural photo aerosol production and continental intrusions of aerosols. Single channel aerosol results indicate a nocturnal increase in surface sea salt concentration attributed to thermal constriction of the MBL (reduction in mixing volume) over the GBR surface mixed zone with implications for surface measurements. The ratio of the small to the large aerosols increases in close association with solar insolation. On a diel scale, proportioning of the day time aerosol size ratio variations between small aerosol production and solar driven lower boundary layer mixing could not be resolved. Seasonally, the ratio of the two aerosol sizes varies in close association with dimethylsulfide, reinforcing the suggested role of DMS as a major contributor to the reef background aerosol.



Cloud brightening studies over the Great Barrier Reef using WRF-Chem

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Abstract

One of the seven wonders of the natural world, the Great Barrier Reef (GBR) is a breathtaking beauty of the world's largest coral reef. Like many ecosystems around the world, climate change is having adverse effects on the GBR with severe coral bleaching events having occurred in the last two consecutive years.

In order to offset the surface temperature increase due to increased greenhouse gas forcing, Latham (1990) proposed a geo-engineering method popularly referred to as marine cloud brightening (MCB). MCB deliberately increases the reflectivity of clouds with addition of cloud condensation nuclei (CCN) through increased emissions of sea-salt delivered via ships. The additional CCN has the potential to increase cloud albedo (the Twomey effect) and/or lifetime (Albrecht effect).

Here, in this study, we present preliminary results of a modelling study of the feasibility of localised MCB as a mitigation methodology for coral bleaching on the GBR, the idea of which was first explored by Harrison (2018). Using the Weather Research and Forecasting Chemistry model (WRF-Chem), we simulate the change in cloud albedo for model simulations with different sea-salt fluxes from various 'stations' around the GBR. The simulated data will eventually be used as input into a biogeochemical model (eReefs) which will be used to study impact of increased MCB on the coral health.

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Identifying coral reef-derived atmospheric dimethylsulfide

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Abstract

The global oceans are the major source of atmospheric dimethylsulfide (DMS_a) derived from sea-to-air transfer, which is estimated to annually account for 28.1 Tg (range 17.6 – 34.4) of sulfur [Lana *et al*., 2011]. Phytoplankton is recognised as the major biogenic source of this oceanic-derived DMS_a, which, via its atmospheric oxidation products, can contribute to the pool of cloud condensation nuclei, and alter the microphysical properties of marine clouds to enhance their albedo [Ayers and Gillett, 2000]. Coral reefs are indicated to be another source of DMS_a; however, convincing environmental evidence of this has been lacking due to the difficulty of distinguishing coral reef DMS_a source contributions from the oceanic-derived DMS_a background signal using low frequency grab-sampling. In order to examine short-term variability of DMS_a at a coral reef location, an automated gas chromatograph was constructed and validated for deployment to the Heron Island Research Station on the southern Great Barrier Reef [Swan *et al*., 2015]. The instrument had a cycle time of 30 minutes and was continuously operated for 2-3 week periods during the 2012 wet season (March) and the 2013 dry season (July-August). In conjunction with meteorological, tidal, and air mass back-trajectory observations, it was possible, with this instrument, to observe occasional plumes of DMS_a that were strongly indicated to originate from the coral reef. These plumes were detected as chromatographic spikes above the oceanic DMS_a background continuum signal. The DMS_a spikes were highly variable irregular events generally occurring at low tide when conditions exist that can stress the coral reef (e.g. Figure 1). In most instances, the low tide DMS_a spikes were detected under low wind speeds of <2 m s^{-1} when dilution from the prevailing SE trade winds was least. The majority of these DMS_a spikes were indicated to originate from the lagoonal platform reef surrounding the island, although evidence of longer range transport of DMS_a from a 70 km stretch of coral reefs to the SE of Heron Island was also obtained under higher wind speeds. During the 2013 dry season campaign, a direct relationship between low water tide height (-0.1 to 0.8 m) and DMS_a mixing ratio was demonstrated (Figure 2). During this season the most intense DMS_a spike was detected when precipitation from a short convection-generated storm fell onto the aerially exposed coral reef at low tide. This co-occurrence of events appeared to biologically shock the coral resulting in a seasonally aberrant extreme DMS_a spike concentration of 45.9 nmol m^{-3} (1122 pmol mol^{-1}) above a steady 1.0-1.5 nmol m^{-3} (24-37 pmol mol^{-1}) background DMS_a signal. Seasonal DMS emission fluxes for the 2012 wet season and 2013 dry season campaigns at Heron Island were estimated using a photochemical/mass balance box model previously applied by Ayers *et al*. [1995] at Cape Grim. Fluxes for the 2012 wet and 2013 dry seasons were estimated to be 5.0 and 1.4 µmol m^{-2} d^{-1}, respectively, of which the coral reef was estimated to contribute 4 % during the wet season and 14 % during the dry season to the dominant oceanic flux [Swan *et al*., 2017]. To support this abstract of information, the circumstances surrounding specific instances of DMS_a spikes indicated to originate from the coral reef during the 2012 and 2013 field campaigns at Heron Island will be presented.

Figure 2 shows median DMS_a mixing ratios over the low tide height range that allows the coral reef to be aerially exposed. The median values were derived from DMS_a measurements made ~1 h either side of low tide for the entire dataset (n = 923). The low water tidal level controls the extent and duration of coral reef aerial exposure, which was shown to have a direct relationship to the DMS_a mixing ratio at Heron Island on the southern Great Barrier Reef.

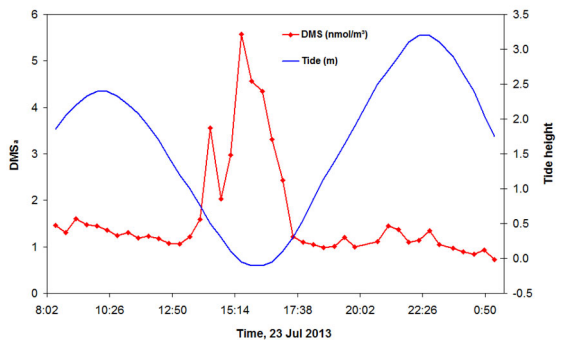


Figure 1. Time-line magnification of a -0.1 m low tide induced DMS_a spike from the Heron Island fringing coral reef on 23 July 2013 between 13:31 and 17:28

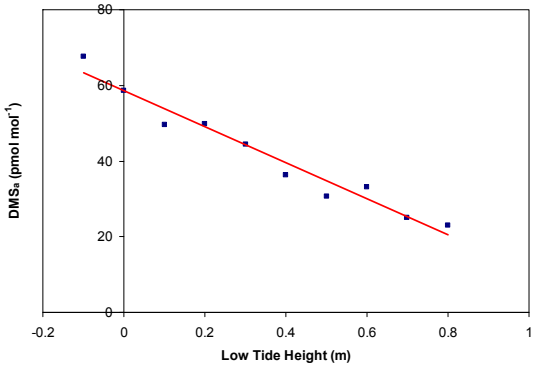


Figure 2. Median DMS_a mixing ratios plotted against low tide seawater height for the Heron Island dry season dataset 18 July to 5 August 2013

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Atmospheric DMS, methanethiol and acetone over the South West Pacific during the SOAP voyage

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Abstract

Atmospheric concentrations of dimethyl sulfide (DMS), methanethiol (MeSH) and acetone are reported from the Surface Ocean Aerosol Production (SOAP) voyage in the South West Pacific during the Austral summer of 2012. DMS and MeSH are the two main products of dimethylsulfoniopropionate (DMSP) degradation however there are few measurements of atmospheric MeSH over the ocean. A PTR-MS instrument was used to measure m/z 63 (DMS), m/z 49 (MeSH) and m/z 59 (acetone) during the voyage. Very high concentrations of DMS were observed with concentrations close to 1 ppb. DMS and MeSH atmospheric concentrations correlated throughout the voyage, and diurnal cycles of DMS and MeSH showed similar behaviour with the lowest concentration in mid-afternoon, likely due to photochemical destruction. The DMS diurnal cycle shows similar behaviour to historical DMS measurements at Cape Grim, Tasmania, but with higher concentrations (factor of 2-4 times higher). Acetone and DMS atmospheric concentrations correlated during phytoplankton bloom 1. Ocean sources of atmospheric DMS, MeSH and acetone are explored by correlating atmospheric measurements with seawater biogeochemical parameters such as dominant phytoplankton type, dissolved CO_2, pH, Chlorophyll *a* and mixed layer depth. Finally, the MeSH sea-air flux during the voyage is estimated.

COALA-JOEYS – Characterising Organic Aerosol Loading in Australia – Joint Organic Emissions Year-long Study

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Abstract

The Joint Organic Emissions Year-long Study (JOEYS) is one of three planned projects under the umbrella campaign COALA (Characterising Organic Aerosol Loading in Australia). In this talk, the progress so far within JOEYS will be outlined, including a description of the measurement program at ANSTO and the trial measurements made at Cataract Scout Camp with the AIRBOX. It is hoped that this talk will lead to a discussion of how best we can collaborate to maximise the benefits from both JOEYS and the larger opportunities that will come from the full COALA campaign.

Performance and deployment of low cost sensor SMOG units

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Abstract

Particles in the atmosphere are a leading cause of asthma and other respiratory and/or cardiovascular health problems. Urbanisation, prescribed burns and bushfires are often a significant source of fine particles resulting in poor air quality. Emerging sensor technology is opening up opportunities to monitor air quality on a much larger scale and engaging communities in the conversation of air quality impacts around their area.

The SMoke Observation Gadget (SMOG) is a unit that comprises a Plantower Laser $PM_{2.5}$ dust sensor PMS3003 and a digital temperature and humidity sensor. The Plantower dust sensor provides continuous measurements of particle concentrations for PM_1, $PM_{2.5}$ and PM_{10}. The sensors are interfaced via a printed circuit board (PCB) to a microcontroller, a Raspberry Pi Model 3B (RPi). All components are housed in a waterproof enclosure to facilitate outdoor deployment. Figure 1 shows an assembled SMOG unit.

A total of 28 SMOG units were tested at Aspendale laboratories in February/March 2018. In May/June 2018, the SMOG units were deployed to Northeast Victoria to capture smoke plume events due to prescribed burns and stubble burns. Two SMOG units were co-located at 15 locations in the Hume region.

The results showed high correlations between individual SMOG units for $PM_{2.5}$ concentrations (R=0.93-0.99) with higher variability observed for PM_{10} concentrations (R=0.52-0.99). Correlations of the SMOG units with E-samplers were more moderate (r^2 = 0.65–0.83). SMOG units followed the $PM_{2.5}$ concentration trends of the co-located E-samplers, indicating that the response time of the SMOG units is comparable to that of the E-samplers and that peaks are captured correctly. Overall the SMOG units overestimate $PM_{2.5}$ concentrations, and seem to level off at high $PM_{2.5}$ concentrations.



Figure 1. Assembled SMoke Observation Gadget (SMOG)

Using Cape Grim data in a Year 11 Programming Course

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Abstract