Atmospheric Composition & Chemistry Observations & Modelling Conference

incorporating the

Cape Grim Annual Science Meeting 2017

Abstracts

8-10 November 2017

hosted by

University of Wollongong

Murramarang Beachfront Nature Resort
South Durras, NSW, Australia



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

Citation

Author, A. B., A. B. Author and A. B. Author, Abstract Title, in Atmospheric Composition & Chemistry Observations & Modelling Conference incorporating the Cape Grim Annual Science Meeting 2017 [abstract], 8-10 November 2017, Murramarang, NSW, N. Derek and P. B. Krummel (eds.), Bureau of Meteorology and CSIRO Oceans and Atmosphere, Climate Science Centre, Melbourne, Australia, page#, 2017.

Day 1: Wednesday, 8 November 2017

12:00	**Lunch**	**Poolside**
13:00	**Convenors**	**Welcome & general information on arrangements etc**
Chair	**Clare Paton-Walsh**	**Session 1 – Joint session with IGAC SSC**
13:10	Hiroshi Tanimoto	The International Global Atmospheric Chemistry (IGAC) Project and the IGAC Monsoon Asia and Oceania Networking Group (MANGO)
13:25	Jenny Fisher	Alkyl nitrates distribution and impacts constrained by aircraft observations and chemical transport modelling
13:40	Kathryn Emmerson	The Australian Biogenic Canopy and Grass Emissions Model
13:55	Paul Krummel	The 2017 Antarctic ozone hole
14:10	Judith Hoelzemann	Studying the transport of Saharan dust and sub-Sahelian biomass burning particles over South America by ground- and satellite based Lidar aerosol retrievals in the region of northeast Brazil
14:25	Robyn Schofield	Working towards a Southern Hemisphere observations data network - SHACCQ
14:40	**Afternoon Tea**	**Poolside**
Chair	**Paul Krummel**	**Session 2 – Oral Presentations**
15:10	Paul Fraser	Short-lived chlorocarbons: multiple threats to ozone layer recovery
15:25	Brian Vasel	Changes in the NOAA Atmospheric Baseline Observatory Network
15:40	Alastair Williams	Seasonal variations in 'deep baseline' radon over the Southern Ocean
15:55	Scott Chambers	Characterising tropospheric influences near coastal Antarctica with ^{222}Rn
16:10	Michael Harvey	Clouds and aerosols: Ship observations targeting Southern Ocean processes
16:25	Ruhi Humphries	Southern Ocean aerosols – a seasonal perspective from Macquarie Island
16:40	Paul Beukes	An overview of activities of the Atmospheric Chemistry Research Group, South Africa – possibilities for collaboration with the Australian atmospheric research community
16:40	**End of Day 1**	
19:00	**Dinner**	**Beach Bistro**

Day 2: Thursday, 9 November 2017

08:00	**Breakfast**	**Beach Bistro (to 09:00)**
Chair	**Jenny Fisher**	**Session 3 – Oral Presentations**
09:00	Melita Keywood	Cape Grim Multiphase Atmospheric Chemistry (MAC) sub-program: review
09:30	Peter Nelson	Shipping emissions in the ports of Tianjin and Qingdao and their contributions to air quality
09:45	Clare Paton-Walsh	The western air-shed particulate study for Sydney – a project of the Clean Air and Urban Landscapes Hub
10:00	Elise-Andrée Guerétte	An update on the evaluation of regional air quality models over Sydney, Australia
10:15	Steven Utembe	Hot summers: effect of elevated temperatures on air quality in Sydney in 2013
10:30	**Morning Tea**	**Poolside**
Chair	**Zoë Loh**	**Session 4 – Oral Presentations**
11:00	Doreena Dominick	Particles observation during MUMBA campaign
11:15	Erin Dunne	Design of a study to measure air quality during hydraulic fracturing operations in the Surat Basin, Queensland
11:30	Sarah Lawson	Coal seam gas and air quality in the Surat Basin, Queensland: update from the monitoring program
11:45	Christopher Roulston	Reduction in particulate emission factors as peat burns progress and age due to generation of a filtering ash layer
12:00	Fabienne Reisen	Evaluation of black carbon aerosols at Cape Grim: Seasonal trends and potential sources
12:15	Jesse Greenslade	Isoprene emissions estimates inferred from OMI over Australia
12:30	**Lunch**	**Poolside**
Chair	**Kathryn Emmerson**	**Session 5 – Oral Presentations**
13:30	Gabriel da Silva	Isomerization and decomposition chemistry of isoprene hydroxy nitrates
13:45	Tao Wang	Field observations of N_2O_5 and $ClNO_2$ in southern and northern China
14:00	Scott Kable	Photochemical production of H_2 from aldehydes

14:15	Meredith Jordan	Atmospheric photochemistry - getting to the ground state
14:30	Grant Edwards	An update on the Cape Grim mercury measurements 2013 to present
14:45	Neil Page	Using observations and modelling to quantify mercury biogeochemical cycling in the Australian context

Day 2: Thursday, 9 November 2017 – Poster Session

Chair	**Ruhi Humphries**	**Session 6 – Poster Session**
15:00	Poster summaries	Each presenter to give a 1-2 minute, 1-slide poster summary
15:30	**Afternoon Tea**	**Includes Posters**
Kellie Cook		A comparative analysis of Reactive Mercury measurements using two methodologies and environmental correlates in an urban setting
Maggie Corrigan		Intersystem crossing in carbonyl compounds
Ian Galbally		Measurements of nitrogen oxides (NO_x) in the air at Cape Grim: recent activities
Alan Griffiths		The uncertainty balance between radon emissions and model simulations
Alan Griffiths		Radon tracer flux measurements of CO_2, N_2O and CH_4 in an agricultural region
Ruhi Humphries		Exhaust identification on the RV Investigator
Katrina Macsween		Reconsidering mercury emissions from Australian biomass burning
Matthieu Miller		Update on atmospheric reactive mercury concentrations at the Cape Grim Baseline Air Pollution Station and Macquarie University
Frances Phillips		Open path FTIR spectroscopy to measure gaseous species relevant to urban air quality
Robert Ryan		Vertically resolved pollution monitoring in Melbourne using MAX-DOAS measurements
Jack Simmons		Aerosol number concentrations crossing the polar front off east Antarctica
Yohanna Villalobos		Inverse modelling of CO_2 surface fluxes over Australia inferred from OCO-2 XCO2 satellite retrievals
Blair Welsh		Photolytic production of H_2 from aldehydes
Matthew Woodhouse		A new mechanistic parameterisation for dry deposition of ozone to the ocean, and revised oceanic and global deposition estimates
17:30		**End Day 2**
19:00	**Dinner**	**Beach Bistro**

Day 3: Friday, 10 November 2017

08:00	**Breakfast**	**Beach Bistro (to 09:00)**
Chair	**Matthew Woodhouse**	**Session 7 – Oral Presentations**
09:00	Ian Galbally	Tropospheric Ozone Assessment Report: Global metrics for climate change, human health and crop/ecosystem research – results from a global collaboration
09:15	Stephen Wilson	SRAD2 – the new UV-B spectrometer system at Cape Grim
09:30	Zoë Loh	An update on comparisons of *in situ* carbon dioxide and methane measurements at Cape Grim
09:45	Chris Perrella	Real-time accurate optical measurements of CO_2 number density
10:00	Beata Bukosa	The imprint of ENSO on total column greenhouse gas measurements
10:15	Lingxi Zhou	Estimated ratios of GHG emissions observed over the Yellow Sea and the East China Sea during a spring 2017 cruise
10:30	**Morning Tea**	**Poolside**
Chair	**Fabienne Reisen**	**Session 8 – Oral Presentations**
11:00	David Thornton	Measurements of gases in ice at Patriot Hills, West Antarctica
11:15	Ray Langenfelds	Air archiving: recent research and operational developments
11:30	Paul Fraser	Carbonyl sulfide (COS) pollution at Aspendale: what are the local sources?
12:00	**Lunch**	**Poolside – End of meeting, safe travels, we hope you enjoyed Murramarang**

Day 1 – Wednesday, 8 November 2017

Session 1 – Joint session with IGAC SSC

The International Global Atmospheric Chemistry (IGAC) Project and the IGAC Monsoon Asia and Oceania Networking Group (MANGO) – H. Tanimoto, K. Oanh, M. Naja, M. G. Lawrence and M. L. Melamed 1

Alkyl nitrates distribution and impacts constrained by aircraft observations and chemical transport modelling – J. A. Fisher, E. L. Atlas, D. Blake, C. Thompson, T. Ryerson, J. Peischl, Z. A. Tzompa-Sosa and L. T. Murray 2

The Australian Biogenic Canopy and Grass Emissions Model – K. M. Emmerson, M. E. Cope, I. E. Galbally, S. Lee and P. F. Nelson 3

The 2017 Antarctic ozone hole – P. B. Krummel, P. J. Fraser, A. R. Klekociuk, M. B. Tully and N. Derek 4

Studying the transport of Saharan dust and sub-sahelian biomass burning particles over South America by ground- and satellite based Lidar aerosol retrievals in the region of Northeast Brazil – J. J. Hoelzemann, F. J. S. Lopes, A. G. Guedes, E. Landulfo, M. P. A. Silva, R. S. S. Santos, J. L. Guerrero-Rascado and L. Alados-Arboledas 5

Working towards a Southern Hemisphere observations data network - SHACCQ – R. Schofield 7

Session 2 – Oral Presentations

Short-lived chlorocarbons: multiple threats to ozone layer recovery – P. J. Fraser, B. L. Dunse, B. Mitrevski, P. B. Krummel, L. P. Steele, N. Derek, M. Rigby and X. Fang 8

Changes in the NOAA Atmospheric Baseline Observatory Network – B. A. Vasel 9

Seasonal variations in 'deep baseline' radon over the Southern Ocean – A. G. Williams, S. D. Chambers, A. D. Griffiths, Z. M. Loh and P. B. Krummel 10

Characterising tropospheric influences near coastal Antarctica with ^{222}Rn – S. D. Chambers, R. S. Humphries, A. G. Williams, S. Preunkert, Z. M. Loh, P. B. Krummel, A. D. Griffiths, I. E. Galbally, S. B. Molloy, R. Weller and I. Levin 11

Clouds and aerosols: ship observations targeting Southern Ocean processes – M. J. Harvey, A. J. McDonald, O. Morgenstern, L. T. Cravigan, S. Hartery, P. Kuma, S. J. Lawson, S. Parsons, J. A. McGregor, A. Shuddeboom, V. Varma and J. Williams 13

Southern Ocean aerosols – a seasonal perspective from Macquarie Island – R. S. Humphries, M. D. Keywood, J. P. Ward, J. N. Harnwell, G. Brettingham-Moore, E. W. Crocker and S. Alexander 14

An overview of activities of the Atmospheric Chemistry Research Group, South Africa – possibilities for collaboration with the Australian atmospheric research community – J. P. Beukes and P. G. van Zyl 15

Day 2 – Thursday, 9 November 2017

Session 3 – Oral Presentations

Cape Grim Multiphase Atmospheric Chemistry (MAC) sub-program: review – M. D. Keywood, F. Reisen, P. W. Selleck, J. C. Powell, R. W. Gillett, J. P. Ward and G. C. Edwards 16

Shipping emissions in the ports of Tianjin and Qingdao and their contributions to air quality – D. Chen, X. Wang, P. F. Nelson, Y. Li, N. Zhao, Y. Zhao, J. Lang, Y. Zhou and X. Guo 17

The Western Air-Shed Particulate Study for Sydney – a project of the Clean Air and Urban Landscapes Hub – C. Murphy (Paton-Walsh), F. A. Phillips, T. Naylor, E.-A. Guérette, S. R. Wilson, D. Dominick, H. Forehead, P. Perez, I. Wadlow, A. Kuhar, L. Spicer, J. Xu, K. Sneesby, S. Beaupark, O. Gendek, J. Kirkwood, M. Riley, Y. Scorgie, J. Silver and P. J. Rayner 18

An update on the evaluation of regional air quality models over Sydney, Australia – E.-A. Guérette, K. Monk, S. R. Utembe, J. D. Silver, K. M. Emmerson, A. D. Griffiths, H. Duc, L. Tzu-Chi Chang, T. Trieu, N. Jiang, Y. Scorgie, M. E. Cope, C. Paton-Walsh and P. J. Rayner 19

Hot summers: effect of elevated temperatures on air quality in Sydney in 2013 – S. R. Utembe, E.-A. Guérette, J. Silver, P. J. Rayner and C. Murphy 21

Session 4 – Oral Presentations

Particles observation during MUMBA Campaign – D. Dominick, S. R. Wilson, N. B. Jones, C. Paton-Walsh, R. S. Humphries, E.-A. Guérette, M. D. Keywood and B. Marwick 22

Design of a study to measure air quality during hydraulic fracturing operations in the Surat Basin, Queensland – E. Dunne, M. D. Keywood, J. C. Powell, P. W. Selleck and J. P. Ward 23

Coal seam gas and air quality in the Surat Basin, Queensland: update from the monitoring program – S. J. Lawson, J. C. Powell, M. F. Hibberd, M. Cheng, P. W. Selleck, E. Dunne, M. D. Keywood, J. N. Harnwell, J. A. Noonan and D. M. Etheridge 26

Reduction in particulate emission factors as peat fires progress and age due to generation of a filtering ash layer – C. T. Roulston, C. Murphy and T. E. L. Smith 27

Evaluation of black carbon aerosols at Cape Grim: seasonal trends and potential sources – F. Reisen, J. L. Gras, J. P. Ward and M. D. Keywood 28

Isoprene emissions estimates inferred from OMI over Australia – J. Greenslade, J. A. Fisher and L. Surl 29

Session 5 – Oral Presentations

Isomerization and decomposition chemistry of isoprene hydroxy nitrates – G. da Silva 30

Field observations of N_2O_5 and $ClNO_2$ in southern and northern China – T. Wang and the study team 31

Photochemical production of H_2 from aldehydes – A. Harrison, M. Shaw, A. Kharazmi, M. J. T. Jordan and S. H. Kable 32

Atmospheric photochemistry - getting to the ground state – M. J. T. Jordan, M. Corrigan, B. Nikoobakht and S. H. Kable 33

An update on the Gape Grim mercury measurements 2013 to present – G. C. Edwards, M. D. Keywood, D. A. Howard, M. B. Miller, M. S. Gustin and J. C. Powell 34

Using observations and modelling to quantify mercury biogeochemical cycling in the Australian context – N. Page, J. A. Fisher, I. Dion, G. C. Edwards, D. A. Howard, P. Nelson, A. Morrison, M. D. Keywood and L. Martin 35

Session 6 – Poster Presentations

A comparative analysis of reactive mercury measurements using two methodologies and environmental correlates in an urban setting – K. Cook, M. B. Miller and G. C. Edwards 36

Intersystem crossing in carbonyl compounds – M. Corrigan, B. Nikoobakht and M. J. T. Jordan 37

Measurements of nitrogen oxides (NO_x) in the air at Cape Grim: recent activities – I. E. Galbally and S. B. Molloy ..... **Error! Bookmark not defined.**

The uncertainty balance between radon emissions and model simulations – A. D. Griffiths, S. D. Chambers, and A. G. Williams 39

Radon tracer flux measurements of CO_2, N_2O and CH_4 in an agricultural region – A. D. Griffiths, D. W. T. Griffith, S. R. Wilson, S. D. Chambers, A. G. Williams, S. Werczynski, O. Sisoutham, J. Howitt, D. Reardon and R. Leuning 40

Exhaust identification on the RV Investigator – R. S. Humphries, I. McRobert, W. Ponsonby, J. P. Ward, M. D. Keywood, Z. M. Loh, P. B. Krummel and J. N. Harnwell 41

A new mechanistic parameterisation for dry deposition of ozone to the ocean, and revised oceanic and global deposition estimates – A. K. Luhar, I. E. Galbally and M. T. Woodhouse 42

Reconsidering mercury emissions from Australian biomass burning – K. MacSween, D. A. Howard and G. C. Edwards 43

Update on atmospheric reactive mercury concentrations at the Cape Grim Baseline Air Pollution Station and Macquarie University – M. B. Miller, G. C. Edwards and M. S. Gustin 44

Open Path FTIR Spectroscopy to measure gaseous species relevant to urban air quality – F. A. Phillips, T. Naylor, C. Paton-Walsh and D. W. T Griffith 45

Vertically resolved pollution monitoring in Melbourne using MAX-DOAS measurements – R. G. Ryan, S. K. Rhodes, M. B. Tully and R. Schofield 46

Aerosol number concentrations crossing the Polar Front off east Antarctica – J. B. Simmons, R. S. Humphries and S. R. Wilson 47

Inverse modelling of CO_2 surface fluxes over Australia inferred from OCO-2 XCO2 satellite retrievals – Y. Villalobos, S. Tomas and P. J. Rayner 48

Photolytic production of H_2 from aldehydes – B. A. Welsh, A. D. C. F. Lee, A. W. Harrison, A. Kharazmi, M. F. Shaw, M. J. T. Jordan and S. H. Kable 49

Day 3 – Friday, 10 November 2017

Session 7 – Oral Presentations

Tropospheric Ozone Assessment Report: global metrics for climate change, human health and crop/ecosystem research – results from a global collaboration – I. E. Galbally, the TOAR SSC, TOAR authors and the TOAR Oceania and Antarctica Working Group 50

SRAD2 – the new UV-B spectrometer system at Cape Grim – S. R. Wilson 51

An update on comparisons of *in situ* carbon dioxide and methane measurements at Cape Grim – Z. M. Loh, P. B. Krummel, L. P. Steele, D. A. Spencer, P. J. Fraser, R. L. Langenfelds, M. V. van der Schoot, N. T. Somerville and J. Ward 52

Real-time accurate optical measurements of CO_2 number density – S. K. Scholten, C. Perrella, J. D. Anstie, R. T. White, N. B. Hébert, W. Al-Ashwal, J. Genest and A. N. Luiten 53

The imprint of ENSO on total column greenhouse gas measurements – B. Bukosa, N. M. Deutscher, J. A. Fisher, D. W. T. Griffith, V. A. Velazco, P. Wennberg, G. Toon, D. Feist, M. Kumar Sha and M. de Maziére 54

Estimated ratios of GHG emissions observed over the Yellow Sea and the East China Sea during a spring 2017 cruise – Y. Liu, L. Zhou, P. P. Tans, K. Zang and S. Cheng 55

Session 8 – Oral Presentations

Measurements of gases in ice at Patriot Hills, West Antarctica – D. P. Thornton, D. M. Etheridge, M. Rubino, C. S. M. Turney and C. J. Fogwill 56

Air archiving: recent research and operational developments – R. L. Langenfelds, L. P. Steele, P. J. Fraser, B. Mitrevski, J. Ward[2] and N. T. Somerville 57

Carbonyl sulfide (COS) pollution at Aspendale: what are the local sources? – P. J. Fraser, B. L. Dunse, B. Mitrevski, P. B. Krummel, L. P. Steele and N. Derek 59

Page left blank intentionally

The International Global Atmospheric Chemistry (IGAC) Project and the IGAC Monsoon Asia and Oceania Networking Group (MANGO)

H. Tanimoto[1*], K. Oanh[2], M. Naja[3], M. G. Lawrence[4] and M. L. Melamed[5]

[1] Center for Global Environmental Research, National Institute for Environmental Studies, Tsukuba, Japan
[2] Asian Institute of Technology, Bangkok, Thailand
[3] Aryabhatta Research Institute of Observational Sciences, Nainital, Uttarakhand, India
[4] Institute for Advanced Sustainability Studies, Potsdam, Germany
[5] IGAC International Project Office, University of Colorado/CIRES, Boulder, Colorado, USA

[*] corresponding author: Hiroshi Tanimoto [tanimoto@nies.go.jp]

Abstract

The atmosphere is an integrator connecting the components of the Earth system. Human emissions of pollutants and long-lived greenhouse gases into the atmosphere have caused dramatic transformations of the planet, altering air quality, climate, the cryosphere, elemental cycles and nearly every ecosystem worldwide. Understanding the global atmosphere requires an international network of scientists providing intellectual leadership in areas of atmospheric chemistry that need to be addressed, promoted and would benefit from research across disciplines and/or geographical boundaries. Acknowledgement of this need led to the formation of the International Global Atmospheric Chemistry (IGAC) Project in 1990. Since 1990, IGAC has fostered a community of several thousand students, scientists, policy makers, and stakeholders that actively collaborate across geographical boundaries and disciplines in order to contribute to addressing the most pressing global environmental change and stainability issues through scientific research. IGAC's mission is to facilitate atmospheric chemistry research towards a sustainable world by fostering community, building capacity, and providing leadership.

As part of IGAC's efforts to build capacity, IGAC sponsors national/regional working groups to create a strong cohesive community of atmospheric scientists in emerging countries/regions that together have a sum greater than their parts and connects these scientists to the larger IGAC community to foster international collaboration. The IGAC Monsoon Asia and Oceania Networking Group (MANGO) is one of IGAC's sponsored regional working groups. IGAC MANGO aims to enhance communication and collaborations between scientists, and explore opportunities for funding and infrastructure to foster scientific research, capacity building, and regional collaborations.

This talk will provide the Australian scientific community with an overview of, and explore opportunities for engagement in IGAC and IGAC MANGO.

Alkyl nitrates distribution and impacts constrained by aircraft observations and chemical transport modelling

J. A. Fisher[1*], E. L. Atlas[2], D. Blake[3], C. Thompson[4], T. Ryerson[4], J. Peischl[4], Z. A. Tzompa-Sosa[5] and L. T. Murray[6]

[1] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia
[2] Department of Atmospheric Sciences, University of Miami, Miami, Florida, USA
[3] Department of Chemistry University of California at Irvine, Irvine, California, USA
[4] National Oceanographic and Atmospheric Administration, Boulder, Colorado, USA
[5] Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA
[6] Department of Earth and Environmental Sciences, University of Rochester, Rochester, New York, USA

[*] corresponding author: Jenny A. Fisher [jennyf@uow.edu.au]

Abstract

Nitrogen oxides (NO + NO_2 = NO_x) are precursors in the formation of tropospheric ozone, contribute to the formation of aerosols, and enhance nitrogen deposition to ecosystems. While direct emissions tend to be localised over continental source regions, a significant source of NO_x to the remote troposphere comes from degradation of other forms of reactive nitrogen. Long-lived, small chain alkyl nitrates ($RONO_2$) including methyl, ethyl and propyl nitrates may be particularly significant forms of reactive nitrogen in the remote atmosphere as they are emitted directly by the ocean in regions where reactive nitrogen is otherwise very low. They may also act as NO_x reservoir species, sequestering NO_x in source regions and releasing it far downwind—and through this process may become increasingly important reservoirs as methane, ethane, and propane emissions grow. However, small $RONO_2$ are not consistently included in global atmospheric chemistry models, and their distributions and impacts remain poorly constrained. In this presentation, we will describe a new $RONO_2$ simulation in the GEOS-Chem chemical transport model evaluated using a large ensemble of aircraft observations collected over a 20-year period. The observations are largely concentrated over the Pacific Ocean, beginning with PEM-Tropics in the late 1990s and continuing through the recent HIPPO and ATom campaigns. Both observations and model show enhanced $RONO_2$ in the tropical Pacific boundary layer that is consistent with a photochemical source in seawater. The model reproduces a similarly large enhancement over the southern ocean by assuming a large pool of oceanic $RONO_2$ here, but the source of the seawater enhancement in this environment remains uncertain. We find that including marine $RONO_2$ in the simulation is necessary to correct a large underestimate in simulated reactive nitrogen throughout the Pacific marine boundary layer. We also find that the impacts on NO_x export from continental source regions are limited as $RONO_2$ formation competes with other NO_x reservoirs such as PAN, leading to re-partitioning of reactive nitrogen rather than a net reactive nitrogen source. Further implications for NO_x and ozone, as well as the impacts of recent changes in the global distribution of methane, ethane, propane, and NO_x emissions, will also be discussed.

The Australian Biogenic Canopy and Grass Emissions Model

K. M. Emmerson[1*], M. E. Cope[1], I. E. Galbally[1], S. Lee[1] and P. F. Nelson[2]

[1] CSIRO Ocean and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[2] Department of Environmental Sciences, Macquarie University, Sydney, NSW, Australia

[*] corresponding author: Kathryn Emmerson [kathryn.emmerson@csiro.au]

Abstract

One of the key challenges in atmospheric chemistry is to reduce the uncertainty of biogenic emission estimates from vegetation to the atmosphere. In Australia, eucalypt trees are a primary source of biogenic emissions, but their contribution to Australian air sheds is poorly quantified [Emmerson *et al*., 2016]. CSIRO developed the Australian Biogenic Canopy and Grass Emissions Model (ABCGEM) 15 years ago to investigate this issue. For comparison, biogenic emissions are calculated by the well-accepted Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther *et al*. [2012]) for the same region using the same meteorological inputs.

The two models use independent inputs of Leaf Area Index (LAI), Plant Functional Type (PFT) and emission factors. We find that LAI, a proxy for leaf biomass, has a small role in spatial, temporal and inter-model biogenic emission variability, particularly in urban areas for ABCGEM. After removing LAI as the source of the differences, we found large differences in the emission activity function for monoterpenes. In MEGAN monoterpenes are partially light dependent, reducing their dependence on temperature. In ABCGEM monoterpenes are not light dependent, meaning they continue to be emitted at high rates during hot summer days, and at night. Comparison with observations suggests that monoterpenes emitted from Australian vegetation may not be as light dependent as vegetation globally, as assumed in MEGAN.

The simplified ABCGEM model is comparable with the state-of-the-art MEGAN model when measured by normalised mean bias values between the models and observed atmospheric isoprene and monoterpene observations. Observed ratios of isoprene to monoterpene carbon in south east Australia are approximately unity. ABCGEM replicates this ratio for both emission rates and predicted concentrations, while MEGAN over-estimates by a factor of 4. This suggests the correct balance between isoprene and monoterpene emissions in ABCGEM, but their magnitudes need further assessment. We estimate the uncertainty in Australian BVOC emissions to be a factor of 2 for isoprene and 3 for monoterpenes.

This study identifies the uncertainties associated with the ABCGEM emission estimates, and data requirements necessary to improve isoprene and monoterpene emissions estimates for the application of both ABCGEM and MEGAN in Australia.

References

Emmerson, K. M., I. E. Galbally, A. B. Guenther, C. Paton-Walsh, E. A. Guerette, M. E. Cope, M. D. Keywood, S. J. Lawson, S. B. Molloy, E. Dunne, M. Thatcher, T. Karl and S. D. Maleknia, Current estimates of biogenic emissions from eucalypts uncertain for southeast Australia, *Atmos. Chem. Phys.*, 16, 6997-7011, doi:10.5194/acp-16-6997-2016, 2016.

Guenther, A. B., X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons, and X. Wang, The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5, 1471-1492, doi:10.5194/gmd-5-1471-2012, 2012.

The 2017 Antarctic ozone hole

P. B. Krummel[1*], P. J. Fraser[1], A. R. Klekociuk[2], M. B. Tully[3] and N. Derek[1]

[1] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[2] Australian Antarctic Division, Hobart, Tasmania, Australia
[3] Australian Bureau of Meteorology, Melbourne, Victoria, Australia

* corresponding author: Paul Krummel [paul.krummel@csiro.au]

Abstract

The 2017 ozone hole developed in the first week of August and rose sharply to reach a peak size in early September, this was then followed by a significant warming event which reduced the overall areal extent of the ozone hole considerably. If this peak area in early September turns out to be the maximum for 2017, then the 2017 ozone hole will be one of the smallest recorded for many years and similar in size to the ozone holes observed in the mid- to late-1980s. During the presentation an update to this will be given which will incorporate the latest data available. The development and recovery of the 2017 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 2017 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 20% 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.

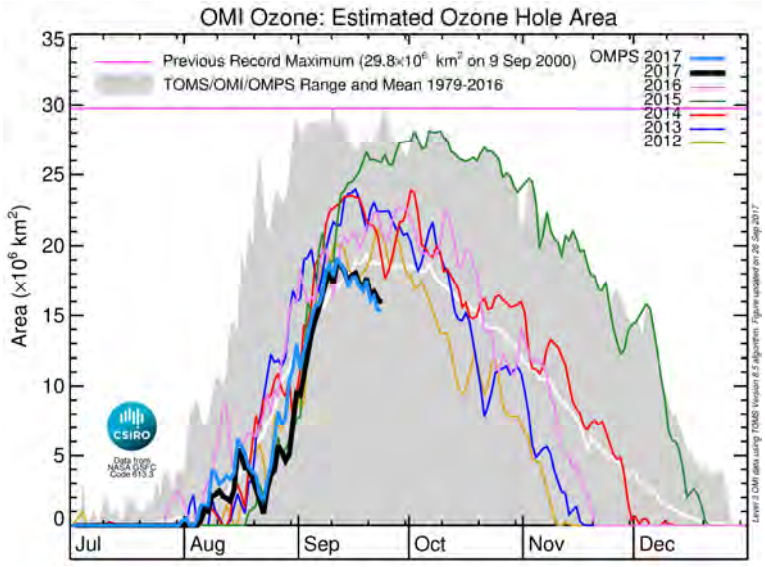


Figure 1. The Antarctic ozone hole area as of 23 September 2017, showing the relatively small areal extent of the ozone hole this year.

Studying the transport of Saharan dust and sub-sahelian biomass burning particles over South America by ground- and satellite based Lidar aerosol retrievals in the region of Northeast Brazil

J. J. Hoelzemann[1*], F. J. S. Lopes[2], A. G. Guedes[3], E. Landulfo[2], M. P. A. Silva[3], R. S. S. Santos[3], J. L. Guerrero-Rascado[4] and L. Alados-Arboledas[4]

[1] DCAC/CCET/UFRN - Department of Atmospheric and Climate Sciences, Federal University of Rio Grande do Norte, Brazil
[2] IPEN - Institute of Energy and Nuclear Research, São Paulo, Brazil
[3] Graduate Program in Climate Sciences, Federal University of Rio Grande do Norte, Brazil
[4] Andalusian Institute for Earth System Research, University of Granada, Spain

[*] corresponding author: Judith Hoelzemann [judith.hoelzemann@ccet.ufrn.br]

Abstract

In January 2016 a fourth Brazilian Lidar station of the Latin American LALINET network (Latin American LIdar system NETwork) [Guerrero-Rascado *et al*. [2014], Landulfo *et al*. [2016] was installed in Natal (5° 50´ 29´´ S, 35° 11´ 57´´ W, sea level), the capital of the state of Rio Grande do Norte in the most Northeastern part of Brazil. The goal of LALINET is to measure dust transport, biomass burning plumes, and volcanic ashes into and out of the continent, mapping the vertical distribution of aerosols and its optical properties. Since then, the instrument in Natal, a depolarization Lidar named DUSTER, the first in Brazil of its kind, has been measuring the atmosphere over Natal for aerosols. DUSTER is projected to operate with 4 channels, one at 1064 nm wavelength, two channels at 532 nm (parallel and perpendicular) and the last channel at 355 nm.

During the months of December to February the meteorological conditions are more prone to transport saharan and sub-sahelian air to the southwest, over the Atlantic Ocean to Natal. During this period in 2016/2017, the first intensive campaign was conducted, named MOLOTOV I, resulting in a first data base that is currently being analyzed in a number of different studies on dust particles, biomass burning particle transport, as well as cirrus cloud studies. First case studies have already shown interesting transport features of aerosol layers as can be seen in Figure 1 and which could also be observed in the perpendicular channel, indicating dust type aerosol, corroborated by trajectory modelling, tracing the air parcel back to the African continent.

In addition to the ground-based Lidar, CALIPSO satellite Lidar data based on the same technique is being analyzed for validation purposes, and time series of CALIPSO aerosol data from 2016-today are being processed to assess aerosol behavior over the region for the first time. Together with the Lidar DUSTER, a CIMEL sun-photometer that is part of the AERONET network was also installed in Natal to provide complementary measurements to the Lidar. Aerosol data from both the Natal AERONET station and the only other AERONET station of this region located in Petrolina (9° 23’ 39” S, 40° 30’ 35” W), state of Pernambuco, Brazil are currently being analyzed and compared to the other instruments.

In this context we present the LALINET network, particularly the DUSTER in Natal and its group and collaborators and examples of the ongoing aerosol studies that are being conducted over the Northeast of Brazil as well as provide an outlook on planned activities.

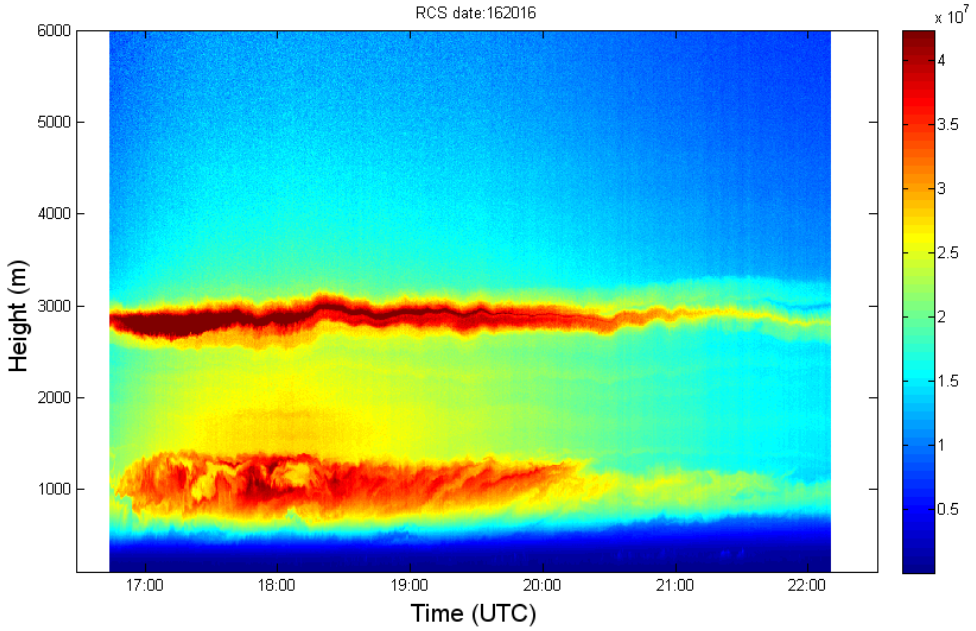


Figure 1. Dust layer identified over Natal on 1 June 2016. There were two layers, one around 1,000 m and another above, at 3,000 m. Natal has strong and continuous winds (trade winds) due its closeness to the ITCZ line.

References

Guerrero-Rascado, J. L., E. Landulfo, J. C. Antuña, H. de Melo Jorge Barbosa, B. Barja, Á. E. Bastidas, A. E. Bedoya, R. F. da Costa, R. Estevan, R. Forno, D. A. Gouveia, C. Jiménez, E. G. Larroza, F. J. da Silva Lopes, E. Montilla-Rosero, G. de Arruda Moreira, W. M. Nakaema, D. Nisperuza, D. Alegria, M. Múnera, L. Otero, S. Papandrea, J. V. Pallota, E. Pawelko, E. J. Quel, P. Ristori, P. F. Rodrigues, J. Salvador, M. F. Sánchez and A. Silva, Latin American Lidar Network (LALINET) for aerosol research: Diagnosis on network instrumentation, *J. Atmos. Solar-Terrestrial Phys.,* 138–139, 112–120, doi:10.1016/j.jastp.2016.01.001, 2016.

Landulfo, E., F. J. S. Lopes, E. Montilla, A. G. Guedes, J. J. Hoelzemann, J. H. Fernandez, L. Alados-Arboledas and J. L. Guerrero-Rascado, DUSTER lidar: transatlantic transport of aerosol particles from the Sahara and other sources: first results from the recently installed lidar and sunphotometer in Natal/Brazil, in *Lidar Technologies, Techniques, and Measurements for Atmospheric Remote Sensing XII*, edited by U. N. Singh and D. N. Nicolae, Proceedings of SPIE Vol. 10006, (SPIE, Bellingham, WA, 2016), 1000607, doi:10.1117/12.2241386; 2016.

Working towards a Southern Hemisphere observations data network - SHACCQ

R. Schofield

School of Earth Sciences, University of Melbourne, Melbourne, Victoria

* corresponding author: Robyn Schofield [robyn.schofield@unimelb.edu.au]

Abstract

Body Text

References

Author1, A. A., B. B. Author2 and C. C. Author3, Title, *Publication,* Volume, xx-xx, doi:xxxxxxxxxx, year.

Short-lived chlorocarbons: multiple threats to ozone layer recovery

P. J. Fraser[1*], B. L. Dunse[1], B. Mitrevski[1], P. B. Krummel[1], L. P. Steele[1], N. Derek[1], M. Rigby[2] and X. Fang[3]

[1] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[2] School of Chemistry, University of Bristol, Bristol, United Kingdom
[3] Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, MA, USA

[*] corresponding author: Paul Fraser [paul.fraser@csiro.au]

Abstract

Over the past 50 years, long-lived trace gases in the atmosphere containing chlorine, such as the chlorofluorocarbons (e.g. CFC-12, CCl_2F_2) and carbon tetrachloride (CCl_4), have been a significant source of stratospheric chlorine and a major contributor to depletion of the stratospheric ozone layer. Today, successful implementation of the Montreal Protocol has resulted in substantial reductions in emissions of these long-lived trace gases, such that the stratospheric chlorine loading is now in decline and signs of ozone layer recovery are emerging.

Short-lived, largely anthropogenic chlorocarbons such as dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), 1,2-dichloroethane (CH_2ClCH_2Cl),) and perchloroethylene (CCl_2CCl_2) have made a small, but significant, approximately constant-in-time, contribution to stratospheric chlorine. Recent publications [Hossaini *et al*., 2017; Oram *et al*., 2017] and a presentation at *AGAGE 56*, Bologna, Italy, October 2017 [Fang *et al*., 2017] suggest that global emissions of these species, whose production and consumption are not regulated under the Montreal Protocol, are increasing rapidly and pose a potential threat to future recovery of stratospheric ozone.

These recent findings will be summarised and possible causes discussed.

References

Hossaini, R., M. P. Chipperfield, S. A Montzka, A. A. Leeson, S. S. Dhomse and J. A. Pyle, The increasing threat to stratospheric ozone from dichloromethane, *Nature Communications*, 8:15962, doi:10.1038/ncomms15962, 2017.

Oram, D. E., M. J. Ashfold, J. C. Laube, L. J. Gooch, S. Humphrey, W. T. Sturges, E. Leedham-Elvidge, G. L. Forster, N. R. P. Harris, M. I. Mead, A. A. Samah, S. M. Phang, C.-F. Ou-Yang, N.-H. Lin, J.-L. Wang, A. K. Baker, C. A. M. Brenninkmeijer and D. Sherry, A growing threat to the ozone layer from short-lived anthropogenic chlorocarbons, *Atmos. Chem. Phys*, 17:1, 1-13, doi:10.5194/acp-17-1-2017, 2017.

Fang, X., S. Park, T. Saito, S. Li, M. Rigby, P. Yu, R. W. Portmann, R. Tunnicliffe, A. L. Ganesan, Y. Yokouchi, R. F. Weiss, P. B. Krummel, P. J. Fraser, J. Mühle, C. M. Harth, P. K. Salameh, S. O'Doherty, D. Young, M. Lunt, A. Gressent and R. G. Prinn, A growing threat to the ozone layer due to rapid increase in chloroform emissions in China, presented at *AGAGE 56*, Bologna, Italy, 2-6 October, 2017.

Changes in the NOAA Atmospheric Baseline Observatory Network

B. A. Vasel

NOAA Global Monitoring Division (GMD), Boulder, Colorado, USA

Abstract

NOAA established the Mauna Loa and South Pole Atmospheric Baseline Observatories in the mid-1950s followed by Barrow and American Samoa in the early 1970s. In 2002 and 2005 baseline observatories were established at Trinidad Head, California and Summit, Greenland. The observatory locations were selected in order to provide sampling of very clean air, away from sources of pollution, so that the background atmosphere could be monitored, resulting in, for example, the iconic Mauna Loa CO_2 time series. As the need for a better understanding of the climate system increases, the collaboration of the NOAA Atmospheric Baseline Observatories with global cooperative networks will become even more crucial to the study of atmospheric composition as it influences climate change.

In 2017, the GMD revisited the scientific priorities for our global research networks and the two 'newest' baseline observatory sites, Trinidad Head and Summit, were downgraded to sampling sites. At Trinidad Head, aerosol measurements were not representative of the free troposphere and CO_2 measurements adversely influenced by recirculation from land. The Trinidad Head surface and ozonesonde data are excellent and these measurements remain, as do the halocarbon flask measurements. At Summit, the *in situ* halocarbon gas chromatograph (GC) was removed as the weekly flask measurements produced essentially the same data. Surface ozone, black carbon and aerosols measurements were retained as were the carbon cycle and halocarbon flask programs. Ozonesonde flights and surface radiation programs were also terminated.

In 2018, GMD is looking further at the scientific value of the various measurement programs and the operational costs for the baseline observatory network with the possibility of increased cost reimbursement options from our partners. The long-term goal for the sites is to increase facility efficiencies, continue to install green technologies, and maximize their overall value to the global scientific community.



Figure 2. NOAA GMD Atmospheric Baseline Observatory Network Logo.

Seasonal variations in 'deep baseline' radon over the Southern Ocean

A. G. Williams[1*], S. D. Chambers[1], A. D. Griffiths[1], Z. M. Loh[2] and P. B. Krummel[2]

[1] Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, Australia
[2] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia

[*] corresponding author: Alastair Williams [agw@ansto.gov.au]

Abstract

Continued improvement and expansion of ANSTO's collaborative network of radon detectors for long-term high-sensitivity monitoring in the Southern Hemisphere is enhancing the scientific community's ability to quantify terrestrial influences (including anthropogenic pollution) upon Southern Ocean and Antarctic air masses.

Observed seasonality in Rn-222 (radon) concentrations at Southern Ocean sites may be due to variations in:

1. air-sea radon fluxes, induced by changes in sea state (chiefly wind speed related) or suspended sediment loads in surface currents (which contain Ra-226, radon's parent element);
2. large-scale atmospheric circulation patterns, bringing air with varying vestigial terrestrial signatures across the Southern Ocean; or
3. marine boundary layer mixing depth and venting (modulated by clouds).

In an attempt to start to tease apart some of these possibilities, we are bringing together multi-annual records of radon and long-lived trace gases from a range of Southern Ocean sites. The intention is to initially perform time series characterisations and statistical comparisons of the data sets, and then to move on to more sophisticated studies including regional and hemispheric model evaluations, and possibly new data collection programs (e.g. surface ocean water sampling for analysis of Ra-226 content).

This presentation will introduce ANSTO's Southern Ocean radon program and then show results from a pilot study using data sets from Cape Grim, Macquarie Island and the *RV Investigator*. Following an initial survey of the data records and their seasonality, an analysis of trace gas percentile distributions as a function of binned radon concentrations is presented for Macquarie Island and Cape Grim for summer and winter separately. The results are discussed with a focus on the possible origins of Southern Ocean seasonal variability in radon, and what this might (or might not) tell us about atmospheric circulation patterns, marine clouds, ocean currents and/or sea state.

Characterising tropospheric influences near coastal Antarctica with ^{222}Rn

S. D. Chambers[1], R. S. Humphries[3], A. G. Williams[1], S. Preunkert[2], Z. M. Loh[3], P. B. Krummel[3], A. D. Griffiths[1], I. E. Galbally[3], S. B. Molloy[3], R. Weller[4] and I. Levin[5]

[1] Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, Australia
[2] Centre National de la Recherche Scientifique, St. Martin d'Hères, France
[3] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[4] Alfred-Wegener-Institut Helmholtz-Zentrum für Polar-und Meeresforschung, Bremerhaven, Germany
[5] Institut für Umweltphysik, Heidelberg University, Heidelberg, Germany

* corresponding author: Scott Chambers [szc@ansto.gov.au]

Abstract

High-latitude tropospheric subsidence is an important mechanism for the indirect transport of nutrients and pollutants to the remote Antarctic continent. Continued improvement and expansion of the international network of radon detectors for long-term monitoring in the Southern Hemisphere [e.g. Chambers *et al*. 2014; Weller *et al*. 2014], as well as the recent installation of an ANSTO dual-flow-loop two-filter radon detector aboard the CSIRO Research Vessel Investigator, is improving our ability to quantify terrestrial influences in tropospheric incursions to the atmospheric boundary layer in coastal Antarctic regions.

Between January 2015 and March 2017 the *RV Investigator* completed five Southern Ocean transects between 50°-180°E (Figure 1a), adding important detail to a related transect previously reported by Polian *et al*. [1986]. Particular features of interest included intermittent radon enhancement of marine boundary layer air in the vicinity of the Polar Front (often attributable to synoptic-related tropospheric subsidence events; see also Humphries *et al*., [2016], and increasing radon concentrations in the immediate vicinity of the Antarctic coastline (attributable in part to enhanced radon concentrations in tropospheric subsidence related to Antarctic katabatic drainage events; Figure 1b).

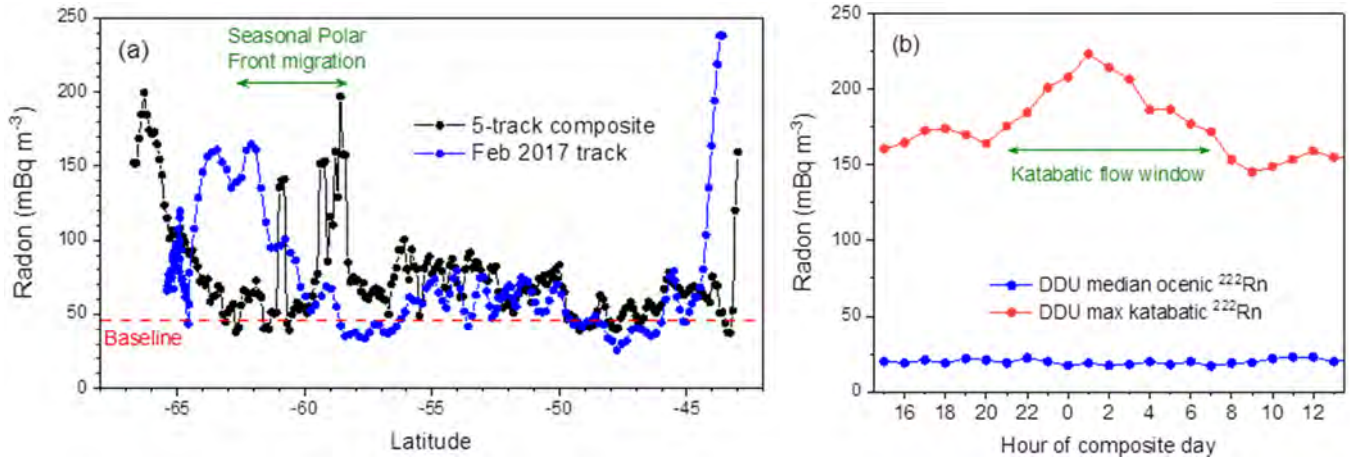


Figure 1. (a) Comparison of composite south-north Southern Ocean radon concentrations to the February 2017 voyage, and (b) diurnal composite Dumont d'Urville (DDU) ^{222}Rn for oceanic fetch and katabatic flow conditions.

The recent development of a simple experimental technique to separate katabatic, oceanic and local/coastal Antarctic air masses more effectively than with back trajectory analysis alone [Chambers *et al*., 2017] has demonstrated a seasonally and spatially varying terrestrial influence in the Antarctic troposphere as observed in katabatic drainage flows. Critically, the above technique is able to clearly distinguish between downslope flow of katabatic origin as opposed to synoptically-forced downslope flow.

In this presentation seasonal cycle amplitudes of terrestrial influence in the coastal Antarctic boundary layer are compared between Dumont d'Urville and Neumayer stations, and summertime concentrations of select

atmospheric trace species are compared between air masses of recent tropospheric and remote oceanic origin. These findings highlight the potential value of establishing a long-term, high-sensitivity, direct radon monitoring program at Casey Station, in order to complement monitoring at Cape Grim, Macquarie Island, aboard the *RV Investigator*, and proposed monitoring on the planned replacement of the *RV Aurora Australis*.

References

Chambers, S. D., S.-B. Hong, A. G. Williams, J. Crawford, A. D. Griffiths and S.-J. Park, Characterising terrestrial influences on Antarctic air masses using Radon-222 measurements at King George Island, *Atmos. Chem. Phys*., 14:18, 9903–9916, doi:10.5194/acp-14-9903-2014, 2014.

Chambers. S. D., T. Choi, S.-J. Park, A.G. Williams, S.-B. Hong, L. Tositti, A. D. Griffiths, J. Crawford and E. Pereira, Investigating local and remote terrestrial influence on air masses at contrasting Antarctic sites using Radon-222 and back trajectories, *J. Geophys. Res. – Atmos.*, *in press*, 2017.

Humphries, R. S., A. R. Klekociuk, R. Schofield, M. Keywood, J. Ward and S. R. Wilson, Unexpectedly high ultrafine aerosol concentrations above East Antarctic sea ice, *Atmos. Chem. Phys*., 16:4, 2185–2206, doi:10.5194/acp-16-2185-2016, 2016.

Polian, G., G. Lambert, B. Ardouin and A. Jegou, Long-range transport of continental radon in sub-Antarctic and Antarctic areas, *Tellus*, 38B:3-4, 178-189, doi:10.3402/tellusb.v38i3-4.15126, 1986.

Weller, R., I. Levin, D. Schmithüsen, M. Nachbar, J. Asseng and D. Wagenbach, On the variability of atmospheric ^{222}Rn activity concentrations measured at Neumayer, coastal Antarctica, *Atmos.Chem. Phys*., 14:8, 3843–3853, doi:10.5194/acp-14-3843-2014, 2014.

Clouds and aerosols: ship observations targeting Southern Ocean processes

M. J. Harvey[1*], A. J. McDonald[2], O. Morgenstern[1], L. T. Cravigan[3], S. Hartery[1,2], P. Kuma[2], S. J. Lawson[4], S. Parsons[2], J. A. McGregor[1], A. Shuddeboom[2], V. Varma[1] and J. Williams[1]

[1] National Institute of Water and Atmospheric Research (NIWA), Wellington, New Zealand
[2] Department of Physics and Astronomy, University of Canterbury, Christchurch, New Zealand
[3] International Laboratory for Air Quality and Health, Queensland University of Technology, Brisbane, Queensland
[4] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia

[*] corresponding author: Mike Harvey [mike.harvey@niwa.co.nz]

Abstract

Current climate models display a consistent deficit of reflected shortwave radiation over the Southern Ocean associated with erroneous clouds. One hypothesis is that the cloud schemes in GCMs are trained on Northern-Hemisphere data characterized by substantial anthropogenic and terrestrial aerosol-related influences which are almost completely absent in the Deep South. We seek to improve process understanding and hence implement parameterisation improvements in the New Zealand Earth System Model. Data are sparse, and new observations from research voyages are planned as part of the Deep South National Science Challenge (http://www.deepsouthchallenge.co.nz/), a New Zealand government initiative that aims to investigate the role of Antarctic and Southern Ocean processes and impacts on New Zealand's weather and climate.

For aerosol, an evolving understanding challenges some established ideas and suggests roles for marine biology in aerosol-cloud interaction through aerosol nuclei as:

Ice nuclei: the underestimation of supercooled liquid water in low- and medium-level clouds can affect cloud lifetime, precipitation and radiative properties. The influence and sources of ice nucleating aerosol on cloud phase are poorly understood. Mineral dust levels are low; but is there an ocean biogenic source of ice nuclei with nucleating potential?

Cloud Condensation nuclei: low-level cloud properties are strongly dependent on CCN numbers which may be limited and are seasonally varying with summer maxima. Can volatile marine organic compounds either alone or in conjunction with sulfuric acid be important to new particle formation and hence CCN numbers and cloud properties?

A voyage to polar waters of the northern Ross Sea is planned in February – March 2018 with RV Tangaroa. A summary of plans for atmospheric sampling on that voyage will be presented and experimental results of testing a pollution minimising sampling strategy for aerosol will be discussed.

Southern Ocean aerosols – a seasonal perspective from Macquarie Island

R. S. Humphries[1*], M. D. Keywood[1], J. P. Ward[1], J. N. Harnwell[1], G. Brettingham-Moore[2], E. W. Crocker[2] and S. Alexander[3]

[1] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[2] Bureau of Meteorology, Melbourne, Victoria, Australia
[3] Australian Antarctic Division, Kingston, Tasmania, Australia

[*] corresponding author: Ruhi Humphries [ruhi.humphries@csiro.au]

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. These biases are a result of incorrect microphysical representation of clouds in models, in particular, the ability to simulate sufficient low-level cloud regimes. Due to its remoteness and wild environment however, the Southern Ocean is one of the most under-sampled regions of the Earth's atmosphere.

The Antarctic, Clouds and Radiation Experiment (ACRE) includes a two-year intensive measurement campaign that began in March 2016 at Australia's sub-Antarctic research station at Macquarie Island (54.6^{o}S, 158.9^{o}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. Just over 18 months of measurements have been made to date, with very little instrument downtime. 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.

References

Carslaw, K. S., L. A. Lee, C. L. Reddington, K. J. Pringle, A. Rap, P. M. Forster, G. W. Mann, D. V. Spracklen, M. T. Woodhouse, L. A. Regayre and J. R. Pierce, Large contribution of natural aerosols to uncertainty in indirect forcing, *Nature*, *503:*7474, 67–71, doi:10.1038/nature12674, 2013.

An overview of activities of the Atmospheric Chemistry Research Group, South Africa – possibilities for collaboration with the Australian atmospheric research community

J. P. Beukes and P. G. van Zyl

Atmospheric Chemistry Research Group, North-West University, Potchefstroom, South Africa

* corresponding author: Johan Paul Beukes [paul.beukes@nwu.ac.za]

Abstract

The Atmospheric Chemistry Research Group (ACRG), North-West University, Potchefstroom Campus, South Africa, was established in the early 1990's. Initially the group focused mainly on aqueous phase reaction kinetics, but later diversified into ground-based ambient monitoring, deposition measurements, aircraft monitoring and limited modelling. In this paper a concise overview of current/recent scientific results of the ACRG will be presented, with the aims of introducing the ACRG to the Australian atmospheric research community and to promoting possible future collaboration. Australia and South Africa occur at similar latitudes in the Southern Hemisphere, indicating some environmental similarities that should serve as motivation for collaboration. Additionally, south-south collaboration, instead of north-south, collaboration should receive more attention.

The ACRG, together with research partners from the University of Helsinki and the Finnish Meteorological Institute (Finland), operate the Welgegund atmospheric research station, which is the most comprehensively equipped [Beukes *et al*., 2015] long-term atmospheric research station in the South African interior. The station was strategically positioned to be able to distinguish between air masses that had passed over the various industrialised regions of South Africa, as well as the regional background. This station compliments the Cape Point GAW station, which mainly measures Southern Hemisphere background air masses that had passed over the oceans. The ACRG also takes part in bilateral and multilateral research projects that are not associated with the Welgegund measurements, with local South African and international partners. Current/recent scientific topics considered include general air quality, secondary aerosol new particle formation, aerosol chemical composition, aerosol optical properties, black carbon, sulphur (S) and nitrogen (N) deposition and fluxes (CO_2, NO_2, SO_2), ozone (O_3) chemistry, open biomass burning, household combustion, atmospheric trace metals, hexavalent chromium (Cr(VI)), mercury (Hg), volatile organic compounds (VOCs), the vertical structure of the troposphere, long-term trend modelling, complementing ground-based data with satellite measurements and modelling results, and a growing interest in air quality health related matters.

References

Beukes, J. P., A. D. Venter, M. Josipovic, P. G. van Zyl, V. Vakkari, K. Jaars, M. Dunn and L. Laakso, Automated continuous air monitoring, Chapter 6 in *Monitoring of air pollutants – Sampling, sample, preparation and analytical techniques*, P. B. C. Forbes (ed.), *Comprehensive Anal. Chem.*, 70, 183–208, doi:10.1016/bs.coac.2015.09.006, 2015.

Cape Grim Multiphase Atmospheric Chemistry (MAC) sub-program: review

M. D. Keywood[1*], F. Reisen[1], P. W. Selleck[1], J. C. Powell[1], R. W. Gillett[1], J. P. Ward[1] and G. C. Edwards[2]

[1] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria
[2] Department of Environmental Sciences, Macquarie University, Sydney, NSW, Australia

[*] corresponding author: Melita Keywood [melita.keywood@csiro.au]

Abstract

The Cape Grim Baseline Station has been producing high quality data and research outputs on the chemical composition and chemistry of the remote marine boundary layer for 40 years. The regular review of the science programs undertaken at Cape Grim contribute to this excellence. In 2017, it is the turn of the Multiphase Atmospheric Chemsitry (MAC) Program to be reviewed.

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

Activities in the MAC program fall under two categories; long term monitoring and research to understand processes. While the aims of these two categories differ, they are related. It should be noted that the objectives and key scientific issues addressed by the MAC program closely align with those of the Particle Program. In 2016 the two programs were merged into a single program.

The components of the MAC program that are reviewed here include aerosol composition (both $PM_{2.5}$ and PM_{10}), precipitation chemistry, persistent organic pollutants (POPs) and relevant collaborative programs including atmospheric mercury (Macquarie University) and $PM_{2.5}$ elemental composition (ANSTO). The MAC Program was last reviewed in 2009. Some achievements of the MAC Program include a 27 year and 14 year quality-assured record of weekly baseline chemical composition for PM_{10} and $PM_{2.5}$ respectively, a 39 year record of precipitation chemical composition, 5 years of POPs concentrations measured using active sampling, 13 year record of annual passive POPs concentrations, 5 years of gaseous elemental mercury and a 25 year record of $PM_{2.5}$ elemental composition. In addition intensive campaigns were carried out in 2006 (P2P), 2007, 2011 and 2014. The findings from these campaigns highlight the importance of the chemical composition of cloud condensation nuclei (CCN) in understanding the source of CCN in the marine boundary layer and will be discussed. The review will cover (a) the Program scientific objectives; (b) discussion of existing activities and outcomes (c) work in progress (d) future plans and (e) relevance to GAW and Cape Grim.

Shipping emissions in the ports of Tianjin and Qingdao and their contributions to air quality

D. Chen[1,2*], X. Wang[1], P. F. Nelson[2], Y. Li[3], N. Zhao[1], Y. Zhao[1], J. Lang[1], Y. Zhou[1] and X. Guo[1]

[1] Key Laboratory of Beijing on Regional Air Pollution Control, Beijing University of Technology, Beijing, China
[2] Department of Environmental Sciences, Macquarie University, Sydney, NSW, Australia
[3] Transport Planning and Research Institute, Ministry of Transport, Beijing, China

[*] corresponding author: Dongsheng Chen [dschen@bjut.edu.cn]

Abstract

Shipping emissions as a serious source of air pollution have been outlined in various studies worldwide. Air pollutants emitted from ships can be easily spread from sea to land under the action of sea breeze, thus aggravating air pollution and health problems. As advances in electric vehicles in the future lead to reductions in emissions from road transport, shipping and aviation emissions are likely to become the most important mobile sources of air pollutant emissions.

In this work shipping emissions for the large Chinese ports of Tianjin and Qingdao are reported. A detailed exhaust emission inventory of ships using Automatic Identification System (AIS) data was developed for Tianjin Port, one of the top 10 world container ports and the largest port in North China. It was found that in 2014, ship emissions were 2.93×10^4, 4.13×10^4, 4.03×10^3, 3.72×10^3, 1.72×10^3 and 3.57×10^3 tonnes of SO_2, NOx, PM_{10}, $PM_{2.5}$, NMVOC and CO respectively, which are equivalent to 11.07%, 9.40%, 2.43%, 3.10%, 0.43% and 0.16% respectively of the non-ship anthropogenic totals in Tianjin. The total CO_2 emissions is approximately 1.97×10^6 tonnes. The container ships and dry bulk cargo ships contributed about 70% of the total ship emissions of NOx, SO_2 and PM_{10}. Pollutants were mainly emitted during cruise and hotelling modes, and the highest intensities of emissions located in the vicinity of fairways, berth and anchorage areas in Tianjin Port.

For Qingdao, the total estimated ship emissions for SO_2, NO_X, PM_{10}, $PM_{2.5}$, HC and CO in 2014 were 3.32×10^4, 4.29×10^4, 4.54×10^3, 4.18×10^3, 1.85×10^3 and 3.66×10^3 tonnes, respectively. Emissions of SO_2 and NO_X from ships account for 9% and 13% of the anthropogenic totals in Qingdao, respectively. The main contributors to the ship emissions are containers, followed by fishing ships, oil tankers and bulk carriers. The inter-monthly ship emissions varied significantly due to two reasons: stopping of the fishing ship activities during the fishing moratorium and the reduction of freight volume around the Chinese New Year Festival. Emissions from transport vessels concentrated basically along the shipping routes, while fishing ships contributed to massive irregular spatial emissions in the sea. The impact of ship emissions on the ambient air quality was further investigated using the Weather Research and Forecasting with Chemistry (WRF/Chem) model. The results reveal that the contribution of ship emissions to the $PM_{2.5}$ concentrations in Qingdao is the highest in summer (13.1%) and the lowest in winter (1.5%). The impact was more evident over densely populated urban areas, where the contributions from ship emissions could be over 20% in July due to their close range to the docks. These results indicated that the management and control of shipping emissions are required considering their remarkable influence on the air quality and potential negative effects on human health.

The Western Air-Shed Particulate Study for Sydney – a project of the Clean Air and Urban Landscapes Hub

C. Murphy (Paton-Walsh)[1*], F. A. Phillips[1], T. Naylor[1], É.-A. Guérette[1], S. R. Wilson[1], D. Dominick[1], H. Forehead[1], P. Perez[1], I. Wadlow[1], A. Kuhar[1], L. Spicer[1], J. Xu[1], K. Sneesby[1], S. Beaupark[1], O. Gendek[1], J. Kirkwood[2], M. Riley[2], Y. Scorgie[2], J. Silver[3] and P. J. Rayner[3]

[1] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia
[2] NSW Office of Environment and Heritage, Sydney, NSW, Australia
[3] School of Earth Sciences, University of Melbourne, Melbourne, Victoria, Australia

[*] corresponding author: Clare Murphy (Paton-Walsh) clarem@uow.edu.au

Abstract

The Western Air-Shed Particulate Study for Sydney (WASPSS) is a project of the Clean Air and Urban Landscapes hub, which is funded by the National Environmental Science Programme.

In this study we present some of the results from the extended air quality measurement undertaken in this project, including:

1. Open-path measurements extending over a 400m path through central Auburn
2. *In situ* measurements made at one end of the line-of-sight of the open-path instruments at Auburn
3. High-spatial resolution measurements around major roads in Randwick (linked with a traffic study).

We will discuss the relative merits of different technologies and show highlights from the results.

If time allows, we may also present an overview of the main findings of the modelling intercomparison and outline the next steps in this project.

An update on the evaluation of regional air quality models over Sydney, Australia

E.-A. Guérette[1*], K. Monk[1], S. R. Utembe[2], J. D. Silver[2], K. M. Emmerson[3], A. D. Griffiths[4], H. Duc[5], L. Tzu-Chi Chang[5], T. Trieu[5], N. Jiang[5], Y. Scorgie[5], M. E. Cope[3], C. Paton-Walsh[1] and P. J. Rayner[2]

[1] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia
[2] School of Earth Sciences, University of Melbourne, Melbourne, Victoria, Australia
[3] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[4] Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, Australia
[5] Climate and Atmospheric Research, NSW Office of Environment and Heritage, Sydney, NSW, Australia

[*] corresponding author: Elise-Andrée Guérette [eag873@uowmail.edu.au]

Abstract

This is an update on the regional air quality model evaluation project undertaken as part of the Western Air-shed and Particulate Study for Sydney, which is a project of the Clean Air and Urban Landscapes hub, funded by the National Environmental Science Programme.

Regional air quality models are powerful tools to investigate the complex and dynamic interactions between meteorology and chemistry that lead to poor air quality episodes. Ensuring their usefulness for policy scenario analysis, however, requires that model biases be characterised through an extensive performance evaluation. In this project, we are evaluating the performance of several regional air quality models by comparing their output to each other and to observations.

There are two requirements for this evaluation: (1) all models are run over the same geographical domain using the same grid resolution (down to 3 km in the innermost domain over the Greater Sydney area) for three time periods that coincide with intensive measurement campaigns that were conducted within the region in recent years (Sydney Particle Study 1: February-March 2011, Sydney Particle Study 2: April-May 2012 and MUMBA: December 2012 to February 2013) and (2) all models use the 2008 Air Emissions Inventory for the Greater Metropolitan Region in NSW from the NSW EPA [2012] as their anthropogenic emission inventory.

This project leverages regional modelling efforts from several groups, including the University of Melbourne, CSIRO, the NSW Office of Environment and Heritage and ANSTO. Model output is compared to observations on an hourly and daily basis and model performance is assessed against benchmarks sourced from the literature, including other evaluation exercises [e.g. Brunner *et al*. 2015; Im *et al*. 2015], as well as being judged in the context of what is needed in the region.

Here, we give an update on the project and present an assessment of model performance for selected parameters, including surface wind, ozone and PM2.5.

References

Brunner, D., N. Savage, O. Jorba, B. Eder, L. Giordano, A. Badia, A. Balzarini, R. Baró, R. Bianconi, C. Chemel, G. Curci, R. Forkel, P. Jiménez-Guerrero, M. Hirtl, A. Hodzic, L. Honzak, U. Im, C. Knote, P. Makar, A. Manders-Groot, E. van Meijgaard, L. Neal, J. L. Pérez, G. Pirovano, R. San Jose, W. Schröder, R. S. Sokhi, D. Syrakov, A. Torian, P. Tuccella, J. Werhahn, R. Wolke, K. Yahya, R. Zabkar, Y. Zhang, C. Hogrefe and S. Galmarini, Comparative analysis of meteorological performance of coupled chemistry-meteorology models in the context of AQMEII phase 2, Atmos. Environ., 115, 470-498, doi:10.1016/j.atmosenv.2014.12.032, 2015.

Im, U., R. Bianconi, E. Solazzo, I. Kioutsioukis, A. Badia, A. Balzarini, R. Baró, R. Bellasio, D. Brunner, C. Chemel, G. Curci, J. Flemming, R. Forkel, L. Giordano, P. Jiménez-Guerrero, M. Hirtl, A. Hodzic, L. Honzak, O. Jorba, C. Knote, J. J. P. Kuenen, P. A. Makar, A. Manders-Groot, L. Neal, J. L. Pérez, G. Pirovano, G. Pouliot, R. San Jose, N. Savage, W. Schröder, R. S. Sokhi, D. Syrakov, A. Torian, P. Tuccella, J. Werhahn, R. Wolke, K. Yahya, R. Zabkar, Y. Zhang, J. Zhang, C. Hogrefe and S. Galmarini,

Evaluation of operational on-line-coupled regional air quality models over Europe and North America in the context of AQMEII phase 2. Part 1: Ozone, *Atmos. Environ.*, 115, 404-420, doi:10.1016/j.atmosenv.2014.09.042, 2015.

NSW EPA, 2008 Calendar Year Air Emissions Inventory for the Greater Metropolitan Region in NSW, NSW Environment Protection Agency, http://www.epa.nsw.gov.au/air/airinventory2008.htm, 2012.

Hot summers: effect of elevated temperatures on air quality in Sydney in 2013

S. R. Utembe[1*], E.-A. Guérette[2], J. Silver[1], P. J. Rayner[1] and C. Murphy[2]

[1] School of Earth Sciences, University of Melbourne, Melbourne, Victoria, Australia
[2] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia

[*] corresponding author: Steven Utembe[sutembe@unimelb.edu.au]

Abstract

The summer of 2013 was the hottest Australian summer in the observation record. From an air quality perspective, elevated temperatures are usually accompanied by deterioration in air quality, which can be exacerbated by the hot and often (but not always) stagnant meteorological conditions. The area covering western and north-western Sydney is home to Eucalypts in the Greater Blue Mountains Heritage Area, an area covering over a million hectares. These Eucalypts are a huge source of isoprene and other biogenic emissions whose fluxes increase with temperature. In this study we examine the effect of elevated temperatures on air quality in Sydney during the 2013 heatwave during which temperatures at times exceeded 40°C.

Using the Weather Research and Forecasting Chemistry (WRF-Chem) model, we will analyse the effect of elevated temperatures on air quality in Sydney by running the model with biogenic emissions generated by MEGAN and separately running the model with average MEGAN biogenic emissions (for January 2013). Similarly, we will compare results from a standard run with that in which average temperatures (for January 2013) are applied to the chemistry (only).

References

Guenther, A. B., X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons and X. Wang, The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev*., 5, 1471-1492, doi:10.5194/gmd-5-1471-2012, 2012.

Particles observation during MUMBA Campaign

D. Dominick[1*], S. R. Wilson[1], N. B. Jones[1], C. Paton-Walsh[1], R. S. Humphries[1,2], E.-A. Guérette[1], M. D. Keywood[2] and B. Marwick[3]

[1] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia
[2] CSIRO Oceans and Atmosphere, Climate Science Centre, Melbourne, Victoria, Australia
[3] Center for Archaeological Science, University of Wollongong, Wollongong, NSW, Australia

* corresponding author: Doreena Dominick [dd824@uowmail.edu.au]

Abstract

Atmospheric particles were measured in the coastal city of Wollongong, Australia, during an intensive field campaign known as Measurements of Urban, Marine and Biogenic Air (MUMBA) between 16 January 2012 and 15 February 2013. One of the goals of this research was to study the capability of Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) to measure aerosol particles during the campaign. Particle number concentrations over the entire size of 14 nm – 660 nm measured during this campaign were indicative of the interplay between marine environments and urban air. In addition, low $PM_{2.5}$ mass was experienced during the campaign. The daily average mass concentration of $PM_{2.5}$ measured was 6.1 μgm^{-3}, which was low and always below the maximum allowable daily average values by the Australian National Environment Protection (Ambient Air Quality) Measure (25 μgm^{-3}). Overall, four particle formation and growth events were observed during the campaign. MAX-DOAS was not fully successful in detecting aerosol particle numbers measured during the campaign.

Design of a study to measure air quality during hydraulic fracturing operations in the Surat Basin, Queensland

E. Dunne*, M. D. Keywood, J. C. Powell, P. W. Selleck and J. P. Ward

CSIRO Oceans and Atmosphere, Climate Science Centre, Melbourne, Victoria, Australia

* corresponding author: Erin Dunne [erin.dunne@csiro.au]

Abstract

The Surat Basin is an area of intensive coal seam gas (CSG) extraction in Australia with annual CSG production rising from around 11 million cubic metres (Mm^3) in 2005 to almost 15, 000 Mm^3 in 2015 [Qld Government, 2017]. As extraction from higher permeability coal seams reaches its peak, the use of stimulation techniques, such as hydraulic fracturing (HF), to access gas from lower permeability coal seams is likely to become more frequent. In Queensland an estimated ~ 8% of the more than 5,000 conventional and domestic petroleum and gas wells have so far undergone HF (DEHP, 2014). However as the industry expands, 10 - 40% of wells are likely to undergo HF [DEHP 2014]. The potential health and environmental impacts of the CSG industry expansion and more frequent use of HF are issues of particular concern to people living nearby these developments [Cham and Stone, 2013].

CSIRO CSC are leading an Australian-first of air quality study during HF operations at a site in the Surat Basin Queensland as part of a larger project within the Gas Industry Social and Environmental Research Alliance (www.gisera.org.au) investigating the impact of HF on air, water and soil quality.

The air quality measurement program was designed to achieve three main objectives

- **Objective 1**- Quantify enhancements in air pollutant levels above background that occur during HF operations.
- **Objective 2**- Provide information on the contribution of HF and non-HF related sources of air pollutants to local air quality at the selected study site.
- **Objective 3**- Provide comparisons of the air quality observed at a HF site with Australian federal and state air quality objectives, as well as data from other air quality studies undertaken in areas not directly impacted by HF operations both within the Surat Basin and in other locations in Australia.

Here we will present an overview of the study design approach including a conceptual model of the potential sources and pathways to air of pollutants associated with HF activities (Figure 1), a list a key air pollutants to be targeted in the study of air quality impacts from HF (Table 1), a brief overview of the observed HF process, and the measurement systems currently deployed in a gas field site undergoing HF (Figures 2 and 3, Table 1).

References

Cham, S. T., and P. Stone, How can understanding community concerns about hydraulic fracturing help to address them? *Effective and Sustainable Hydraulic fracturing*, Andrew P. Bunger, John McLennan and Rob Jeffrey (eds.), ISBN 978-953-51-1137-5, doi:10.5772/56442, 2013. Available: https://cdn.intechopen.com/pdfs-wm/44211.pdf

DEHP, *Fraccing,* Department of Environment and Heritage Protection, 2014. Available: https://www.ehp.qld.gov.au/management/non-mining/fraccing.html

Queensland Government*, Coal Seam Gas Production, Queensland Government Data*, 2017. Available: https://data.qld.gov.au/dataset/petroleum-gas-production-and-reserve-statistics/resource/63a8a6cc-7fb6-4040-b4e7-9d453b14d3ed

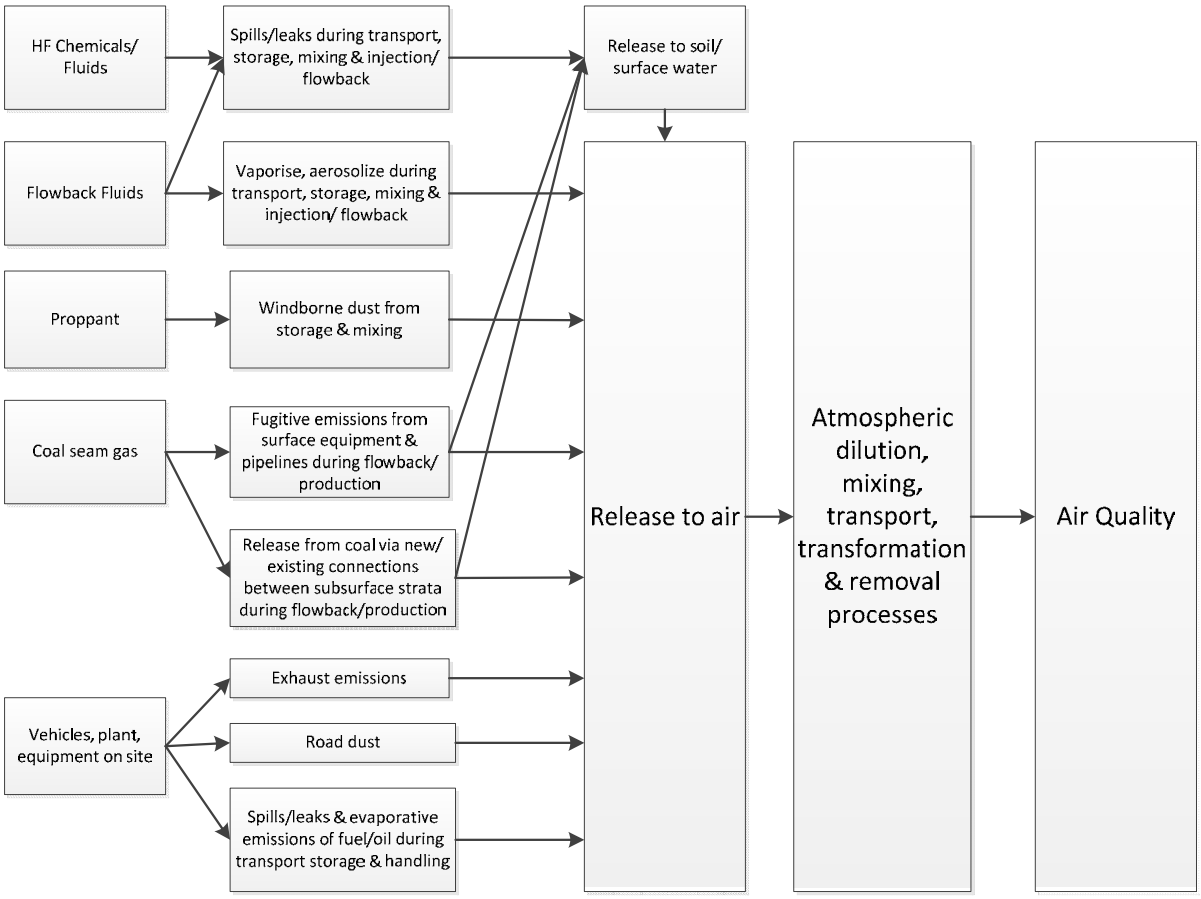


Figure 1. Conceptual model of the potential sources and pathways to air of pollutants associated with H F operations.



Figure 2. The measurement systems deployed comprise two fully instrumented air quality monitoring stations operated by Ecotech Australia and five CSIRO custom-built solar powered air monitoring systems. (Left) Northern air quality monitoring station with well undergoing hydraulic fracturing in the background; (Right) Solar-powered air monitoring system with well undergoing drilling in the background.

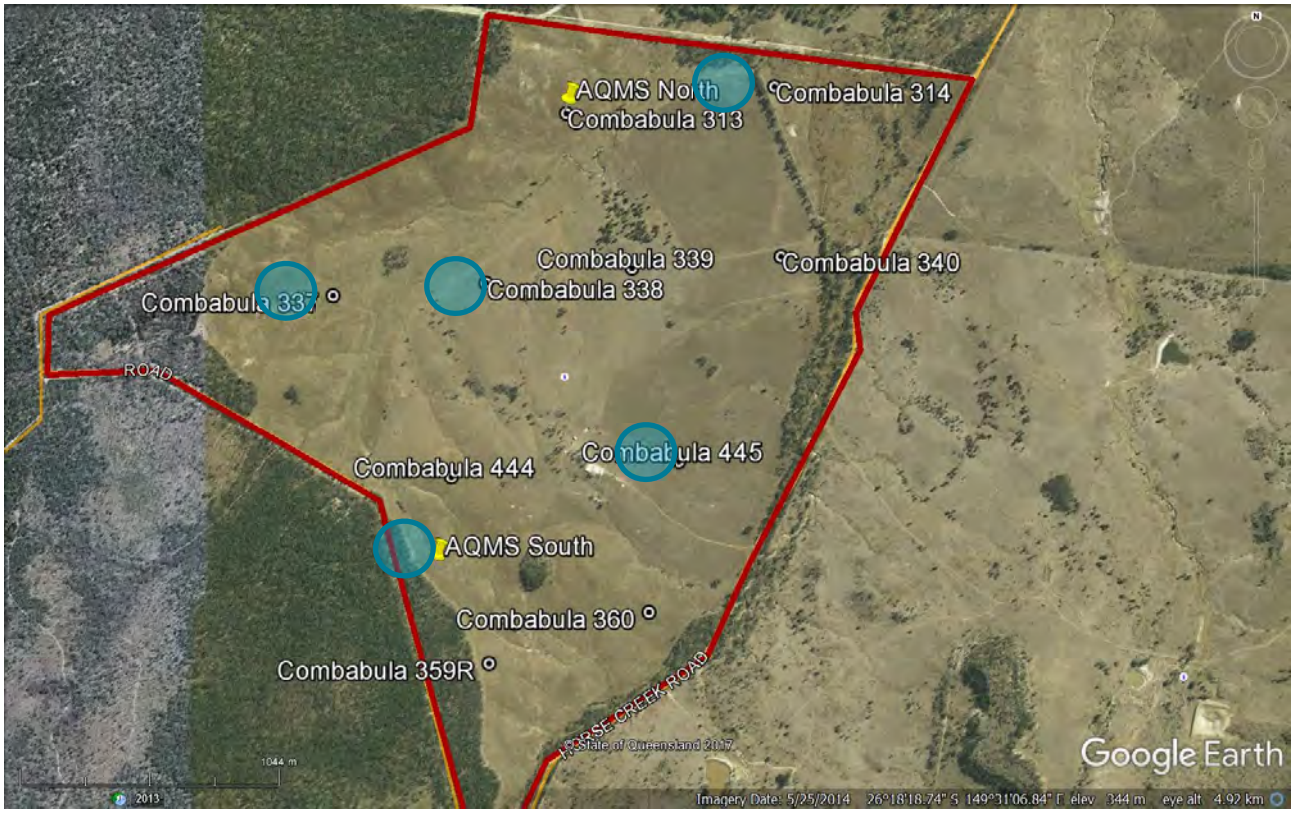


Figure 3. Map showing locations of wells to undergo HF (labelled by Well ID: Combabula ###), and the proposed location of the AQMS (yellow pins) and Perimeter Monitoring Stations (blue circles)

Table 1. Target air pollutants, measurement systems and their locations within the selected study site.

Target Air Pollutants	Measurement system	Location
NOx, O_3, CO, SO_2	Ecotech direct reading analysers	AQMS North and South
Methane	LGR Cavity Ringdown analyser	AQMS North and South
VOCs	PTR-MS	AQMS North
	12h Adsorbent tube sampling with GC-FID-MS analysis	AQMS North and South Four solar powered sites
Aldehydes & ketones	24 h DNPH sampling with HPLC analysis	AQMS North Five solar powered sites
PM 1, 2.5, 4, 10 & TSP	Palas Fidas 200 optical light scattering analyser	AQMS North and South
PM 2.5 sampling	Met-One E Sampler- Light scattering aerosol monitor and weekly integrated mass on 47 mm filter	Five solar powered sites
PM 10 sampling	12 h sampling onto 47 mm Teflon filter with Comde Derenda low vol sampler	AQMS North
	Weekly sampling onto 47mm Teflon filter with Microvol low vol sampler	Five solar powered sites
PM 10 and 2.5 composition analysis	All PM 10 and M 2.5 filters will be analysed via • Gravimetric mass determination • ANSTO Ion beam elemental analysis • Soluble ions • Anhydrous sugars	AQMS North Five solar powered sites
Mercury	Tekran gaseous elemental Hg analyser (Macquarie Uni)	AQMS South
Radon	Dual flow loop 2 filter radon detector (ANSTO)	AQMS South
PAHs	48 h samples on quartz filter and SKC PUF sorbent cartridge via Hi Vol sampler	AQMS South
Meteorology	Temp, RH, Wind speed & direction	All sites

Coal seam gas and air quality in the Surat Basin, Queensland: update from the monitoring program

S. J. Lawson*, J. C. Powell, M. F. Hibberd, M. Cheng, P. W. Selleck, E. Dunne, M. D. Keywood, J. N. Harnwell, J. A. Noonan and D. M. Etheridge

CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia

* corresponding author: Sarah Lawson [sarah.lawson@csiro.au]

Abstract

We provide an update on results from the GISERA (Gas Industry Social and Environmental Research Alliance) Air Quality monitoring program in the Surat Basin (Figure 1), a region of intensive coal seam gas (CSG) production. This comprehensive study is the first of its kind in Australia and involves monitoring NO_x, O_3, total VOCs, CO, CH_4, CO_2, PM2.5 and PM10 at three ambient air quality sites in the centre of the gas fields, from 2015 - current. NO_x, O_3 and CO are also measured at two regional CSIRO sites 10 -20 km from potential CSG emission sources, at monitoring stations commissioned as part of the GISERA Methane Seeps project (Figure 2). Passive fortnightly Radiello measurements of speciated VOCs, aldehydes and H_2S have also been made at ten sites for 16 months (Figure 2).

We will present some air quality guideline exceedance events of PM2.5, PM10 and TSP at each site and attempt to identify the source of the exceedance using emission ratios, meteorology and knowledge of nearby sources (both CSG-related and other sources). We will present and investigate the likely source of the highest methane peaks observed at each of the gas field monitoring sites. The 16 months of passive VOC, aldehyde and H_2S data will be presented, with the species commonly detected including aromatic hydrocarbons, carbon tetrachloride, and oxygenated VOCs. The sources of these commonly detected species will be discussed and concentrations compared with elsewhere in urban and rural Australia. Where possible, emission ratios will be used to identify sources of VOCs observed. Concurrent work including the Surat Basin Air Quality Modelling study will be briefly discussed.

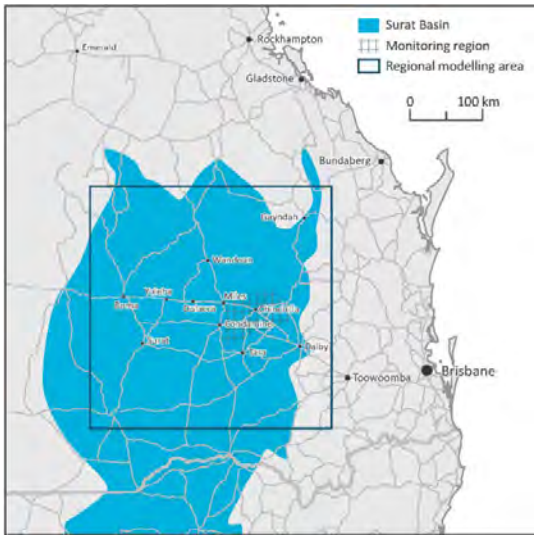


Figure 1. Surat Basin study area [taken from Lawson *et al.*, 2017].

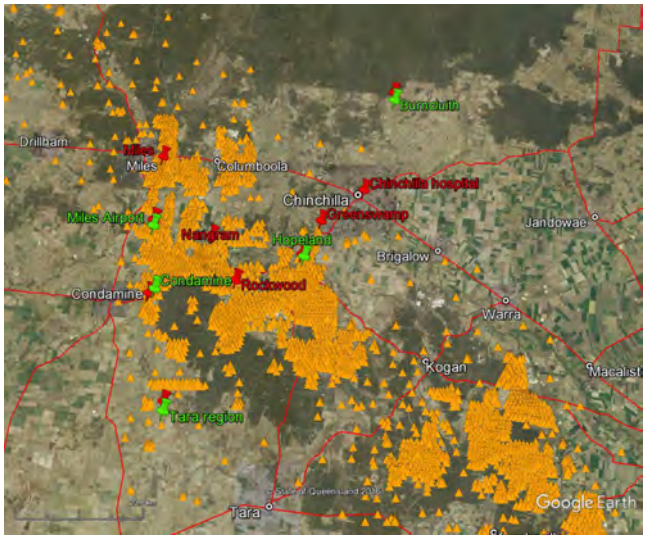


Figure 2. Location of measurement sites. Ambient air monitoring stations (green pins), passive sampler sites (red pins), townships names (white text). Orange triangles represent individual wellheads. Information Source: Queensland Globe, 2016. Figure from Lawson *et al.*, 2017.

References

Lawson, S. J., M. F. Hibberd and M. D. Keywood, Ambient air quality in the Surat Basin: Overview of study design, CSIRO Australia, 2017. Available at https://gisera.org.au/project/ambient-air-quality-in-the-surat-basin/

Reduction in particulate emission factors as peat fires progress and age due to generation of a filtering ash layer

C. T. Roulston[1*], C. Murphy[1] and T. E. L. Smith[2]

[1] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia
[2] Department of Geography, Kings College, London, UK

[*] corresponding author: Christopher Roulston [cr881@uowmail.edu.au]

Abstract

Tropical peatland fires contribute to climate change through greenhouse gas emissions and degrade regional air quality due to significant particulate matter emissions [Page *et al*., 2002; Turetsky *et al*., 2015]. These fires occur seasonally and will often smoulder for many weeks, destroying unique ecosystems and impacting human health [Gaveau *et al*., 2014]. Particulate matter, reactive gases and secondary products such as ozone have a damaging effect on regional economies due to the reduction of solar irradiance that reaches agricultural regions affected by smoke plumes. This effect is estimated to potentially reduce agricultural yields by up to thirty percent annually [Chameides *et al*., 1999]. Particulate matter is also known to reduce industrial productivity.

Despite these devastating effects, very little peer-reviewed research exists for categorising particulate emissions or in determining their emission factors across peatland burns. $PM_{2.5}$ studies of temperate peat and organic soils found significant variability in emission factors between sites, ranging from 9 to 79 $g.kg^{-1}$ [Geron and Hays, 2013]. In 2016, a study of tropical peat emission once again reported emission factors ranging from 15.7 to 29.6 $g.kg^{-1}$ [Stockwell *et al*., 2016]. During our field campaign summarised in Roulston *et. al*. in 2016 (currently in review), the relationship between emission factors and the age of the burn was observed as a possible cause of this variability.

Our study used peat samples burnt in a controlled environment to further investigate the filtering effect, providing evidence to strengthen the hypothesis that particulate emissions reduce over time due to the formation of a filter-like ash layer.

References

Chameides, W. L., H. Yu, S. C. Liu, M. Bergin, X. Zhou, L. Mearns, G. Wang, C. S. Kiang, R. D. Saylor, C. Luo, Y. Huang, A. Steiner and F. Giorgi, Case study of the effects of atmospheric aerosols and regional haze on agriculture: An opportunity to enhance crop yields in China through emission controls?, *Proc. Natl. Acad. Sci.*, 96:24, 13626-13633, doi:10.1073/pnas.96.24.13626, 1999.

Gaveau, D. L. A., M. A. Salim, K. Hergoualc'h, B. Locatelli, S. Sloan, M. Wooster, M. E. Marlier, E. Molidena, H. Yaen, R. DeFries, L. Verchot, D. Murdiyarso, R. Nasi, P. Holmgren and D. Sheil, Major atmospheric emissions from peat fires in Southeast Asia during non-drought years: evidence from the 2013 Sumatran fires, *Scientific Reports*, 4:6112, 7, doi:10.1038/srep06112, 2014.

Geron, C., and M. Hays, Air emissions from organic soil burning on the coastal plain of North Carolina, *Atmos. Environ*., 64, 192-199, doi:10.1016/j.atmosenv.2012.09.065, 2013.

Page, S. E., F. Siegert, J. O. Rieley, H.-D. V. Boehm, A. Jaya and S. Limin, The amount of carbon released from peat and forest fires in Indonesia during 1997, *Nature*, 420:6911, 61-65, doi:10.1038/nature01131, 2002.

Stockwell, C. E., T. Jayarathne, M. A. Cochrane, K. C. Ryan, E. I. Putra, B. H. Saharjo, A. D. Nurhayati, I. Albar, D. R. Blake, I. J. Simpson, E. A. Stone and R. J. Yokelson, Field measurements of trace gases and aerosols emitted by peat fires in Central Kalimantan, Indonesia, during the 2015 El Niño, *Atmos. Chem. Phys.*, 16:18, 11711-11732, doi:10.5194/acp-16-11711-2016, 2016.

Turetsky, M. R., B. Benscoter, S. Page, G. Rein, G. R. Van Der Werf and A. Watts, Global vulnerability of peatlands to fire and carbon loss, *Nature Geoscience*, 8:1, 11-14, doi:10.1038/ngeo2325, 2015.

Evaluation of black carbon aerosols at Cape Grim: seasonal trends and potential sources

F. Reisen*, J. L. Gras, J. P. Ward and M. D. Keywood

CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale Victoria

* corresponding author: Fabienne Reisen [fabienne.reisen@csiro.au]

Abstract

Black carbon (BC) measurements have been made at Cape Grim on the northwest coast of Tasmania using a Mutli-Angle Absorption Photometer (MAAP) since 2007. In 2015 a Photoacoustic Extinctiometer (DMT PAX-870 nm) that measures absorption and scattering at 870 nm and a Tricolor Absorption Photometer (TAP- NOAA/Brecthel) that measures absorption at 467, 528 and 652 nm were installed at Cape Grim.

The presentation will report on the long-term BC measurements at Cape Grim and the comparisons between BC concentrations measured from 2015 and 2017 using three different BC measurement instruments (MAAP, PAX and TAP).

The long-term BC observations (2007-2017) have shown a seasonal trend with lowest levels measured in summer and highest levels measured in winter. The main contributors to BC at Cape Grim were northern Tasmania, Melbourne and eastern Victoria, with low BC concentrations measured during baseline conditions. The largest impact on ground-based BC concentrations was due to the extensive fires in Tasmania in January and February 2016. This resulted in a yearly averaged BC concentration for 2016 of 61 ng/m^3, approximately twice the yearly averaged BC concentrations measured in previous years.

Isoprene emissions estimates inferred from OMI over Australia

J. Greenslade[1*], J. A. Fisher[1,2] and L. Surl[3]

[1] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW
[2] School of Earth and Environmental Sciences, University of Wollongong, Wollongong, NSW
[3] National Centre for Earth Observation, School of Geosciences, University of Edinburgh, Edinburgh, Scotland

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

Abstract

Isoprene emissions in Australia are poorly characterised [Emmerson *et al*., 2016]. The Model of Emissions of Gases and Aerosols from Nature (MEGAN) is used by GEOS-Chem and many other global scale chemistry models. Sparse measurements in Australia makes model evaluation difficult, however HCHO coverage from OMI allows a top-down estimate using the techniques first described by Palmer *et al*. [2003].

To determine isoprene to HCHO yield in Australia I use GEOS-Chem (which includes MEGAN). Using these yields, and the OMI HCHO total columns, I re-calculate isoprene emissions. In this presentation I will discuss a preliminary evaluation of the results, and make a comparison against MEGAN estimates and existing small scale campaign data.

Early results reinforce that MEGAN generally over-predicts biogenic isoprene emissions in Australia. CTMs driven by MEGAN are therefore likely to overestimate ozone and SOA in this region. Further measurements of biogenic emissions are imperative. Accurate quantification of the overestimation will be a high priority goal in future work.

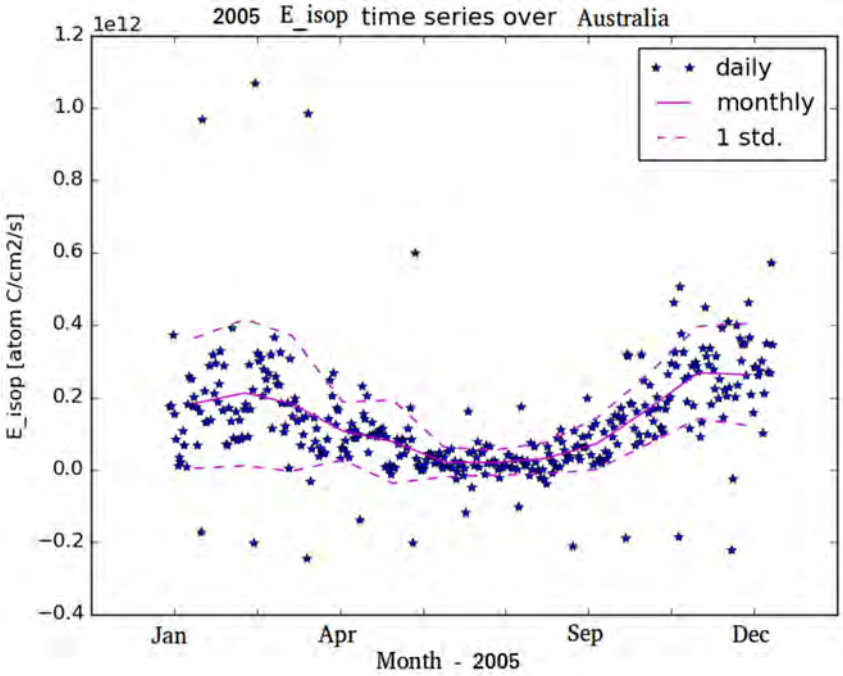


Figure 1. Estimated isoprene emissions using OMI HCHO and GEOS-Chem modelled yields over Australia in 2005. Monthly average and standard deviation shown in magenta.

References

Emmerson, K. M., I. E. Galbally, A. B. Guenther, *et al*., Current estimates of biogenic emissions from eucalypts uncertain for southeast Australia, *Atmos. Chem. Phys*., 16:11, 6997–7011, doi:10.5194/acp-16-6997-2016, 2016.

Palmer, P. I., D. J. Jacob, A. M. Flore, *et al*., Mapping isoprene emissions over North America using formaldehyde column observations from space, *J. Geophys. Res*., 108:D6, doi:10.1029/2002jd002153, 2003.

Isomerization and decomposition chemistry of isoprene hydroxy nitrates

G. da Silva

Department of Chemical Engineering, University of Melbourne, Parkville, Victoria, Australia

* corresponding author: Gabriel da Silva [gdasilva@unimelb.edu.au]

Abstract

Atmospheric oxidation of isoprene produces significant yields of eight unique nitrate compounds, each with a β- or δ-hydroxy group. These isoprene hydroxy nitrates (ISOPNs) significantly impact upon global NO_x budgets, O_3 levels, and aerosol formation. Uncertainties exist, however, in our understanding of ISOPN chemistry, particularly in their yields from the reaction of isoprene peroxyl radicals with NO. This study describes novel isomerization reactions of the ISOPNs, identified through the application of computational chemistry techniques. These reactions produce saturated polycyclic orthonitrite compounds via attack of the R–NO_2 group on the vinyl moiety. For the δ-hydroxy nitrates, low-energy isomerization pathways exist to six-membered ring compounds that are around 5 kcal mol^{-1} exothermic. These reactions proceed with barriers around 15 kcal mol^{-1} below the respective peroxyl radical + NO reactants and yield orthonitrites that can further isomerize to β-hydroxy ISOPNs. Moreover, the δ-hydroxy nitrates can directly interconvert with their β substituted counterparts via NO_3 group migration, with barriers that are lower yet. It follows that β-hydroxy nitrates may be stabilized in the δ-hydroxy form, and *vice versa*. Moreover, the lowest-energy pathway for dissociation of the δ-hydroxy ISOPNs is for the formation of β-hydroxy alkoxyl radicals, and because of this established branching fractions between the various isoprene peroxyl radicals may require re-evaluation. The results presented here also suggest that ISOPNs may be stabilized to some extent in their saturated orthonitrite forms, which has implications for both the total nitrate yield and for their subsequent removal by OH, O_3, and photolysis.

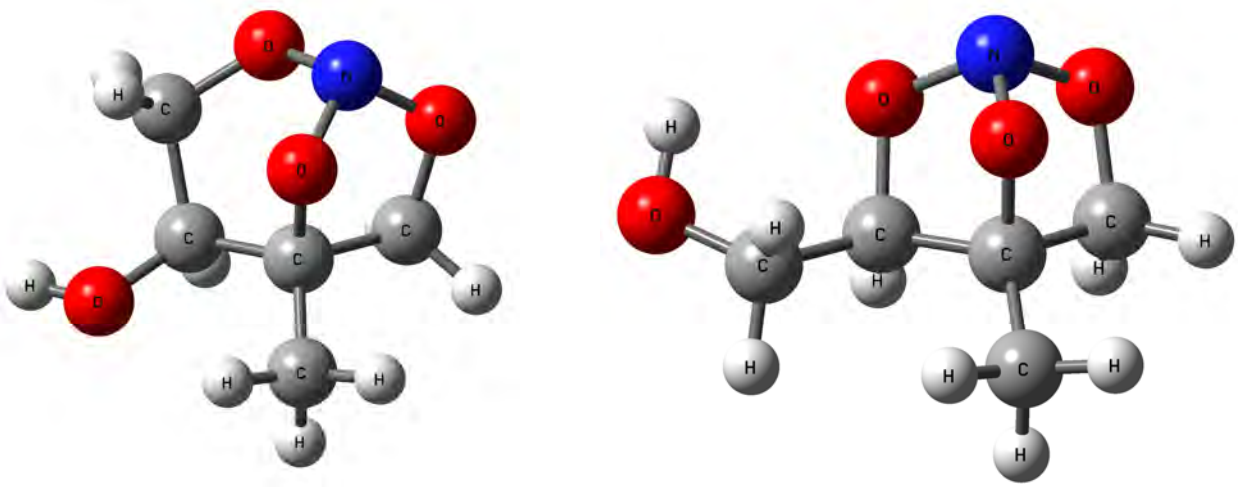


Figure 1. Example isoprene orthonitrites formed following external (left) and internal (right) OH radical addition to isoprene.

Field observations of N_2O_5 and $ClNO_2$ in southern and northern China

T. Wang* and the study team

[1] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China

* corresponding author: Tao Wang [cetwang@polyu.edu.hk]

Abstract

Heterogeneous uptake of dinitrogen pentoxide (N_2O_5) on aerosol at night and subsequent production of nitryl chloride ($ClNO_2$) and nitrate impact the oxidative capacity, NOx fate, and the formation of ozone and aerosol. However, the detailed processes and effects are not completely understood in diverse environments. To further understand the chemical processes of these compounds in China, two intensive measurement campaigns were conducted at a semi-rural site in the Pearl River delta (South China) in January 2017 and at an urban site in Beijing in May 2017. Key parameters related to N_2O_5 and $ClNO_2$, including aerosol ionic composition and size, volatile organic compounds as well as ozone, NO_x and NO_y, were measured during the campaigns. This talk will present preliminary results, including concentrations and meteorological influence, derived uptake coefficient of N_2O_5 and $ClNO_2$ yields, and contribution of night-time N_2O_5 uptake to nitrate formation compared to the daytime NO_2+OH pathway. The results suggest importance of the N_2O_5 heterogeneous processes in atmospheric chemistry and nitrate formation in polluted environment.

References

Wang, T; Y. J. Tham, L.K. Xue, Q.Y. Li, Q.Z. Zha, Z. Wang, S. C. N. Poon, W. P. Dubé, D. R. Blake, P. K. K. Louie, C. W. Y. Luk, W. Tsui and S. S. Brown, Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, *J. Geophys. Res. – Atmos.*, 121:5, 2476-2489, doi:10.1002/2015JD024556, 2016.

Tham, Y. J., Z. Wang, Q.Y. Li, H. Yun, W.H. Wang, X.F. Wang, L.K. Xue, K.D. Lu, N. Ma, B. Bohn, X. Li, S. Kecorius, J. Größ, M. Shao, A. Wiedensohler, Y.H. Zhang and T. Wang, Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, *Atmos. Chem. Phys.*, 16, 14959–14977, doi:10.5194/acp-16-14959-2016, 2016.

Li, Q.Y., L. Zhang, T. Wang, Y. J. Tham, R. Ahmadov, L.K. Xue, Q. Zhang and J.Y. Zheng, Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: improvement and application of the WRF-Chem model in southern China, *Atmos. Chem. Phys.*, 16, 14875–14890, doi:10.5194/acp-16-14875-2016, 2016.

Zhang, L., Q.Y. Li, T. Wang, R. Ahmadov, Q. Zhang, M. Li and M.Y. Lv, Combined impacts of nitrous acid and nitryl chloride on lower tropospheric ozone: new module development in WRF-Chem and application to China, *Atmos. Chem. Phys.,* 17, 9733-9750, doi:10.5194/acp-17-9733-2017 2017.

Photochemical production of H_2 from aldehydes

A. Harrison[1], M. Shaw[2], A. Kharazmi[1], M. J. T. Jordan[2] and S. H. Kable[1*]

[1] School of Chemistry, University of New South Wales, Kensington, NSW
[2] School of Chemistry, University of Sydney, Camperdown, NSW

[*] corresponding author: Scott Kable [s.kable@unsw.edu.au]

Abstract

Atmospheric models provide the predictive power to assist in control, regulation and understanding of important issues such as climate change, urban pollution and the recovery of the Antarctic ozone hole. Models, of course, are only as good as the chemistry and physics that comprise them. But the atmosphere is chemically complex – over 2 billion tonnes of organic material, with over a million chemical structures, is emitted to the atmosphere every year. Models are, accordingly, also very complex; for example the Master Chemical Mechanism chemical model for the atmosphere (U. Leeds, UK) contains over 17,000 reactions.

Photochemical reactions carried out in a molecular beam are ideal for characterizing the disposal of the photon energy into the products. This energy disposal can be used, in combination with theory, to determine the reaction mechanism. The collision-free environment also ensures that the reaction is a primary photochemical process; bimolecular events are negligible. However, quantum yields are very difficult to measure (we know a reaction happens for sure, but not whether it is important!). Reactions in gas bulbs can be used to determine absolute quantum yields, but untangling the complex chemistry is more difficult (we know how much products are formed, but not always how). The combination of the two techniques can yield both mechanism and importance.

In this seminar, we will explain some of our recent studies on reaction mechanisms for laser-induced photochemistry of carbonyls, both in molecular beams and gas bulbs. We have measured the mechanism quantum yield for H_2 production in a variety of carbonyls, including linear aliphatic, branched aliphatic, and unsaturated (e.g. methacrolein). Quantum yields vary between 1 and 10% and the mechanism can be quite different in the different compounds.

Atmospheric models currently underestimate the observed amount of H_2 in the atmosphere by about a factor of two. The missing H_2 source is believed to be photolytic. The combination of H_2 production in photolysis of many aldehydes in a molecular beam, and measurement of quantum yields of co-products in the bulb leads us to consider the possibility that the missing H_2 production might arise from photochemistry of carbonyls.

Atmospheric photochemistry - getting to the ground state

M. J. T. Jordan[1*], M. Corrigan[1], B. Nikoobakht[1] and S. H. Kable[2]

[1] School of Chemistry, University of Sydney, Camperdown, NSW
[2] School of Chemistry, University of New South Wales, Kensington, NSW

[*] corresponding author: Meredith Jordan [meredith.jordan@sydney.edu.au]

Abstract

The fate of an atmospheric molecule excited by an actinic UV photon has been assumed to be either (i) reaction (dissociation) of the electronically excited molecule or collisional stabilisation back to the original parent molecule. In the last 10 years, the importance of 'hot' ground state reactions of photoexcited species has been demonstrated experimentally and these reactions have been found to impact in atmospheric chemistry models, such as the Master Chemical Mechanism model (U. Leeds, UK). The route of a photoexcited molecule back to the ground state, however, is not obvious. Depending on the spin-state of an electronically excited molecule, it can cross back to the ground state by internal conversion or intersystem crossing. Here we consider these two mechanisms in small carbonyl molecules and show that intersystem crossing provides a fast and viable route back to the ground state, with minimal loss of internal energy. Thus 'hot' ground state reactions of small carbonyls, with very different products and intermediates to those expected on electronic excited states, should be included in atmospheric chemistry models.

An update on the Gape Grim mercury measurements 2013 to present

G. C. Edwards[1*], M. D. Keywood[2], D. A. Howard[1], M. B. Miller[1,3], M. S. Gustin[3] and J. C. Powell[2]

[1] Department of Environmental Sciences, Macquarie University, Sydney, NSW, Australia
[2] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[3] Department of Natural Resources and Environmental Science, University of Nevada-Reno, Reno, NV, USA

[*] corresponding author: Grant Edwards [grant.edwards@mq.edu.au]

Abstract

In 2013 the United Nations Environment Program (UNEP) Minamata Convention was promulgated with a mission to protect human health and the environment from mercury and its compounds throughout the lifecycle of this potent neurotoxin. Implications of the convention are profound towards the control of anthropogenic releases of mercury globally. The Minamata Convention as of August 2017 been brought into force and thereby is a legally binding treaty. Australia is a signatory to the treaty. The treaty provides a foundation to set policy and regulation to reduce Hg effects on humans and the environment**.**

The atmosphere, a global common, is the central conduit for transport, transformation, emission, deposition, and re-emission of mercury and mercury complexes amongst Earth's ecosystems. Mercury in the atmosphere is found as three operationally defined chemical forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM). PBM and GOM are quantified together as reactive mercury (RM = GOM + PBM). Commonly the terms Total gaseous mercury (TGM= GOM +GEM) and reactive gaseous mercury (RGM=GOM) are also used.

Since 2011 Cape Grim station has undertaken continuous measurements of atmospheric levels of GEM and since 2015 concurrent measurements of RM. As the atmosphere represents the dominant pathway for distribution of mercury globally the Cape Grim mercury atmospheric composition measurements will play an increasingly important role in the assessment of the impact of the Minamata treaty as well as contributing to improving the understanding of the global mercury cycle. The complete suite of atmospheric mercury data now collected at Cape Grim is critical to improving our understanding of mercury biogeochemical cycling.

The Cape Grim mercury measurements have already made a significant contribution to the understanding of background levels of TGM in the Southern Hemisphere [Slemr *et al*., 2015] where it is shown that these levels are significantly lower than previously thought. This finding has significant implications to global mercury modelling and inter-hemispheric transport of atmospheric mercury. This presentation is an up-to date summary of recent findings and progress with the mercury measurement program at Cape Grin since the Slemr paper with a focus on the mercury measurements since 2013.

Reference

Slemr, F., H. Angot, A. Dommergue, O. Magand, M. Barret, A. Weigelt, R. Ebinghaus, E.-G. Brunke, K. A. Pfaffhuber, G. Edwards, D. Howard, J. Powell, M. Keywood and F. Wang, Comparison of mercury concentrations measured at several sites in the Southern Hemisphere, *Atmos. Chem. Phys*., 15:6, 3125–3133, doi:10.5194/acp-15-3125-2015, 2015.

Using observations and modelling to quantify mercury biogeochemical cycling in the Australian context

N. Page[1*], J. A. Fisher[1,2], I. Dion[1,3], G. C. Edwards[4], D. A. Howard[4], P. Nelson[4], A. Morrison[4], M. D. Keywood[5] and L. Martin[6]

[1] School of Earth & Environmental Sciences, University of Wollongong, Wollongong NSW Australia
[2] Centre for Atmospheric Chemistry, School of Chemistry, University of Wollongong, Wollongong NSW Australia
[3] now at: CNRM-GAME, Météo-France/CNRS UMR 3589, Toulouse, France
[4] Department of Environmental Sciences, Macquarie University, Sydney, NSW, Australia
[5] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[6] South African Weather Service, Pretoria, South Africa

[*]corresponding author: Neil Page [ncp532@uowmail.edu.au]

Abstract

The GEOS-Chem biogeochemical Hg model (like every other major Hg model) has historically been developed and evaluated using observations from the northern hemisphere, which are significantly more abundant than observations in the southern hemisphere. A recent evaluation of GEOS-Chem against a global database of Hg observations found significant biases in the simulation of Hg in the southern hemisphere; however, only three southern hemisphere sites were included and none were in Australia. To date, model performance in Australia has not been evaluated due to a lack of available Hg observations. Five years of continuous atmospheric gaseous elemental mercury (GEM) data have now been collected at the Cape Grim Baseline air pollution station located at the northwest tip of Tasmania. Additional time series of ambient GEM, ranging in duration from 2 to 4 years, have been measured at several locations in Australia: a tropical baseline site at Gunn Point NT, a site located near coal-fired power plants and open pit coal mining in Glenville, NSW. These diverse, newly available atmospheric mercury datasets are compared to data from southern hemisphere background sites at Amsterdam Island in the Indian Ocean and Cape Point, South Africa. The datasets provide an opportunity to test our understanding of the Hg cycle in Australia as embedded in global models. Here, we will present an evaluation of the GEOS-Chem model using the new Hg observations along with sensitivity simulations designed to reveal uncertainties, constraints and controlling factors that govern model performance in Australia. Our evaluations to date show that the model is able to simulate observed latitudinal gradients and seasonality, and that all Australian sites are highly sensitive to treatment of ocean Hg exchange. Uncertainties remain in simulating the southern hemisphere GEM background and the air-surface exchange over terrestrial Australian landscapes, and these are the focus of ongoing and future work.

A comparative analysis of reactive mercury measurements using two methodologies and environmental correlates in an urban setting

K. Cook, M. B. Miller and G. C. Edwards

Department of Environmental Sciences, Macquarie University, Sydney, NSW, Australia

* corresponding author: Kellie Cook [kellie.cook@hdr.mq.edu.au]

Abstract

Accurate quantification of atmospheric mercury (Hg) is critical for understanding the Hg biogeochemical cycle and for the development of effective policy and management. However it is increasingly being acknowledged that reactive mercury (RM, defined as GOM + PBM) measured by the Tekran speciation system (2537/1130/1135) is found to measure biased low [Gustin *et al*., 2013]. There is also evidence to suggest that environmental parameters affect the accurate quantification of RM, including relative humidity and tropospheric ozone (O_3). This study, undertaken at an urban site in Sydney over three seasons, presents a method comparison between the Tekran speciation system and the University of Nevada Reno Reactive Mercury Active System (UNRRMAS). Additionally, we explored the dependence of RM on environmental variables, and investigate possible sources of RM events. Mean RM background concentrations at this location as determined by the Tekran speciation system were found to be 31.89±16.90 pg m^{-3} , while RM captured by the UNRRMAS was found to be 17.63±6.94 pg m^{-3}. We also found that tropospheric ozone and absolute humidity were not significant influencing factors to either measurement methodologies.

References

Gustin, M. S., J. Huang, M. B. Miller, C. Peterson, D. A. Jaffe, J. Ambrose, B. D. Finley, S. N. Lyman, K. Call, R. Talbot, D. Feddersen, H. Mao and S. E. Lindberg, Do we understand what the mercury speciation instruments are actually measuring? Results of RAMIX, *Environ. Sci. Technol*., 47, 7295–7306, doi:10.1021/es3039104, 2013.

Intersystem crossing in carbonyl compounds

M. Corrigan, B. Nikoobakht and M. J. T. Jordan*

School of Chemistry, University of Sydney, Camperdown, NSW, Australia

* corresponding author: Meredith Jordan [meredith.jordan@sydney.edu.au]

Abstract

Formaldehyde and acetaldehyde are key organic components of the atmosphere [Goldstein and Galbally, 2007]. Understanding their photochemistry is critical to understanding the chemistry of the atmosphere. Current models effectively ignore the ground state chemistry of these molecules by assuming collisional cooling will be faster than internal conversion or intersystem crossing, and deactivate the molecule before it reaches its ground state [Le Breton *et al*., 2014; Paulot *et al*., 2011; Atkinson *et al*., 2006]. However, experimental and theoretical evidence suggests this is not the case [Fu *et al*., 2011; Hobday *et al*., 2013]. I will present results showing that intersystem crossing in formaldehyde and acetaldehyde is fast, and allows these molecules to return quickly to S_0. This is driven by high T_1-S_0 spin orbit coupling, which is a consequence of the orbital structure of the carbonyl group. Subsequently this result should be common to all carbonyl-containing compounds. I will also show some preliminary results in larger molecules (propanal, butanal, acetone, butanone), which suggest aldehydes and ketones have fundamentally different photochemical behaviour because of small differences in T_1-S_0 spin orbit coupling between these functional groups.

References

Goldstein, A. H. and I. E. Galbally, Known and unexplored organic constituents in the Earth's atmosphere, *Environ. Sci. Technol.*, 41:5, 1514–1521, doi:10.1021/es072476p, 2007.

Le Breton, M., A. Bacak, J. Muller, P. Xiao, B. M. A. Shallcross, R. Batt, M. C. Cooke, D. E. Shallcross, S. J.-B. Bauguitte, J. C. Percival, Simultaneous airborne nitric acid and formic acid measurements using a chemical ionization mass spectrometer around the UK: Analysis of primary and secondary production pathways, *Atmos. Environ.,* 83, 166-175, doi:10.1016/j.atmosenv.2013.10.008, 2014.

Paulot, F., D. Wunch, J. D. Crousen, G. C. Toon, D. B. Millet, P. F. DeCarlo, C. Vigouroux, N. M. Deutscher, G. González Abad, J. Notholt, T. Warneke, J. W. Hannigan, C. Warneke, J. A. de Gouw, E. J. Dunlea, M. De Mazière, D. W. T. Griffith, P. Bernath, J. L. Jimenez and P. O. Wennberg, Importance of secondary sources in the atmospheric budgets of formic and acetic acids, *Atmos. Chem. Phys.,* 11, 1989-2013, doi:10.5194/acp-11-1989-2011, 2011.

Atkinson, R., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, and IUPAC Subcommittee, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, *Atmos. Chem. Phys.,* 6, 3625-4055, doi:10.5194/acp-6-3625-2006, 2006.

Fu, B., B. C. Shepler and J. M. Bowman, Three-State trajectory surface hopping studies of the photodissociation dynamics of formaldehyde on ab initio potential energy surfaces, *J. Amer. Chem. Soc.,* 133:20, 7957-7968, doi:10.1021/ja201559r, 2011.

Hobday, N., M. S. Quinn, K. Nauta, D. U. Andrews, M. J. T. Jordan, and S. H. Kable, Experimental and theoretical investigation of triple fragmentation in the photodissociation dynamics of H2CO, *J. Phys. Chem. A*, 117:46, 12091-12103, doi:10.1021/jp404895y, 2013.

Measurements of nitrogen oxides (NOx) in the air at Cape Grim: recent activities

I. E. Galbally* and S. B. Molloy

CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia

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

Abstract

Nitrogen oxides have key roles in the chemistry of the troposphere including as a:

- precursor in the formation of ozone,
- precursor to aerosol formation,
- nutritional substance for the biosphere, and
- contributor to the acidity of aerosol, rainwater and wet and dry deposition.

Consequently, to understand the dynamics of the environment there is a need for global monitoring of nitrogen oxides. This is acknowledged in the World Meteorological Organisation Global Watch Program, GAW, [WMO, 2009; Schultz *et al*., 2016].

Cape Grim, Australia's GAW station, has conducted research into the development of methods to measure nitrogen oxides and more recently into monitoring these nitrogen oxides in the background atmosphere of the Southern Hemisphere, where concentrations are amongst the lowest found worldwide,.

This poster presents the equipment, measurement techniques, and guidelines currently used to monitor nitrogen oxides at Cape Grim and results and scientific analyses for the years 2015 and 2016.

The uncertainty balance between radon emissions and model simulations

A. D. Griffiths*, S. D. Chambers, and A. G. Williams

Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, Australia

* corresponding author: Alan Griffiths [alan.griffiths@ansto.gov.au]

Abstract

The usefulness of radon–222 measurements for testing atmospheric transport models depends on the balance between: how well radon emissions are known; and how well transport and mixing are simulated in a particular model. If radon emissions are well known, then radon measurements can be used as a strong test of models. Conversely, a good model, when combined with measurements, can be used to improve our understanding of the spatiotemporal variability of radon emissions.

This modelling study looks at where the balance lies between the offline transport model Flexpart [Stohl *et al*., 2005] version 9, and radon measurements from Cape Grim and the *RV Investigator*. It complements observation-driven work, reported at this conference by Williams *et al*. and Chambers *et al*., and aims to show which processes need to be included to improve simulations relative to a base case.

Processes of potential importance are both model and source related. Model related processes include: moist convection; long-range transport (e.g. Figure 1, showing an event seen in the measurements); and high-latitude tropospheric subsidence. Source related processes include: spatiotemporal variation in ocean emissions (due to the radium distribution in the upper ocean; modulation of ocean-atmosphere gas exchange by sea state and winds); spatiotemporal variation in land emissions (due to variations of radium in soil and soil moisture); and emissions from Antarctic rock outcrops [Burton-Johnson *et al*., 2016].

This poster shows early results from the study. We show that neither model errors nor radon emissions overwhelm the other, and that radon measurements can inform aspects of both.

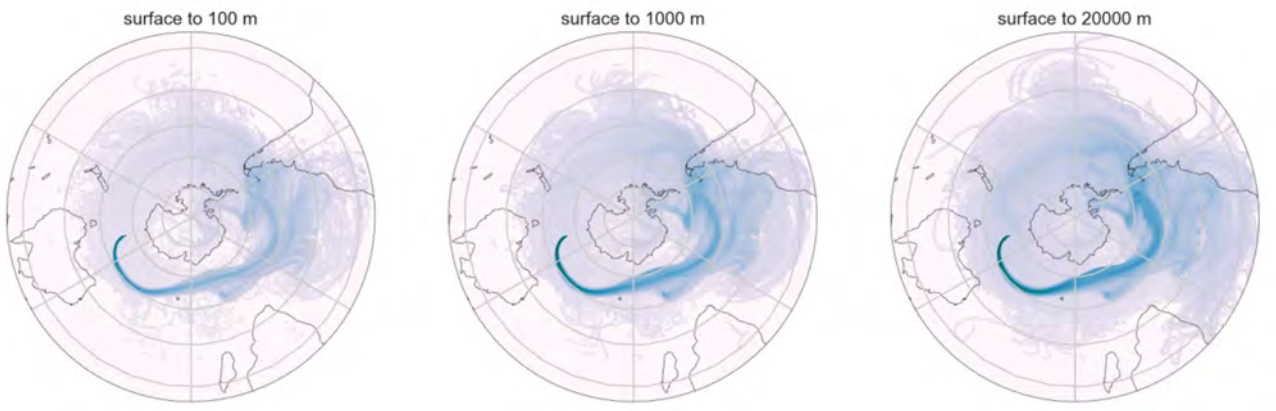


Figure 1. The potential source region of a radon measurement on the *RV Investigator*, south of Tasmania, showing long range transport from South America. Shading indicates the relative residence time of particles in a backwards dispersion simulation using Flexpart (non-linear colour scale, with emphasis on low values, and weighted by radon's 3.8 d half-life, and integrations ran for 30 days prior to measurement).

References

Burton-Johnson, A., M. Black, P. T. Fretwell and J. Kaluza-Gilbert, An automated methodology for differentiating rock from snow, clouds and sea in Antarctica from Landsat 8 imagery: a new rock outcrop map and area estimation for the entire Antarctic continent, *The Cryosphere*, 10:4, 1665-1677, doi:10.5194/tc-10-1665-2016, 2016.

Stohl, A., C. Forster, A. Frank, P. Seibert and G. Wotawa, Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, *Atmos. Chem. Phys.*, 5:9, 2461-2474, doi:10.5194/acp-5-2461-2005, 2005.

Radon tracer flux measurements of CO_2, N_2O and CH_4 in an agricultural region

A. D. Griffiths[1*], D. W. T. Griffith[2*], S. R. Wilson[2], S. D. Chambers[1], A. G. Williams[1], S. Werczynski[1], O. Sisoutham[1], J. Howitt[3], D. Reardon[3] and R. Leuning[4#]

[1] Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, Australia
[2] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia
[3] School of Agricultural and Wine Sciences, Charles Sturt University, Wagga Wagga, NSW, Australia
[4] CSIRO Oceans and Atmosphere, Canberra, ACT, Australia (see footnote)

[*] corresponding authors: Alan Griffiths [alan.griffiths@ansto.gov.au], David Griffith [griffith@uow.edu.au]

Abstract

Estimating regional scale emissions of nitrous oxide from agricultural environments to refine greenhouse gas budgets and inventories remains a difficult task because of the low atmospheric concentrations, small fluxes and small concentration gradients of N_2O. In this work we made measurements in a mixed-farming region typical of large areas of SE Australia. We combined continuous flux measurements of tracer species Radon and CO_2 (by chamber and eddy covariance, respectively) with concentration measurements of these gases as well as N_2O and CH_4 on a 10 m tower in a grassed paddock. We utilised correlations between the trace gases and tracers as they build up in the nocturnal boundary layer (NBL). Under favourable conditions, the NBL is capped by a low inversion and acts as a km-scale 'megachamber'; if the flux of tracer and ratio of concentrations of trace gas and tracer are measured, the unknown nocturnal flux of the target trace gas can be calculated assuming similar source distributions of the unknown and tracer. This allows the measurement of regionally averaged soil N_2O emission fluxes at the low levels typical of low-nitrogen Australian soils.

The measurement campaign ran from August – December 2016, using radon flux and concentration measurements from ANSTO, FTIR and LGR analysis of trace gases from UoW and CSU, and local support and infrastructure from CSU. We will present the measurements with preliminary results and calculations of fluxes.

[#] Ray Leuning (1948-2016)

Exhaust identification on the RV Investigator

R. S. Humphries[1*], I. McRobert[2], W. Ponsonby[2], J. P. Ward[1], M. D. Keywood[1], Z. M. Loh[1], P. B. Krummel[1] and J. N. Harnwell[1]

[1] CSIRO Oceans an Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[2] CSIRO Marine National Facility, Hobart, Tasmania, Australia

[*] corresponding author: Ruhi Humphries [Ruhi.Humphries@csiro.au]

Abstract

Ship based measurements are vital in understanding the global atmosphere. The recent commissioning of the purpose built, Australian blue-water *Research Vessel (RV) Investigator*, with two dedicated atmospheric laboratories, represents an unprecedented opportunity for high quality measurements of the marine atmosphere. A common problem that plagues ship-based measurements is mitigating the influence of the platform's exhaust on sampling. This poster outlines the algorithm recently developed for the RV Investigator that aims to distinguish between exhaust from the platform, and ambient air of interest which could include clean background, continental or urban air. The algorithm avoids using ancillary data such as wind speed and direction, and instead utilises components of the exhaust itself - aerosol number concentration, black carbon mass concentration, and carbon monoxide mixing ratio. The exhaust signal is identified within each of these parameters individually before they are combined and an additional window filter is applied. The algorithm relies heavily on statistical methods, rather than setting thresholds that are too rigid to accommodate potential temporal changes. The algorithm is more effective than traditional wind-based filters in removing exhaust data without removing exhaust-free data which commonly occurs with traditional filters.

A new mechanistic parameterisation for dry deposition of ozone to the ocean, and revised oceanic and global deposition estimates

A. K. Luhar*, I. E. Galbally and M. T. Woodhouse

CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia

* corresponding author: Ashok Luhar [ashok.luhar@csiro.au]

Abstract

Dry deposition at the Earth's surface is an important sink of atmospheric ozone. Presently, dry deposition of ozone to the ocean surface in atmospheric chemistry models has the largest uncertainty compared to deposition to other surface types, with implications for global tropospheric ozone budget and associated radiative forcing. Most models assume that the dominant term of surface resistance in the parameterisation of ozone dry deposition velocity at the oceanic surface is constant at approximately 2000 s m^{-1} based on Wesely [1989]. We have developed a consistent, process-based parameterisation scheme for air-sea exchange in which the surface resistance incorporates the simultaneous waterside processes of ozone solubility, molecular diffusion, turbulent transfer, and a first-order chemical reaction of ozone with dissolved iodide. The asymptotic behaviour of the new scheme is consistent with the known limits [Fairall *et al*., 2007] when either chemical reaction or turbulent transfer dominates. The new scheme improves upon the scheme presented at the 2016 Cape Grim meeting and reported in Luhar *et al*. [2017a]. It has been incorporated into the ACCESS-UKCA global chemistry-climate model and the results are evaluated against dry deposition velocities from currently best available open-ocean measurements [Helmig *et al*., 2012]. In order to better quantify the global dry deposition loss and its interannual variability, the modelled 3-h ozone deposition velocities are combined with the 3-h MACC (Monitoring Atmospheric Composition and Climate) reanalysis ozone for the years 2003–2012. The ozone dry deposition is found to be 98.4 ± 4.5 Tg O3 yr^{-1} for the ocean and 722.8±20.9 Tg O3 yr^{-1} globally. The new estimate of the ocean component is approximately a third of the current model estimates. This reduction corresponds to an approximately 20% decrease in the total global ozone dry deposition, which is equivalent to an increase of approximately 5% in the modelled tropospheric ozone burden and a similar increase in tropospheric ozone lifetime. More details of this work are provided in Luhar *et al*. [2017b].

References

Fairall, C. W., J. E. Hare, D. Helmig and L. Ganzveld, Water-side turbulence enhancement of ozone deposition to the ocean, *Atmos. Chem. Phys*., 7, 443–451, doi:10.5194/acp-7-443-2007, 2007.

Helmig, D., E. K. Lang, L. Bariteau, P. Boylan, C. W. Fairall, L. Ganzeveld, J. E. Hare, J. Hueber and M. Pallandt, Atmosphere-ocean ozone fluxes during the TexAQS 2006, STRATUS 2006, GOMECC 2007, GasEx 2008, and AMMA 2008 cruises, *J. Geophys. Res.*, 117, D04305, doi:10.1029/2011JD015955, 2012.

Luhar, A. K., I. E. Galbally, M. T. Woodhouse and M. Thatcher, An improved parameterisation of ozone dry deposition to the ocean and its impact in a global climate-chemistry model, *Atmos. Chem. Phys*., 17, 3749–3767, doi:10.5194/acp-17-3749-2017, 2017a.

Luhar, A. K., M. T. Woodhouse and I. E. Galbally, Revising global ozone dry deposition estimates based on a new mechanistic parameterisation for air-sea exchange and the multi-year MACC composition reanalysis, *Atmos. Chem. Phys. Discuss.*, submitted, 2017b.

Wesely, M., Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical-models, *Atmospheric Environment*, 23, 1293–1304, doi:10.1016/0004-6981(89)90153-4, 1989.

Reconsidering mercury emissions from Australian biomass burning

K. MacSween*, D. A. Howard and G. C. Edwards

Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University

* corresponding author: Katrina MacSween [katrina.macsween@students.mq.edu.au]

Abstract

Estimates of Australian mercury (Hg) emissions from biomass burning range considerably throughout the literature. However, these estimates are based on global modelled enhancement of CO and a global average emission ratio(ER) of $1.54x10^{-7}$, as reported by Friedli *et al*. [2009]. It is therefore highly likely that these estimates do not accurately represent Australia's actual contributions of Hg released from biomass burning to the atmosphere. In January and February of 2016, the north-west of Tasmania experienced extensive bush fire burning. In total over 97,000 ha of natural vegetated areas were affected by the fires. Throughout this period, CGBAPS sampled air masses that were affected by the fires, with corresponding increases in CO_2, CO and GEM observed. ER of GEM to CO_2 and CO were calculated using linear least squares regressions for enhanced GEM concentrations against measured enhancements of CO_2/CO. HYSPLIT back trajectories were modelled in order to identify potential regions that had an impact on the air masses seen at CGBAPS. These were coupled with MODIS hotspot data, used to identify regions that were actively burning. For the two largest events Mean GEM enhancements were 2.39 and 0.98 ng m^{-3}, with peak enhancements of 6.99 and 2.89 ng m^{-3}. ER for GEM/CO_2 and GEM/CO were 10.22 ±0.09 $X10^{-9}$ and 0.581 ±0.006$x10^{-7}$, respectively. Evasion of GEM from the soil during this burning event was also found to be minimal and therefore thought not to be contributing significantly to the observed ER at CGBAPS. This result indicates that the influence of GEM volatilisation from soils is low from eucalypt vegetation during wild biomass burning events. The observed ER values are considerably lower than previous ER used in modelling emission of Hg from biomass burning in Australia. This would indicate that real total emissions of Hg from biomass burning in Australia are towards the lower end of current estimates.

References

Friedli, H. R., A. F. Arellano, S Cinnirella and N. Pirrone, Initial estimates of mercury emissions to the atmosphere from global biomass burning, *Environ. Sci. Technol.* 43:10, 3507-3513, doi:10.1021/es802703g, 2009.

Update on atmospheric reactive mercury concentrations at the Cape Grim Baseline Air Pollution Station and Macquarie University

M. B. Miller[1*], G. C. Edwards[1] and M. S. Gustin[2]

[1] Department of Environmental Sciences, Macquarie University, Sydney, NSW, Australia
[2] Department of Natural Resources and Environmental Science, University of Nevada, Reno, Nevada, USA

[*] corresponding author: Matthieu Miller [matthieu.miller@hdr.mq.edu.au]

Reactive mercury is an important component of the global mercury cycle, but there is little data on ambient concentrations in the Southern Hemisphere. The first continuous monitoring sites of reactive mercury concentrations in Australia were established at the Cape Grim Baseline Air Pollution Station in November 2015, and at the Macquarie University meteorological station in April 2016, using a recently developed cation exchange membrane filter collection system. The filter method has a better overall collection efficiency than the standard denuder-based monitoring system. For the 19 months of available data at Cape Grim, the mean ambient concentration of reactive mercury was 16±7 pg m^{-3} and ranged from 9 to 49 pg m^{-3}. In 17 months of sampling at Macquarie University, the mean reactive mercury concentration was 17±6 pg m^{-3}, and ranged from 8 to 32 pg m^{-3}. This suggests background concentrations of reactive mercury in the Southern Hemisphere may be highly uniform, though local site variability is apparent. Ongoing method validation has shown the cation exchange membrane technique to be highly selective and efficient for reactive mercury uptake, with negligible interference from gaseous elemental mercury.

Open Path FTIR Spectroscopy to measure gaseous species relevant to urban air quality

F. A. Phillips, T. Naylor, C. Paton-Walsh and D. W. T Griffith

Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia

* corresponding author: Frances Phillips [francesp@uow.edu.au]

Abstract

As part of the Western Air-Shed and Particulate Study for Western Sydney (WASPSS) within the Clean Air and Urban Landscapes (CAUL) Hub, a measurement site was established on the roof a building in Western Sydney, on the edge of the Auburn CBD. Instrumentation at the site included an Open-Path FTIR spectrometer (OP-FTIR). The spectrometer was located at the measurement site with an array of retro-reflectors, terminating the measurement path, located on the roof of a building within the Auburn CBD and ~400 m from the spectrometer. The OP-FTIR spectrometer measured the integrated mixing-ratio of infrared active gases between the spectrometer and the reflectors, including CO, CO_2, CH_4 and NH_3. The system operated continuously, with a temporal resolution of 5 minutes, from October 2016 to March 2017, and from May 2017 to September 2017. These periods encompassed a summer where Sydney experienced record breaking temperatures, cool winter nights where the use of wood fires for heating was evident and days when heavy atmospheric haze resulted from hazard reduction burns in the nearby Blue Mountains.

Atmospheric NH_3 levels ranged from 0.5 to 20 ppb. A diurnal variation was evident with a maximum in the morning and a smaller peak in the evening. A strong correlation (r^2 = 0.6 to 0.75) between the measured CO and NH_3 was noted. A substantial increase in CH_4 levels (maximum ~4000 ppb) in the evenings with stable atmospheric conditions was also identified.

We report on the initial results from the OP-FTIR spectrometer deployed to measure gases relevant to urban air quality at a high temporal resolution for an extended period. We explore the potential for OP-FTIR spectroscopy to identify and quantify gaseous species from vehicle exhaust emissions and wood smoke relevant to urban air quality.

Vertically resolved pollution monitoring in Melbourne using MAX-DOAS measurements

R. G. Ryan[1], S. K. Rhodes[2], M. B. Tully[2] and R. Schofield[1]

[1] School of Earth Sciences, University of Melbourne, Melbourne, Victoria, Australia
[2] Australian Bureau of Meteorology, Melbourne, Victoria, Australia

[*] corresponding author: Robert Ryan [rgryan@student.unimelb.edu.au]

Abstract

As Australia's urban centres continue to expand, understanding the role of competing urban and rural influences on atmospheric composition will become increasingly important. In particular, modelling of air mass interactions and pollution evolution in urban and urban fringe environments is limited by a lack of vertically resolved measurements. With isolated pollution sources in urban areas, and naturally high biogenic volatile organic compound (VOC) levels, the Australian landscape provides an ideal setting to study the key oxidative species involved in these interactions, such as VOCs, nitrogen oxides (NO_x) and tropospheric ozone.

Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) is a UV-visible spectroscopic technique which has gained considerable recent attention. It is capable of providing vertical concentration profiles of aerosols, nitrogen oxides and VOC oxidation products formaldehyde and glyoxal, among other species. In this study, the first vertical profiles from MAX-DOAS measurements in Broadmeadows, Melbourne are presented for these species. The measurement location in the northern suburbs of Melbourne gives an ideal vantage point to assess the influence of rural and urban air masses on NO_x and VOC levels. Analysed alongside meteorological data, these results provide insight into the vertical evolution of pollution plumes under different VOC and tropospheric ozone formation regimes.

Aerosol number concentrations crossing the Polar Front off east Antarctica

J. B. Simmons[1*], R. S. Humphries[2] and S. R. Wilson[1]

[1] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia
[2] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia

[*] corresponding author: Jack Simmons [js828@uowmail.edu.au]

Abstract

Large uncertainties exist in estimates of direct and indirect aerosol effects on radiative forcing. An increased understanding of aerosol populations in atmospheric environments relatively free from anthropogenic influences has been identified as a promising step towards reducing these uncertainties.

Few aerosol measurement campaigns have been completed over the far Southern Ocean off the coast of the east Antarctic. This study presents results from the second aerosol measurement campaign of the east Antarctic sea ice zone. The RV Investigator, equipped with a suite of instruments including an ultrafine condensation particle counter, travelled to the far Southern Ocean in January-March 2017, as the Polar Cell Aerosol Nucleation Project (PCAN).

Results from the equivalent region in the Weddell Sea, west Antarctica, indicate an aerosol regime containing nitrogen [Dall'Osto *et al*., 2017] and sulphate [Davison, *et al*., 1996] species of biological origins. A previous voyage, the Sea Ice Physics and Ecosystem eXperiment 2012 (SIPEX-2), to the same region sampled in the present study occurred in spring 2012. A surprising step change in aerosol population moving south across the Polar front was observed. Humphries *et al*. [2016] reported a five-fold increase in CN_3 across the polar front, with mean polar cell CN_3 concentrations of 1130 cm^{-3}.

The present study reports a summer comparison to the spring CN_3 results of SIPEX 2. A seasonal comparison is necessary due to the high seasonal variability of insolation at high southern latitudes, creating seasonally varied processes impacting on the local atmosphere.

References

Dall'Osto, M., J. Ovadnevaite, M. Paglione, D. C. S. Beddows, D. Ceburnis, C. Cree, P. Cortés, M. Zamanillo, S. O. Nunes, G. L. Pérez, E. Ortega-Retuerta, M. Emelianov, D. Vaqué, C. Marrasé, M. Estrada, M. M. Sala, M. Vidal, M. F. Fitzsimons, R. Beale, R. Airs, M. Rinaldi, S. Decesari, M. Cristina Facchini, R. M. Harrison, C. O'Dowd and R. Simó, Antarctic sea ice region as a source of biogenic organic nitrogen in aerosols, *Scientific Reports,* 7, 6047, doi:10.1038/s41598-017-06188-x, 2017.

Davison, B., C. O'Dowd, C. N. Hewitt, M. H. Smith, R. M. Harrison, D. A. Peel, E. Wolf, R. Mulvaney, M. Schwikowski and U. Baltensperger, Dimethyl sulfide and its oxidation products in the atmosphere of the Atlantic and southern oceans, *Atmos. Environ.*, 30, 1895-1906, doi:10.1016/1352-2310(95)00428-9, 1996.

Humphries, R. S., A. R. Klekociuk, R. Schofield, M. Keywood, J. Ward and S. R. Wilson, Unexpectedly high ultrafine aerosol concentrations above East Antarctic sea ice, *Atmos. Chem. Phys.*, 16, 2185-2206, doi:10.5194/acp-16-2185-2016, 2016.

Inverse modelling of CO_2 surface fluxes over Australia inferred from OCO-2 XCO2 satellite retrievals

Y. Villalobos[1], S. Tomas[1] and P. J. Rayner[1]

[1]School of Earth Sciences, University of Melbourne, Melbourne, Australia

* corresponding author: Yohanna Villalobos [yvillalobos@student.unimelb.edu.au]

Abstract

Any minor change in the carbon cycle may imply a release CO_2 out of its carbon reservoirs such as land or ocean, and therefore, in warmer temperatures on Earth. Understanding the carbon cycle 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, it remains large uncertainties over its quantification, especially at regional scale. Inverse modelling using atmospheric transport models and atmospheric CO_2 observations is an attractive method to improve the accuracy of CO_2 fluxes. Satellite-based space observations offers an alternative to constraint CO_2 surface fluxes in places that lack ground based measurements. In this study, we propose to quantify optimally CO_2 surface fluxes over Australia continent at a high spatial and temporal resolution from CO_2 column-averaged dry air mole fraction (XCO2) retrieval from the orbiting Carbon Observatory-2 (OCO-2) using a Bayesian variational assimilation system (4DVAR) based on the CMAQ regional chemical transport model and its adjoint using a general solver written in python. We will show the information content of OCO2 measurements for constraining monthly mean 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 Australia continent, but also to understand the recent anomalies ('variability') that the terrestrial carbon sink has experimented in the last years in Australia.

Photolytic production of H_2 from aldehydes

B. A. Welsh[1*], A. D. C. F. Lee[1], A. W. Harrison[1], A. Kharazmi[1], M. F. Shaw[2], M. J. T. Jordan[2] and S. H. Kable[1]

[1] School of Chemistry, University of New South Wales, Kensington, NSW, Australia
[2] School of Chemistry, University of Sydney, Camperdown, NSW, Australia

[*] corresponding author: Blair Welsh [blair.a.welsh@gmail.com]

Abstract

Atmospheric H_2 is considered an indirect greenhouse gas, due to its influence on tropospheric concentrations of OH and O_3, and therefore methane [Barnes *et al*., 2003]. Photochemical production of H_2 accounts for 42.5-82.5% of total H_2 production, half of which is attributed to the photolysis of formaldehyde, while the other half remains unresolved[2]. With such qualitative estimates, and the increasing popularity of H_2 as a sustainable and clean energy source, it is important to establish a more comprehensive understanding of the sources and sinks of atmospheric H_2. Unsaturated aldehydes comprise a large percentage of both first and later generation products of the oxidation of isoprene, which is the most abundant volatile organic compound (VOC) in the atmosphere[3], barring methane. Preliminary results suggest that these larger aliphatic aldehydes could account for the missing photolytic H_2 production.

The recent discovery by this group of a photodissociation channel of acetaldehyde that yielded H_2 and ketene (CH_2CO) led to our hypothesis that H_2 is a general photoproduct from aldehydes. This has been investigated with the use of velocity map imaging (VMI) and FTIR spectroscopy techniques. The H_2 fragment and its associated photodissociation dynamics were probed with the VMI apparatus in unimolecular conditions, while FTIR spectroscopy was performed on the co-fragment under atmospheric conditions in order to determine quantum yields for the process. We have evidence of photolytic production of H_2 from propanal, butanal, isobutanal and 2-methylbutanal, with unsaturated aldehydes such as acrolein, methacrolein and crotonaldehyde the current focus of these studies.

References

Barnes, D. H., S. C. Wofsey, B. P. Fehlau, l. W. Gottlieb, J. W. Elkins, G. S. Dutton, and C. Novelli, Hydrogen in the atmosphere: Observations above a forest canopy in a polluted environment, *J. Geophys. Res. – Atmospheres*, 108:D6, 4197, doi:10.1029/2001JD001199, 2003.

Rhee, T. S., C. A. M. Brenninkmeiger and T. Röckmann, The overwhelming role of soils in the global atmospheric hydrogen cycle, *Atmos. Chem. Phys.*, 6:6, 1611-1625, doi:10.5194/acp-6-1611-2006, 2006).

Carlton, A. G., C. Wiedinmyer and J. H. Kroll, A review of Secondary Organic Aerosol (SOA) formation from isoprene, *Atmos. Chem. Phys.*, 9:14, 4987-5005, doi:10.5194/acp-9-4987-2009, 2009.

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

I. E. Galbally*, the TOAR SSC, TOAR authors and the TOAR Oceania and Antarctica Working Group

CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia

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

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 late 2017/early 2018. 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. TOAR formed regional working groups to gather ozone data for these metrics analyses including a Working Group for Oceania and Antarctica which includes Indonesia, Australia, Papua New Guinea, New Zealand, the Pacific islands and Antarctica.

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. Several other papers are in the pipeline, some being open for public comment at this stage.

This presentation will give an overview of the key results currently available from the TOAR study and a more in-depth look at the Oceania and Antarctica region including Cape Grim.

Further information

http://www.igacproject.org/TOAR

Schultz, M. G., S. Schroder, O. Lyapina.., I. E. Galbally.., R. W. Gillett.., S. Molloy, *et al*., Tropospheric Ozone Assessment Report: Database and metrics data of global surface ozone observations, *Elem. Sci. Anth*., 5:58, 26 pp., doi:10.1525/elementa.244, 2017.

Chang, K.-L., I. Petroppavlovskikh, O. R. Cooper, M. G. Schultz and T. Wang, Regional trend analysis of surface ozone observations from monitoring networks in eastern North America, Europe and East Asia, *Elem. Sci. Anth*., 5:50, 22 pp., doi:10.1525/elementa.243, 2017.

SRAD2 – the new UV-B spectrometer system at Cape Grim

S. R. Wilson*

Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia

* corresponding author: Stephen Wilson [swilson@uow.edu.au]

Abstract

UV-B radiation from the sun is a primary driver of the chemistry of the clean atmosphere. The primary process that it drives is the conversion of ozone to the hydroxyl radical through the formation of an excited oxygen atom ($O\ ^1D$). The rate of production of $O\ ^1D$ at a site like Cape Grim is dependent on a range of environmental factors, including the concentration of ozone and the amount of cloud.

A system for measuring the UV-B at Cape Grim has recently been installed in the radiation enclosure, built around a 0.3 m Horiba Jobin Yvon spectrograph. This is a replacement of the original scanning SRAD spectrometer. [Wilson, 2006; 2015] The components that make up the new system and an initial assessment of the performance of the instrument will be presented.

References

Wilson, S. R., The Cape Grim Scanning UV Spectrometer, in *Baseline Atmospheric Program (Australia) 2003-2004*, J. M. Cainey, N. Derek and P. B. Krummel (eds.), 9-16, Bureau of Meteorology and CSIRO Atmospheric Research, Melbourne, Australia, 2006.

Wilson, S. R., Characterisation of $J(O\ ^1D)$ at Cape Grim 2000–2005, *Atmos. Chem. Phys*., 15:13, 7337-7349, doi:10.5194/acp-15-7337-2015, 2015.

An update on comparisons of *in situ* carbon dioxide and methane measurements at Cape Grim

Z. M. Loh[1*], P. B. Krummel[1], L. P. Steele[1], D. A. Spencer[1], P. J. Fraser[1], R. L. Langenfelds[1], M. V. van der Schoot[1,2], N. T. Somerville[3] and J. Ward[3]

[1] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[2] now at EPA Victoria, Carlton, Victoria, Australia
[3] Cape Grim Baseline Air Pollution Station, Australian Bureau of Meteorology, Smithton, Tasmania, Australia

* corresponding author: Zoë Loh [zoe.loh@csiro.au]

Abstract

The first Picarro cavity ringdown spectrometer (CRDS) providing continuous atmospheric CO_2, CH_4 (and water vapour) measurements was installed at Cape Grim in February 2012. Loh *et al.* [2013] presented the first 18 months of Picarro data. Krummel *et al.* [2014] provided a more complete inter-comparison of the CO_2 records from the Picarro CRDS and the LoFlo NDIR (non-dispersive infra-red), and the CH_4 records from the Picarro CRDS and the Advanced Global Atmospheric Gases Experiment (AGAGE) GC-FID (gas chromatograph – flame ionisation detector).

In January 2017, a second Picarro CRDS instrument was installed at Cape Grim and at that time we transitioned to controlling both Picarro instruments with GCWerks CRDS, which we had long been using as the data processing software for CRDS instruments.

In this presentation, we again update how the Picarro records compare to the longer-term CO_2 (LoFlo NDIR) and CH_4 (GC-FID) records at Cape Grim, and also examine how the parallel Picarro records compare to each other.

References

Loh, Z., M. van der Schoot, A. Stavert, P. Krummel, P. Steele, D. Spencer, N. Somerville and J. Ward, The Cape Grim CO_2/CH_4 Picarro record, in *Atmospheric Composition & Chemistry Observations & Modelling Conference incorporating the Cape Grim Annual Science Meeting 2013* [abstract], 27-29 November 2013, Aspendale, Victoria, Bureau of Meteorology and CSIRO Marine and Atmospheric Research, Melbourne, Australia, 56, 2013.

Krummel, P. B., L. P. Steele, Z. M. Loh, D. A. Spencer, P. J. Fraser, R. L. Langenfelds, N. Somerville and J. Ward, Updated comparisons of *in situ* carbon dioxide and methane measurements at Cape Grim, in *Atmospheric Composition & Chemistry Observations & Modelling Conference incorporating the Cape Grim Annual Science Meeting 2014* [abstract], 12-14 November 2014, CSIRO Oceans and Atmosphere Flagship, Melbourne, Australia, 19, 2014.

Real-time accurate optical measurements of CO_2 number density

S. K. Scholten[1*], C. Perrella[1], J. D. Anstie[1], R. T. White[1], N. B. Hébert[2], W. Al-Ashwal[1], J. Genest[2] and A. N. Luiten[1]

[1] Institute for Photonics and Advanced Sensing, School of Physical Sciences, University of Adelaide, Adelaide, SA, Australia
[2] Centre d'optique, photonique et laser, Université Laval, Québec, Canada

[*] corresponding author: Sarah Scholten [sarah.scholten@adelaide.edu.au]

Abstract

Rapid measurements of gas concentration are potentially beneficial for environmental monitoring, high- precision spectroscopy, medical breath analysis, leak detection and liquid natural gas process monitoring. Here, we demonstrate real-time measurement of CO_2 concentration with a precision better than 10^{-3} and an accuracy of 6×10^{-3} for use in such applications. An optical frequency comb (OFC) is used to perform these measurements as they are near-ideal sources for molecular spectroscopy allowing rapid, broad-spectrum measurements with dense spectral sampling [Adler *et al*., 2010; Scholten *et al*., 2016]. These characteristics allow real-time investigation of the complex species-specific spectra of molecules.

We obtain concentration measurements in < 1 s in a 6.5 m sample cell with relative concentration of CO_2 and optically transparent N_2 buffer gas varied over a ~2 hr period. An OFC is used to interrogate the gas sample, before the light is directed to a high-resolution spectrometer based on a virtually-imaged phased array (VIPA) and sensitive InGaAs camera. This image is combined with reference, dark-background, and frequency-calibration images to produce conventional CO_2 spectra that span ~3 THz (~25 nm) with 2 GHz resolution and excellent signal-to-noise (Figure 1a). Parameters from the HITRAN 2012 database were used to construct a model of the 126 strongest spectral lines of CO_2 [Rothman *et al*., 1998; 2013]. The model is fit to each spectrum for concentration extraction (Figure 1b) with a measurement returned every ~0.9 s.

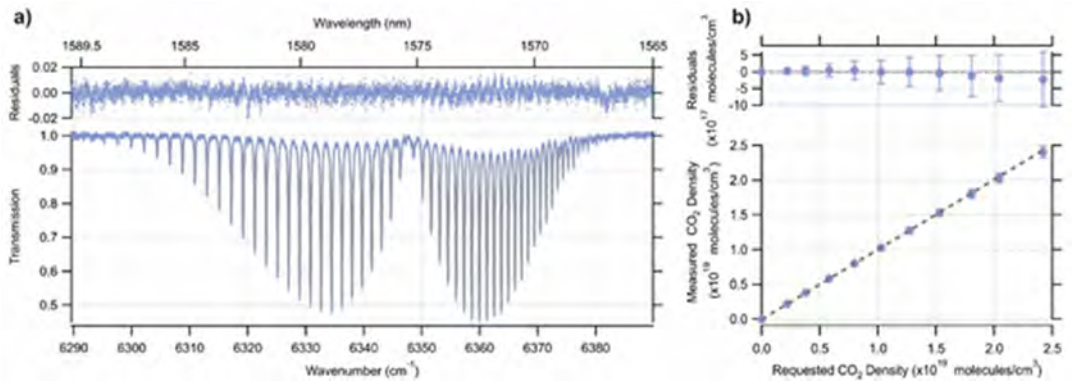


Figure 1. (a) 100% CO_2 spectrum (blue markers) with fit (grey line) acquired and analysed in < 1 s. (b) Comparison of extracted vs requested number densities with expected 1:1 line as concentration is varied over a ~2 hr period. Error bars are from listed uncertainties in model parameters.

References

Adler, A F., M. J. Thorpe, K. C. Cossel and J. Ye, Cavity-enhanced direct frequency comb spectroscopy: technology and applications, *Annu. Rev. Anal. Chem*., 3, 175–205, doi:10.1146/annurev-anchem-060908-155248, 2010.

Scholten, S. K., J. D. Anstie, N. Bourbeau Hébert, R. T. White, J. Genest and A. N. Luiten, Complex direct comb spectroscopy with a virtually imaged phased array, *Opt. Lett.*, 41:6, 1277-1280, doi:10.1364/OL.41.001277, 2016.

Rothman, L. S., C. P. Rinsland, A. Godman *et al*., The HITRAN molecular spectroscopic database and hawks (HITRAN atmospheric workstation): 1996 edition, *J. Quant. Spectrosc. Radiat. Transfer*, 60:5, 665–710, doi:10.1016/S0022-4073(98)00078-8, 1998.

Rothman, L. S., I. E. Gordon, Y. Babikov *et al*., HITRAN2012 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer*, 130, 4-50, doi:10.1016/j.jqsrt.2013.07.002, 2013.

The imprint of ENSO on total column greenhouse gas measurements

B. Bukosa[1], N. M. Deutscher[1], J. A. Fisher[1], D. W. T. Griffith[1], V. A. Velazco[1], P. Wennberg[2], G. Toon[2], D. Feist[3], M. Kumar Sha[4] and M. de Maziére[4]

[1] Centre for Atmospheric Chemistry, University of Wollongong, Wollongong, NSW, Australia
[2] California Institute of Technology, Pasadena, California, USA
[3] Max Planck Institute for Biogeochemistry, Jena, Germany
[4] Royal Belgian Institute for Space Aeronomy, Brussels, Belgium

[*] corresponding author: Beata Bukosa [bb907@uowmail.edu.au]

Abstract

The El Niño–Southern Oscillation (ENSO) is a natural variability of the climate system and it is known to have significant effects on the Australian climate. However, there are still unanswered questions related to its formation and large uncertainties about its impact on future climate and the global carbon cycle.

In this study we use ratios of column average CO and CO_2 ($XCO:XCO_2$) from the Total Carbon Column Observing Network (TCCON) to identify the strength and latitudinal dependence of the impact of different ENSO phases on the carbon cycle. TCCON has global coverage, which allows us to also study the latitudinal change of the ENSO signal. TCCON measurements are sensitive to regional scale processes, and so we complement the column averaged data with long-term surface in-situ measurements, which are sensitive to local scales.

In our analysis we study the inter-annual variability (IAV) of $XCO:XCO_2$ and the correlation of anomalies with El Niño and La Niña events. In order to identify the different processes driving IAV, we perform tagged tracer CO and CO_2 simulations with a global chemical transport model (GEOS-Chem). We also examine the lagged correlation between ENSO and greenhouse gas anomalies to identify the optimal time needed for the manifestation of the different drivers. Our results show strong correlation between ENSO and the $XCO:XCO_2$ IAV in the tropics, with the correlation decreasing towards higher latitudes. Introducing the lag significantly improved the correlation and suggests a delayed response of carbon gas emissions to ENSO forcing.

Estimated ratios of GHG emissions observed over the Yellow Sea and the East China Sea during a spring 2017 cruise

Y. Liu[1], L. Zhou[1*], P. P. Tans[2], K. Zang[1] and S. Cheng[1]

[1] Chinese Academy of Meteorological Sciences (CAMS), CMA, Beijing, China
[2] Earth System Research Laboratory, NOAA, Boulder, Colorado, USA

[*] corresponding author: Lingxi Zhou [zhoulx@cma.cn]

Abstract

We researched the data of atmospheric CO_2, CH_4, CO, and N_2O mixing ratios obtained on the ship over the Yellow Sea laying between north-eastern China and the Korean Peninsula and the East China Sea in the spring 2017. We analysed the variations of the enhancement ratios between every pair of trace gases at different source regions selected by using the NOAA HYSPLIT Model. The voyage was made by the Ocean University of China over the Yellow Sea and the East China Sea in the spring and the observation data of CO_2, CH_4, CO, and N_2O was measured by two Picarro analysers on the ship. The stability of the two instruments was good during sailing. The characteristics of the mole fraction distributions of the four gas species were very similar to each other. The correlations of every pair of gases when the air had remained over the Yellow Sea and the East China Sea are weak. The enhancement ratio of $\Delta CO/\Delta CO_2$ was much higher in big cities like Beijing and Shanghai and it was also higher than the other pairs of gases, whereas the enhancement ratio of $\Delta CH_4/\Delta CO$ was lower, influenced by the high CO emission in the winter and early spring. The ratios of the average enhancements at the Yellow Sea and the East China Sea were caused by the emissions from wide regional areas when compared with the values of NOAA's Marine Boundary Layer (MBL). The ratios of the averages of North (Russia) were on average closer to the MBL. The differences of the enhancement ratios of every pair of gases were influenced by the emissions in different source regions.

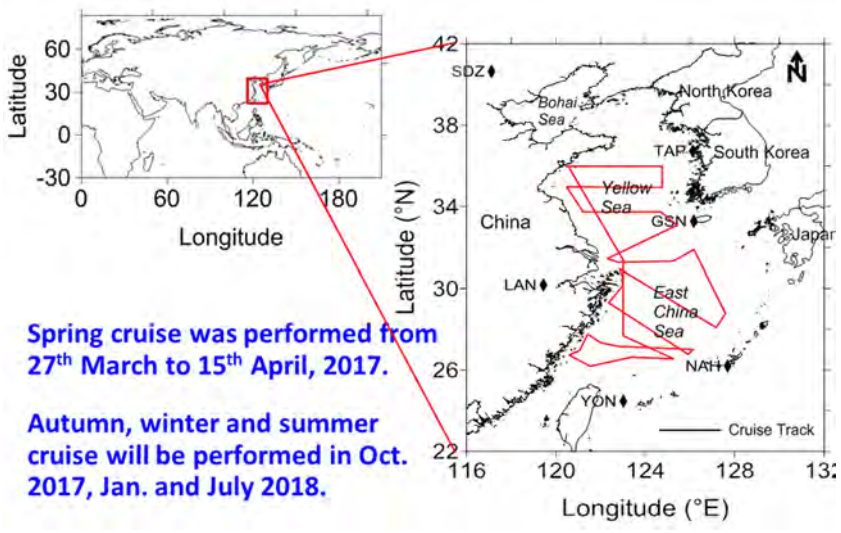


Figure 1. Spring cruise track was between the Pacific Ocean and the Asian continent, and the survey vessel sailed from Qingdao and finally returned to Qingdao.

References

Zang, K.P., L.X. Zhou and J.Y. Wang, Carbon dioxide and methane in the China sea-shelf boundary layer observed by cavity ring-down spectroscopy, *J. Atmos. Oceanic Technol.*, doi:10.1175/JTECH-D-16-0217.1, 2017.

Cheng, S.Y., X.Q. An, L.X. Zhou, P.P. Tans and A. Jacobson, Atmospheric CO_2 at Waliguan station in China: Transport climatology, temporal patterns and source-sink region representativeness, *Atmos. Environ*., 159, 107-116, doi:10.1016/j.atmosenv.2017.03.055, 2017.

Measurements of gases in ice at Patriot Hills, West Antarctica

D. P. Thornton[1*], D. M. Etheridge[1], M. Rubino[1,2], C. S. M. Turney[3] and C. J. Fogwill[3,4]

[1] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[2] Dipartimento di Matematica e Fisica, Università della Campania 'Luigi Vanvitelli', Caserta, Italy
[3] School of Biological, Earth and Environmental Sciences, University of NSW, Sydney, NSW, Australia
[4] School of Geography, Geology and the Environment, Keele University, Staffordshire, UK

[*] corresponding author: David Thornton [david.p.thornton@csiro.au]

Abstract

Ice core programs involve the vertical drilling and collection of ice in order to develop the history of an ice sheet, the atmospheric composition and climate. The extraction and analysis of air within bubbles trapped within the ice matrix to assess past concentrations of trace gases contributes to this endeavour. Blue Ice Areas (BIAs) however provide an opportunity to access ice which has been dynamically tilted, stripped of snow and ablated at the surface via prevailing katabatic airflows.

This upwelling of ancient ice to the surface in effect provides a horizontal ice core, therefore negating the requirements associated with traditionally expensive and logistically complex vertical drilling programs. It also allows access to large volumes of ice for analysis of trace gases and their isotopes that require large sample size. Typically, blue ice areas form where mountains obstruct ice flow and high winds transport an abundance of snow. These conditions cause ice to flow upwards, towards the surface. By walking in the direction of the mountains, we essentially walk back in time over older and older ice.

Patriot Hills, at the end of Horseshoe Valley in the Ellsworth Mountains of West Antarctica, is one such blue ice area providing a unique record of paleo environmental and ice dynamic changes. As part of a wider ice sheet history study, we report on a reconstruction of trace gas concentrations from Patriot Hills. This area initially presented issues with ice core quality (cracks, possible impurities) and made the extraction of air from within ice core bubbles a challenge. However, by matching multiple trace gas concentrations with trace gas records from different Antarctic sites and improving the quality of the ice cores via deeper samples, results thus far suggest our trace gas measurements from Patriot Hills can be used to reconstruct atmospheric and climatic changes through the Holocene and possibly into the last interglacial period.

References

Fogwill, C. J., C. S. M. Turney, N. R. Golledge, D. M. Etheridge, M. Rubino, D. P. Thornton, A. Baker, J. Woodward, K. Winter, T. D. van Ommen, A. D. Moy, M. A. J. Curran, S. Davies, M. E. Weber, M. I. Bird, N. C. Munksgaard, L. Menviel, C. M. Rootes, B. Ellis, H. Millman, J.Vohra, A. Rivera and A. Cooper, Antarctic ice sheet discharge driven by atmosphere-ocean feedbacks at the Last Glacial Termination, *Nature Scientific Reports*, 7:39979, doi:10.1038/srep39979, 2017.

Turney, C., C. Fogwill, T. van Ommen, A. Moy, D. Etheridge, M. Rubino, M. Curran and A. Rivera, Late Pleistocene and early Holocene Change in the Weddell Sea: A New Highly-Resolved Climate Record from Patriot Hills, Ellsworth Mountains, West Antarctica, J. Quat. Sci., 28:7, 697-704, doi:10.1002/jqs.2668, 2013.

Air archiving: recent research and operational developments

R. L. Langenfelds[1*], L. P. Steele[1], P. J. Fraser[1], B. Mitrevski[1], J. Ward[2] and N. T. Somerville[2]

[1] CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia
[2] Cape Grim Baseline Air Pollution Station, Bureau of Meteorology, Smithton, Tasmania, Australia

[*] corresponding author: Ray Langenfelds [ray.langenfelds@csiro.au]

Abstract

The Cape Grim Air Archive (CGAA) is a unique set of high-volume air samples that were collected at Cape Grim under baseline conditions. The archiving program is now in its 40th year of operation. The CGAA continues to be a resource of choice for reconstruction of high quality, multi-decadal atmospheric records of a wide range of trace gases and isotopes.

This talk will describe some of the studies based on measurements of the CGAA in recent years. Analysed species include CFCs [Laube *et al*., 2014, 2016; Allin *et al*., 2015], HCFCs [Schoenenberger *et al*., 2015; Vollmer *et al*., 2015], PFCs [Trudinger *et al*., 2016], halons [Vollmer *et al.*, 2016], clumped isotopes of oxygen [Yeung *et al*., 2016] and isotopes of helium [Mabry *et al*., 2015; Boucher *et al*., in prep.].

Recent operational developments include:

- preparation of a 'seasonal archive', through monthly collection of samples over a full year to enable future reconstruction of trace gas seasonal cycles,
- archiving of old air samples from miscellaneous sites and air mass histories that are separate from, but complementary to, the established CGAA. These samples are variously non-baseline, of urban origin, or from specific sampling programs or campaigns. They are potentially useful for supporting CGAA-derived records, or to define long-term trends in characteristics of trace gas emissions or exchange processes.

References

Allin, S. J., J .C. Laube, E. Witrant, J. Kaiser, E. McKenna, P. Dennis, R. Mulvaney, E. Capron, P. Martinerie, T. Röckmann, T. Blunier, J. Schwander, P. J. Fraser, R. L. Langenfelds and W. T. Sturges, Chlorine isotope composition in chlorofluorocarbons CFC-11, CFC-12 and CFC-113 in firn, stratospheric and tropospheric air, *Atmos. Chem. Phys*., 15:12, 6867–6877, doi:10.5194/acp-15-6867-2015, 2015.

Laube, J. C., M. J. Newland, C. Hogan, C. A. M. Brenninkmeijer, P. J. Fraser, P. Martinerie, D. E. Oram, C. E. Reeves, T. Röckmann, J. Schwander, E. Witrant and W. T. Sturges, Newly detected ozone-depleting substances in the atmosphere, *Nature Geoscience*, 7, 266–269, doi:10.1038/NGEO2109, 2014.

Laube, J. C., N. M. Hanif, P. Martinerie, E. Gallacher, P. J. Fraser, R. Langenfelds, C. A. M. Brenninkmeijer, J. Schwander, E. Witrant, J-L. Wang, C-F. Ou-Yang, L. J. Gooch, C. E. Reeves, W. T. Sturges and D. E. Oram, Tropospheric observations of CFC-114 and CFC-114a with a focus on long-term trends and emissions, *Atmos. Chem. Phys*., 16:23, 15347–15358, doi:10.5194/acp-16-15347-2016, 2016.

Mabry, J. C., T. Lan, C. Boucher, P. G. Burnard, M. S. Brennwald, R. Langenfelds and B. Marty, No evidence for change of the atmospheric helium isotope composition since 1978 from re-analysis of the Cape Grim Air Archive, *Earth Planet. Sci. Lett*., 428, 134–138, doi:10.1016/j.epsl.2015.07.035, 2015.

Schoenenberger, F., M. K. Vollmer, M. Rigby, M. Hill, P. J. Fraser, P. B. Krummel, R. L. Langenfelds, T. S. Rhee, T. Peter, and S. Reimann (2015), First observations, trends, and emissions of HCFC-31 (CH_2ClF) in the global atmosphere, *Geophys. Res. Lett*., 42, 7817–7824, doi:10.1002/2015GL064709, 2015.

Trudinger, C. M., P. J. Fraser, D. M. Etheridge, W. T. Sturges, M. K. Vollmer, M. Rigby, P. Martinerie, J. Mühle, D. R. Worton, P. B. Krummel, L. P. Steele, B. R. Miller, J. Laube, F. S. Mani, P. J. Rayner, C. M. Harth, E. Witrant, T. Blunier, J. Schwander, S. O'Doherty and M. Battle, Atmospheric abundance and global emissions of perfluorocarbons CF_4, C_2F_6 and C_3F_8 since 1800 inferred from ice core, firn, air archive and in situ measurements, *Atmos. Chem. Phys*., 16:18, 11733–11754, doi:10.5194/acp-16-11733-2016, 2016.

Vollmer, M. K., J. Mühle, C. M. Trudinger, M. Rigby, S. A. Montzka, C. M. Harth, B. R. Miller, S. Henne, P. B. Krummel, B. D. Hall, D. Young, J. Kim, J. Arduini, A. Wenger, B. Yao, S. Reimann, S. O'Doherty, M. Maione, D. M. Etheridge, S. Li, D. P.

Verdonik, S. Park, G. Dutton, L. P. Steele, C. R. Lunder, T-S. Rhee, O. Hermansen, N. Schmidbauer, R. H. J. Wang, M. Hill, P.K. Salameh, R. L. Langenfelds, L. Zhou, T. Blunier, J. Schwander, J. W. Elkins, J. H. Butler, P. G. Simmonds, R. F. Weiss, R. G. Prinn and P. J. Fraser, Atmospheric histories and global emissions of halons H-1211 ($CBrClF_2$), H-1301 ($CBrF_3$), and H-2402 ($CBrF_2CBrF_2$), *J. Geophys. Res. – Atmos.*, 121, 3663–3686, doi:10.1002/2015JD024488, 2016.

Vollmer, M. K., M. Rigby, J. C. Laube, S. Henne, T-S. Rhee, L. J. Gooch, A. Wenger, D. Young, L. P. Steele, R. L. Langenfelds, C. A. M. Brenninkmeijer, J-L. Wang, C. F. Ou-Yang, S. A. Wyss, M. Hill, D. E. Oram, P. B. Krummel, F. Schoenenberger, C. Zellweger, P. J. Fraser, W. T. Sturges, S. O'Doherty and S. Reimann, Abrupt reversal in emissions and atmospheric abundance of HCFC-133a (CF_3CH_2Cl), *Geophys. Res. Lett*., 42, 8702–8710, doi:10.1002/2015GL065846, 2015.

Yeung, L. Y, L. T. Murray, J. L. Ash, E. D. Young, K. A. Boering, E. L. Atlas, S. M. Schauffler, R. A. Lueb, R. L. Langenfelds, P. B. Krummel, L. P. Steele and S. D. Eastham, Isotopic ordering in atmospheric O_2 as a tracer of ozone photochemistry and the tropical atmosphere, *J. Geophys. Res. – Atmos*., 121:20, doi:10.1002/2016JD025455, 2016.

Carbonyl sulfide (COS) pollution at Aspendale: what are the local sources?

P. J. Fraser*, B. L. Dunse, B. Mitrevski, P. B. Krummel, L. P. Steele and N. Derek

CSIRO Oceans and Atmosphere, Climate Science Centre, Aspendale, Victoria, Australia

* corresponding author: Paul Fraser [paul.fraser@csiro.au]

Abstract

Carbonyl sulphide (COS) is the most abundant gaseous sulfur species in the atmospheric sulfur cycle, contributing significantly to stratospheric aerosol formation (Montzka *et al*., 2007), and proving useful as a tracer for gross primary productivity (GPP, Campbell *et al*., 2017). Carbonyl sulphide sources are predominantly biological (75%: biomass burning, oceans, soils) and 25% industrial: oxidation of carbon disulphide (CS_2) released during the production of rayon (15%), coal combustion (8%) and aluminium production (2%).

Southern hemispheric industrial COS sources are largely coal combustion and aluminium production. *In situ* measurements of COS at CSIRO Aspendale (2006-2017) on the Medusa GC-MS instrument show clear evidence of local COS sources, likely from both coal burning (Anglesea and LaTrobe Valley power stations) and aluminium production (Point Henry smelter). Following the closures of the Point Henry smelter (2014) and the Anglesea power station (2015), there is little evidence of COS pollution in the Aspendale record. Estimation of the past COS emissions from these sources will require future inverse modelling studies.

The Aspendale, Cape Grim (NOAA) and South Pole COS data are compared, showing very similar baseline behaviour, with mixing ratios reaching a minimum in winter, resulting from a temperature-dependent oceanic source [Montzka *et al*., 2007]. Some recent differences between Cape Grim and South Pole COS data have emerged which need to be resolved in order to continue to use COS data as an indicator of GPP.

References

Campbell, I. E., J. A. Berry, U. Seibt, S. J. Smith, S. A Montzka, T. Launois, S. Belviso, L. Bopp and M. Laine, Large historical growth in global terrestrial gross primary productivity, *Nature,* 544, 84-87, doi:10.1038/nature22030, 2017.

Montzka, S. A., P. Calvert, B. D. Hall, J. W. Elkins, T. J. Conway, P. P. Tans and C. Sweeney, On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2, *J. Geophys. Res*., 112, D09302, doi:10.1029/2006JD007665, 2007