Surface observations of VOCs and aerosol chemical composition over temperate oceans in the Southern Hemisphere

www.cawcr.gov.au

Sarah Lawson, Melita Keywood, Ian Galbally, Paul Selleck, Min Cheng, Mike Harvey, Cliff Law, Jason Ward, Rob Gillett and Zoran Ristovksi

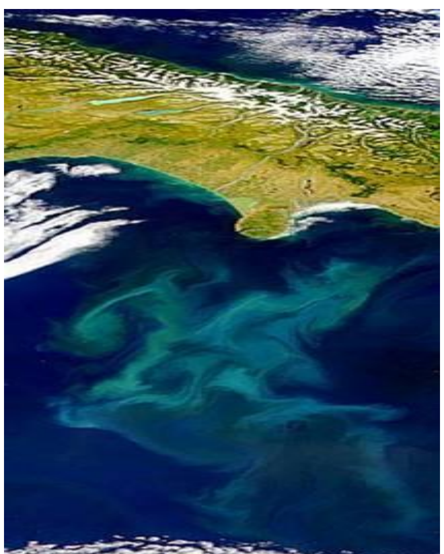
Australian Government
Bureau of Meteorology

The Centre for Australian Weather and Climate Research
A partnership between CSIRO and the Bureau of Meteorology

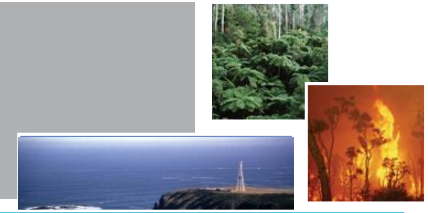
CSIRO

Overview

- VOC results from a research voyage over the South West Pacific (Surface Ocean Aerosol Production)
- Dicarbonyl (incl glyoxal) surface observations over South West Pacific (SOAP voyage), Southern Ocean (Cape Grim Baseline Station)
- Long term aerosol chemical composition record from Cape Grim

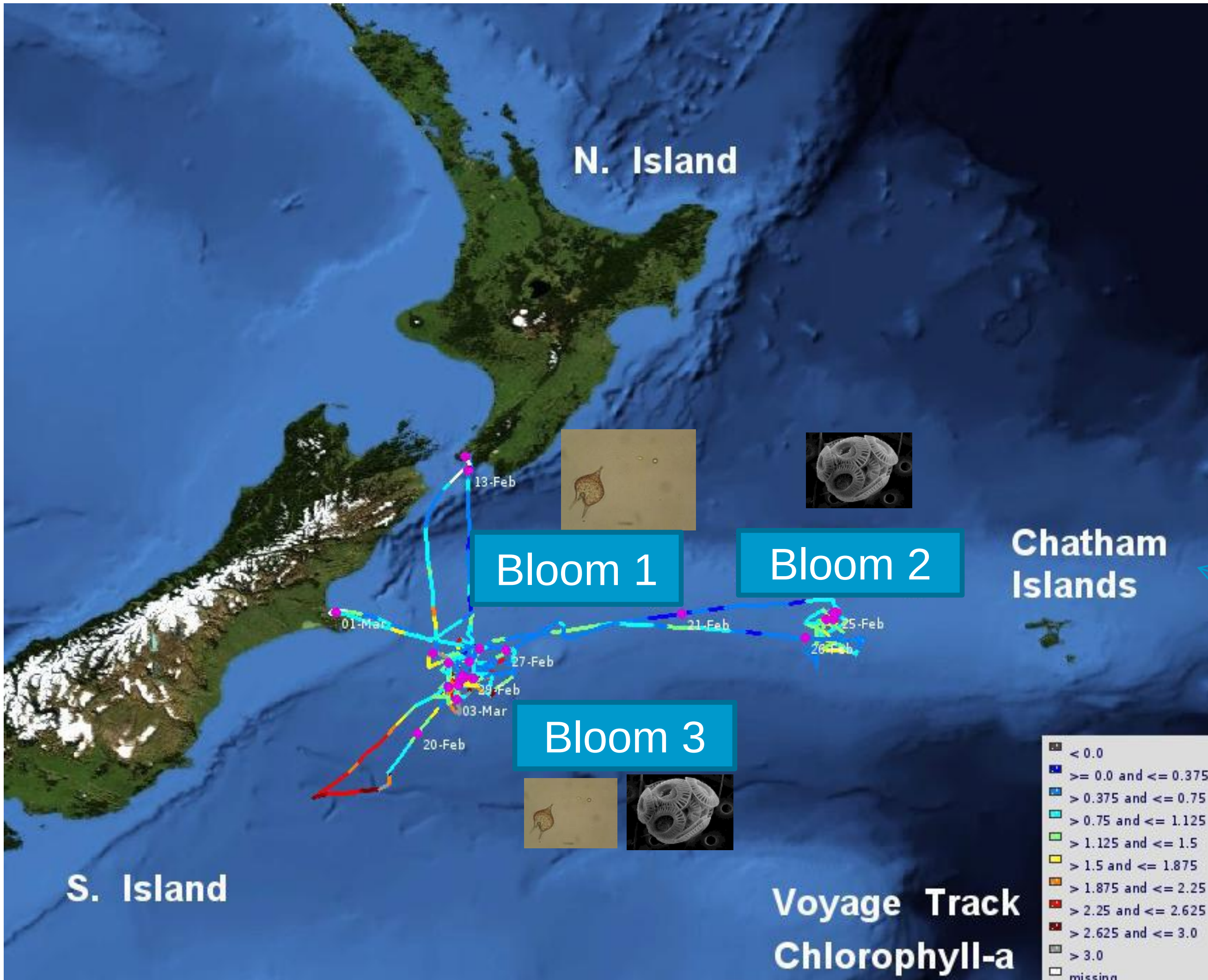


SOAP measurement summary



	Measurement	Organisation
Air Sea Exchange	CO_2/ DMS flux	NIWA, NUIG Ireland, UC Irvine US, IFM-G Germany, U Chapman US, SUNY US
Ocean Biology/ biogeochemistry	SST, Diss. DMS, DMSP, pH, DOM characterisation	NIWA, U Laval Canada
	Chlorophyll-a, bacterial & phytoplankton density/ composition, bacterial enzyme activity, nutrients	NIWA
Atmospheric chemistry	Aerosol nuclei production Aerosol chemical composition (filters) Aerosol size distribution/count Black carbon **Cloud condensation nuclei (CCN)**	UEF Finland NIWA QUT NIWA **CSIRO CMAR**
	Atmospheric DMS	UC Irvine, NIWA, **CSIRO CMAR**
	Halocarbons, I_2, halogen oxides	NIWA University Cambridge
	Volatile organic compounds	**CSIRO CMAR**

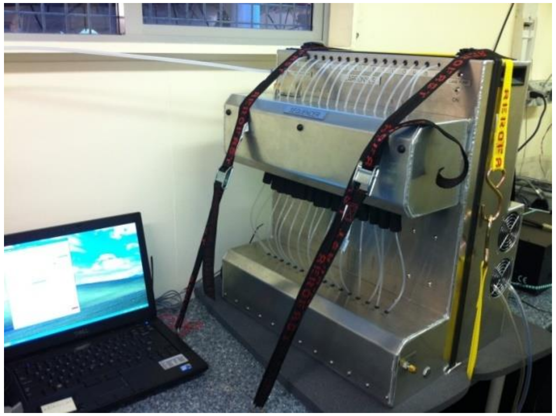
SOAP Voyage track



Chatham Rise: subtropical front: Mixing of water bodies (nutrient rich sub-Antarctic and nutrient depleted sub-tropical)

VOC measurements

Proton Transfer Reaction Mass Spectrometer (PTR-MS). Range of VOCs with 5-20 min resolution

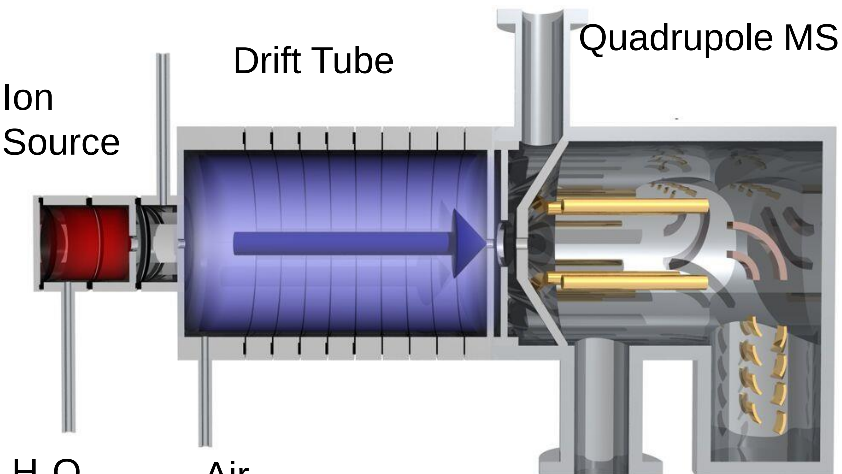


“Sequencer” automatically sampled air on to 2,4-DNPH cartridges for later analysis at Aspendale by and HPLC/diode array

“Baseline” switch developed to avoid sampling concentrated ship exhaust

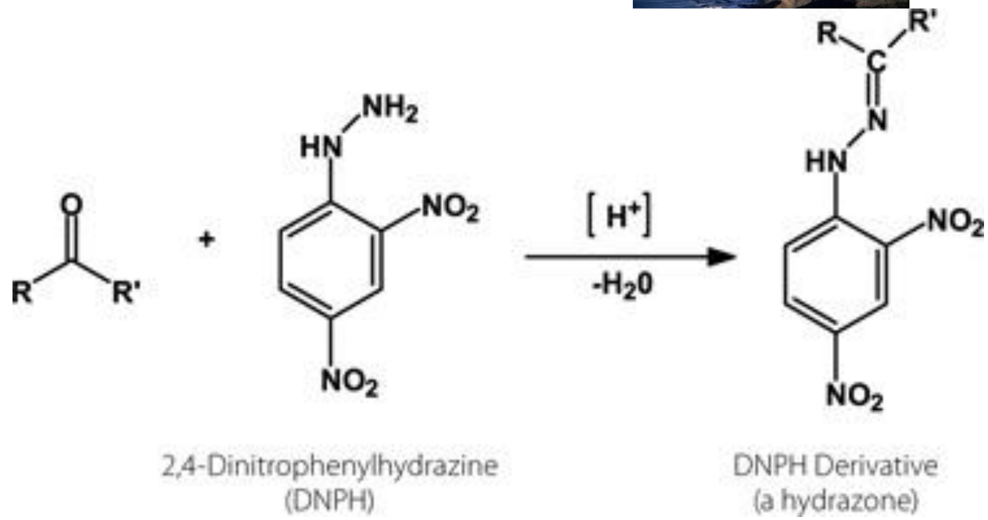
Proton Transfer Reaction Mass Spectrometer (PTR-MS)

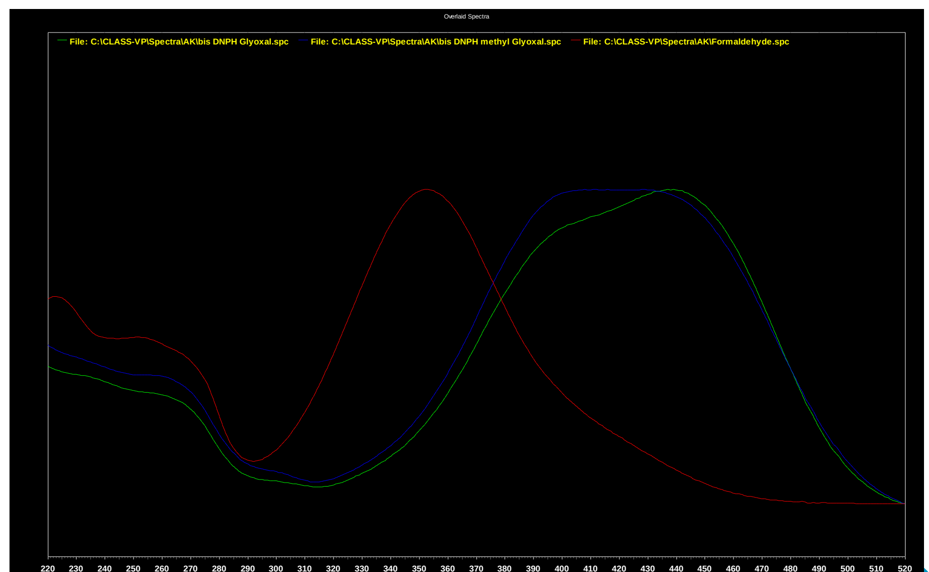
- Online chemical ionisation mass spectrometer
- Ion Source > 98% H_3O^+ (reagent ion) <2% O_2^+
- Primary reaction is:
  $VOC + H_3O^+ \rightarrow VOCH^+ + H_2O$
- detects compounds with proton affinities (PA) greater than H_2O
- Calibrated for formaldehyde, methanol, acetonitrile, acetaldehyde, acrolien, acetone, DMS, isoprene, methacrolein, methyl ethyl ketone, benzene, toluene, m-xylene, tri methyl benzene and alpha-pinene
- several 'zero' measurements per day to determine background signal from interference ions (O_2^+, NO^+, water clusters) and out-gassing from materials
- Detection limits low ppt to 10s of ppt



Carbonyl measurement – DNPH cartridges

- Aldehyde, ketones (up to C8) and dicarbonyls trapped on silica adsorbent coated with 2,4-dinitrophenylhydrazine(2,4-DNPH), and converted to the hydrazone derivatives
- The derivatives are eluted from the cartridge in acetonitrile and analysed by HPLC with diode array detector (EPA Method TO11A)
- MDLs: 1-2 ppt glyoxal and methyl glyoxal for 24 hour sample

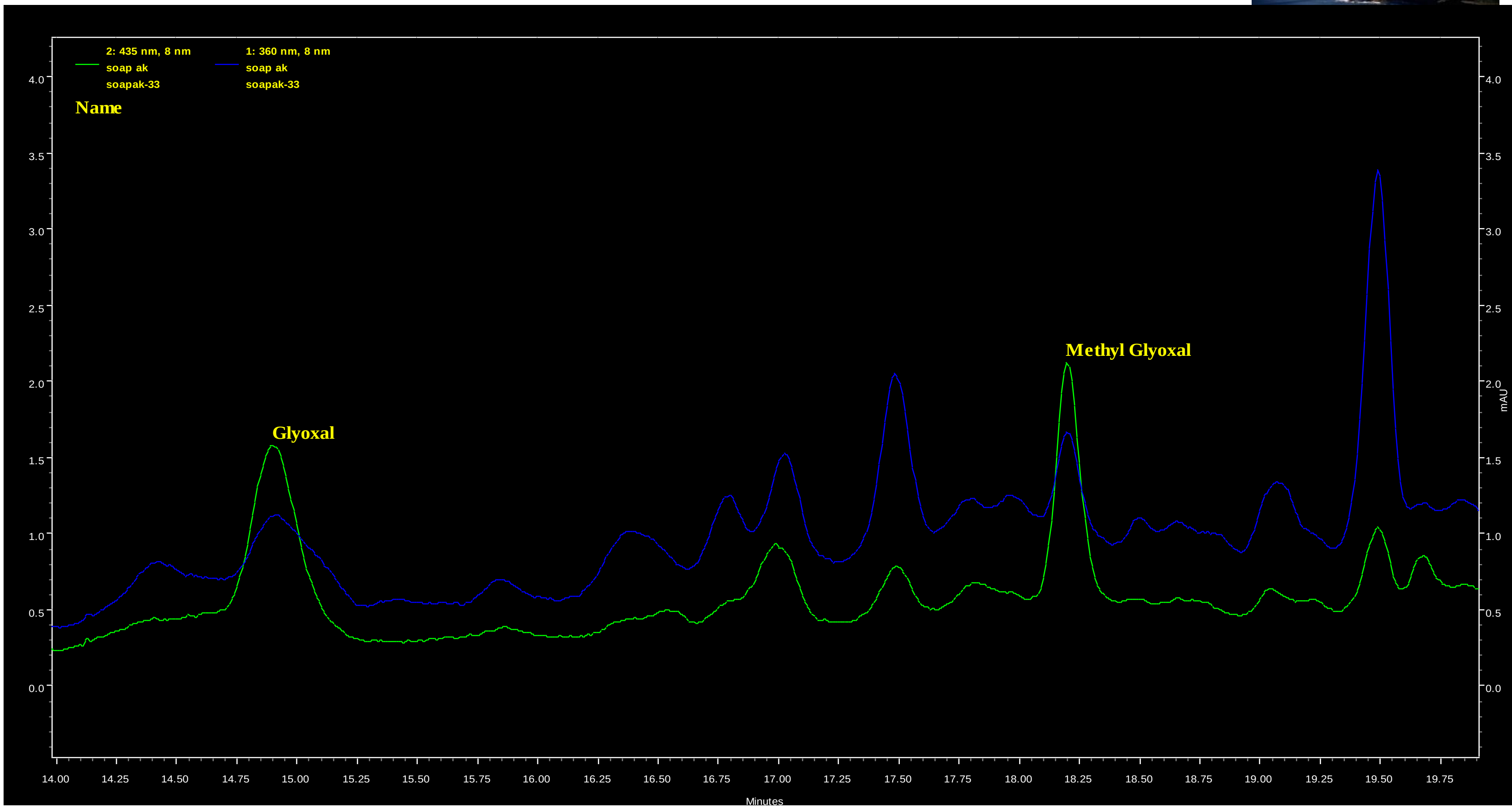




Red: formaldehyde - monocarbonyl (360nm)

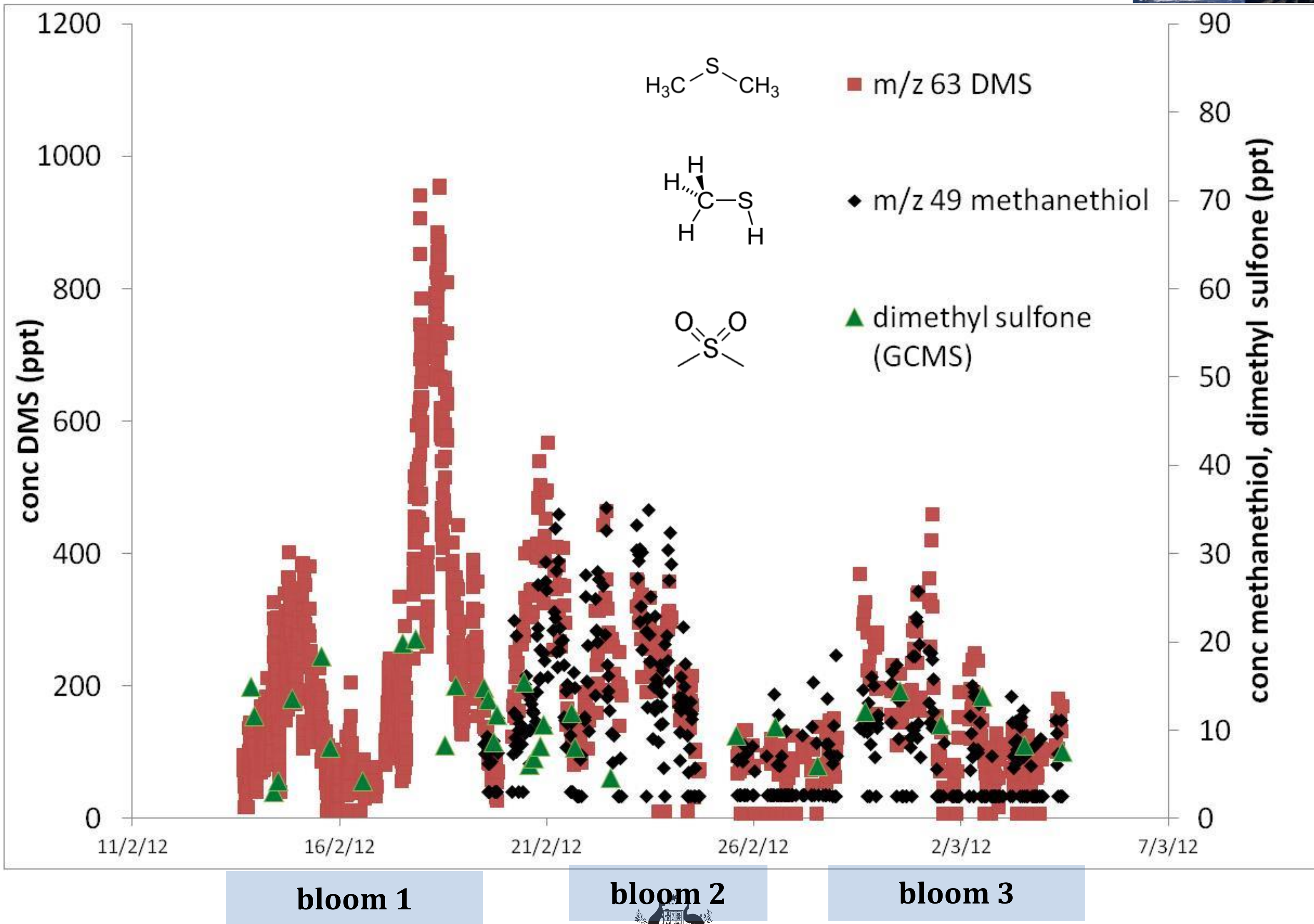
Blue and green: glyoxal and methyl glyoxal - dicarbonyls (435nm)

Sample chromatogram at 360 and 435 nm

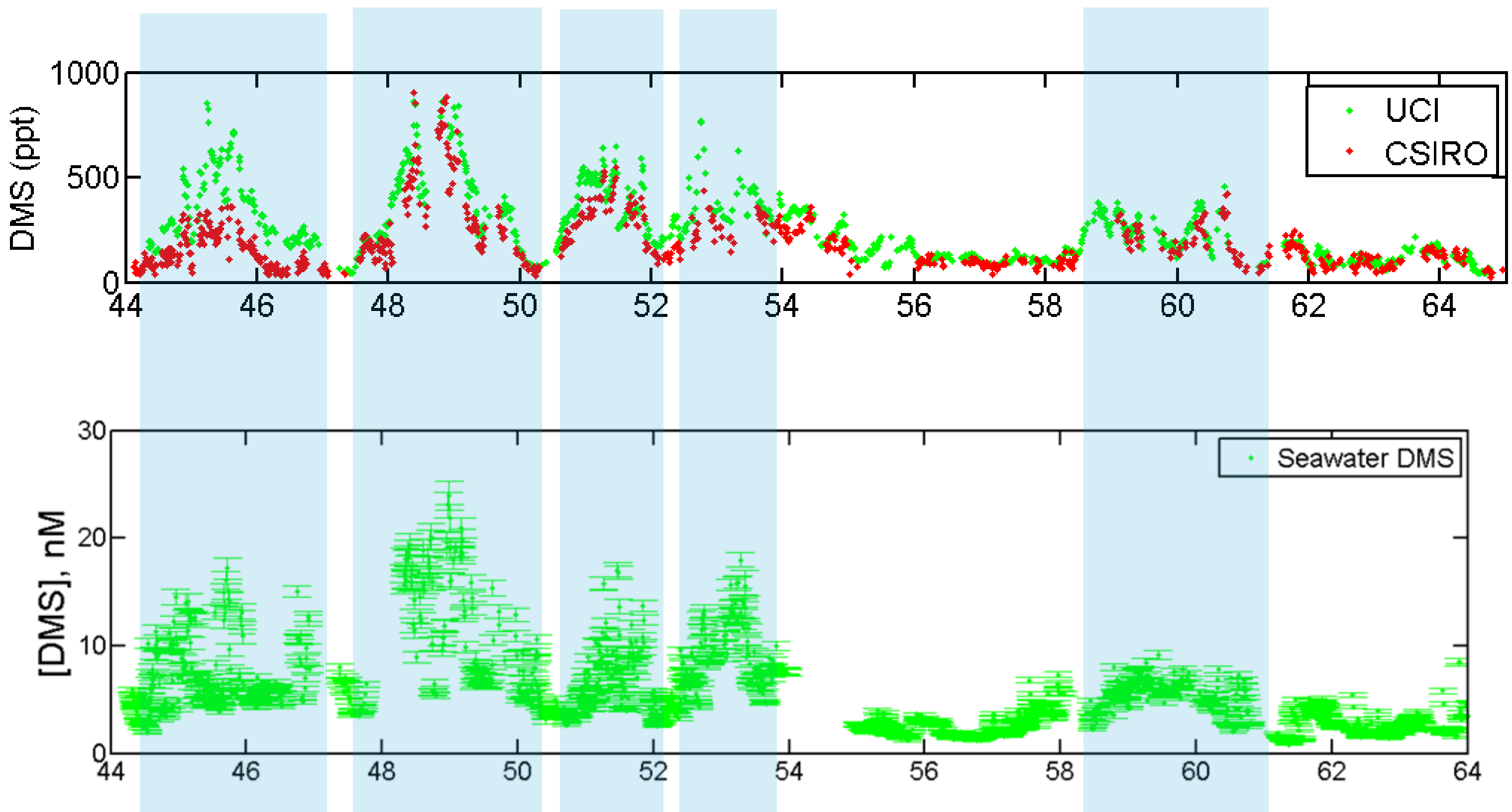


Sample chromatogram – blue 360m, green 435nm

DMS emissions and the sulphur cycle

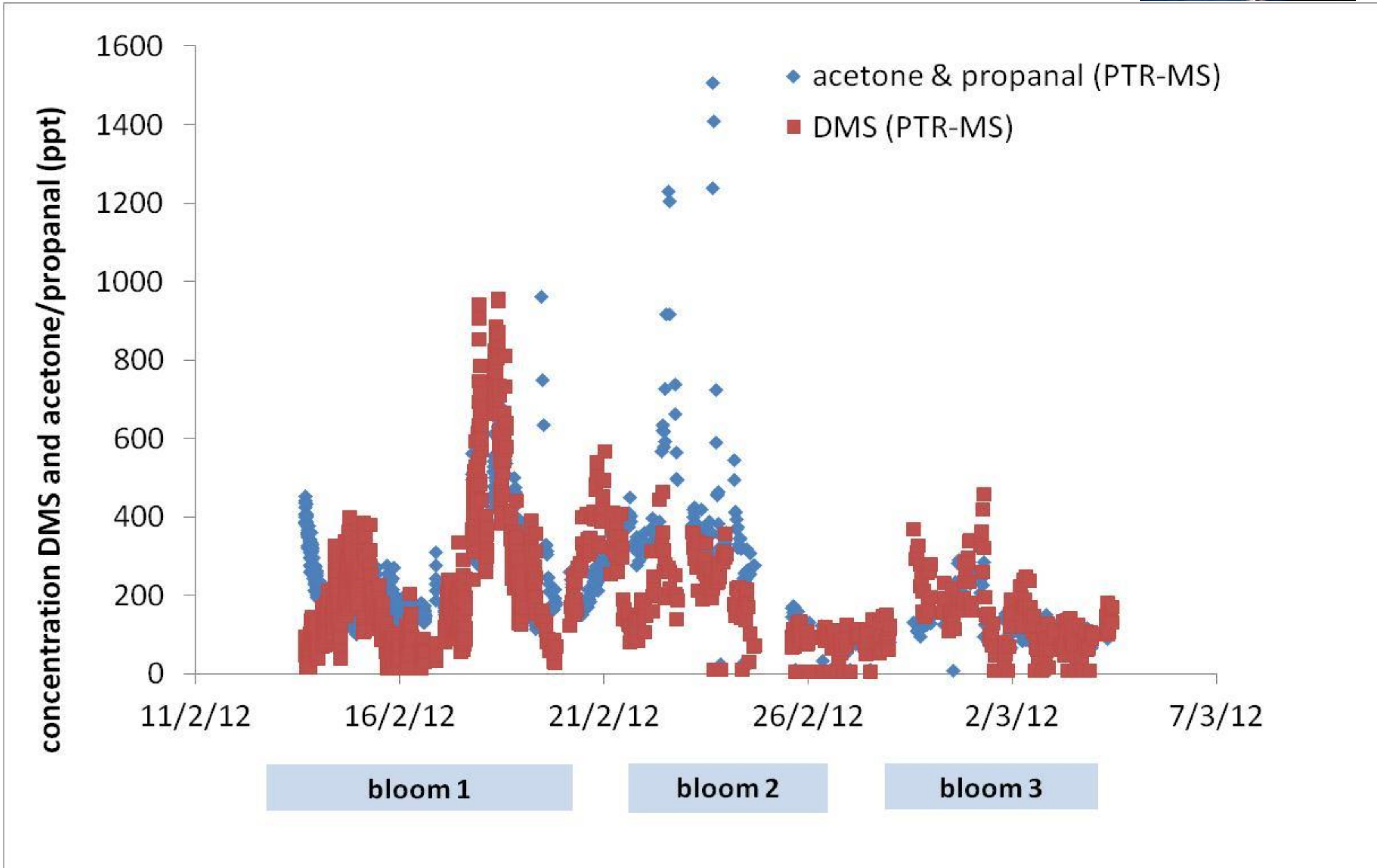


Atmospheric DMS influenced by seawater concs

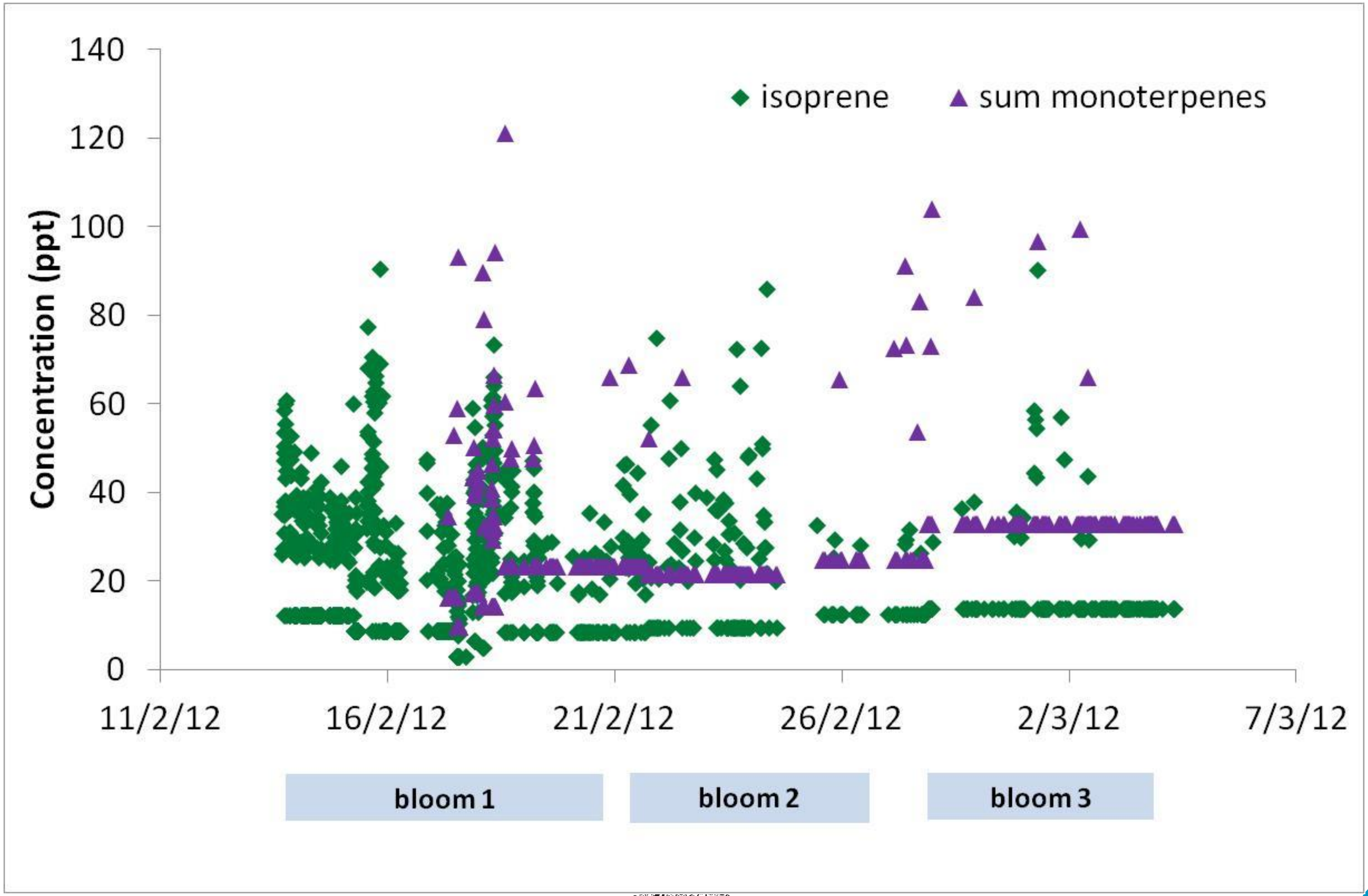


UCI atmospheric and seawater data courtesy of Eric Saltzman and Tom Bell

DMS and acetone – common biological source?



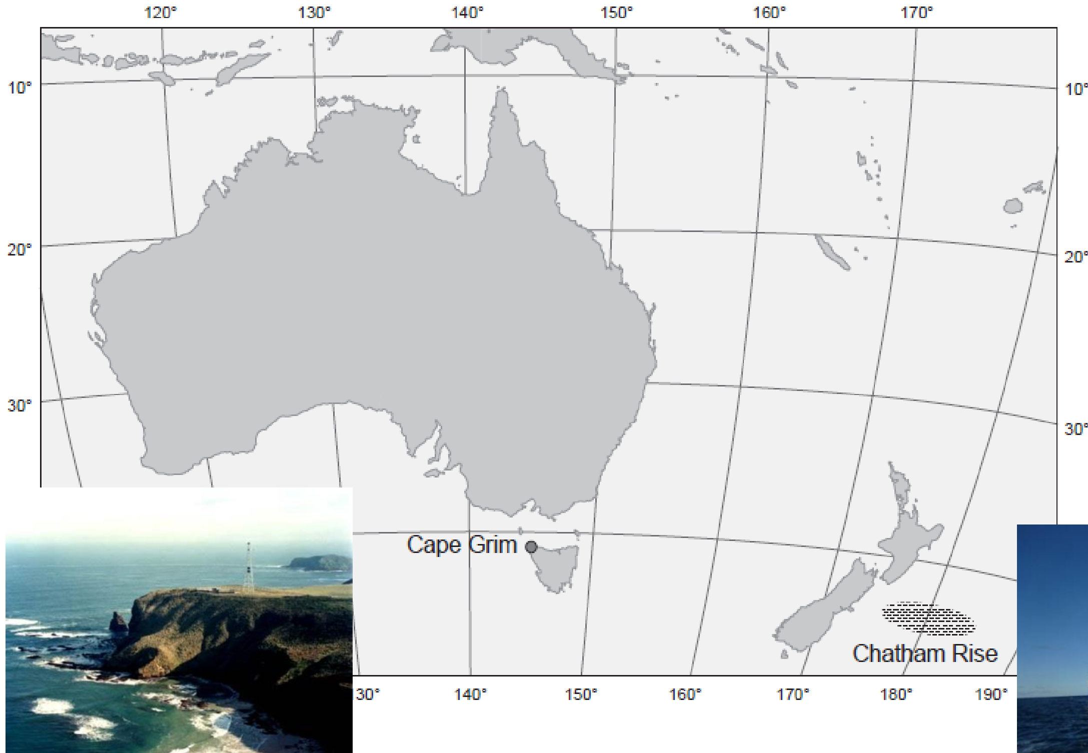
Locally high concentrations of isoprene, monoterpenes



Protonated Mass	Most Probable Compound	SOAP Chatham Rise Oceanic Bloom transects ppt	Cape Grim Oceanic [1] - [3]	Southern Hemisphere Mid-Latitude Oceanic [4]- [7]	Subtropical/ Tropical Oceanic [8]- [14]
33	Methanol	**229 - 1067**	476-633	595-727	575-890
42	Acetonitrile	**27- 55**	25-32	20	111-142
45	Acetaldehyde	**19 - 91**	nd- 53	120	204-500
59	Acetone	**109 - 410**	61-118	100 - 450	350-630
63	DMS	**55 - 484**	~80-95	140-250	50-270
69	Isoprene	**9 - 43**	14-21	30-187	2-120
81/137	Monoterpenes	**14 - 32**	nd-25	5-125	2-80

[1] Galbally *et al* (2007), [2] Lawson *et al* (2011), [3] Ayers *et al* (1997), [4] Colomb *et al* (2009), [5] Williams *et al* (2010), [6] Weller and Schrems (2000), [7] Yassaa et al 2008, [8] Singh *et al* (2004), [9] Williams et al (2004), [10] Warneke et al (2009), [11] Sinreich et al (2010), [12] Zhou and Mopper (1990ab), [13] Zhou and Mopper (1993) [14] Bonsang (1992)

Seasonal glyoxal and methyl glyoxal observations over remote ocean

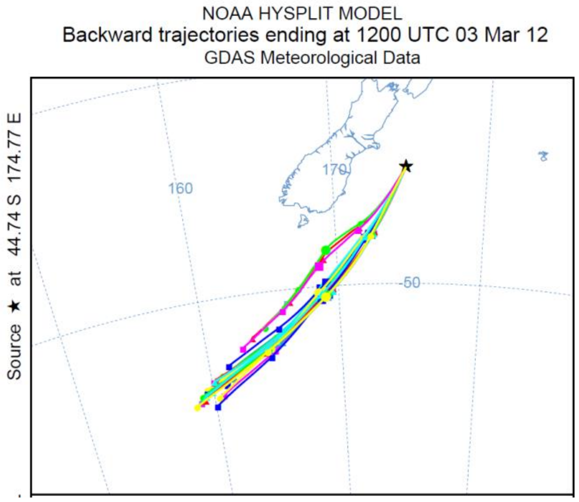


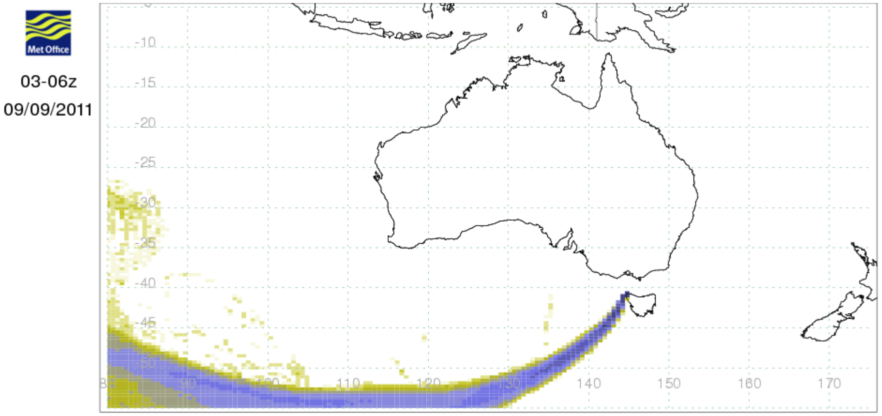
33 DNPH samples (24 hour)
5 'Baseline' days
Winter 2011
Chl a ~0.2 mg m^{-3}

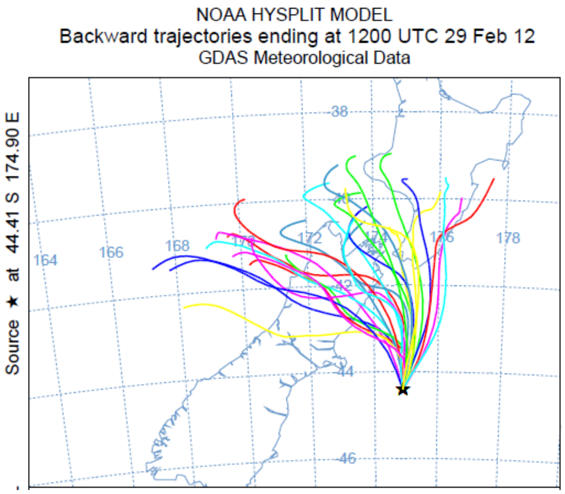
6 DNPH samples (24 hour)
4 'Baseline' days
Summer 2012
Chl a ~1 mg m^{-3}

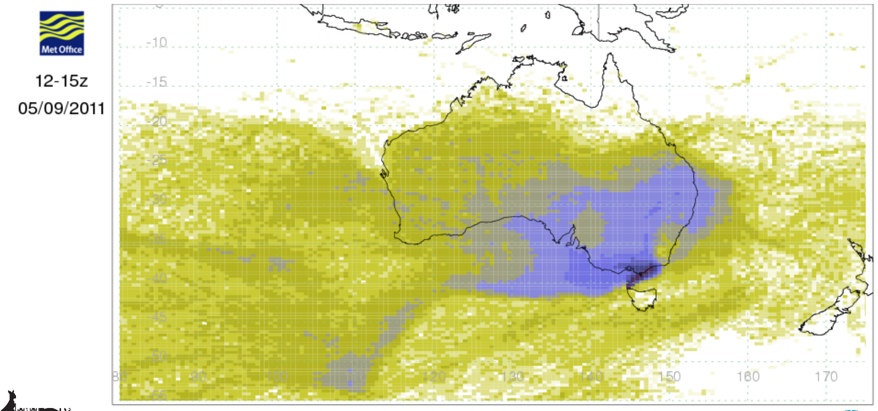
How do we select 'Baseline' samples?

…back trajectories but also wind speed, CO_2, radon, particle concentration

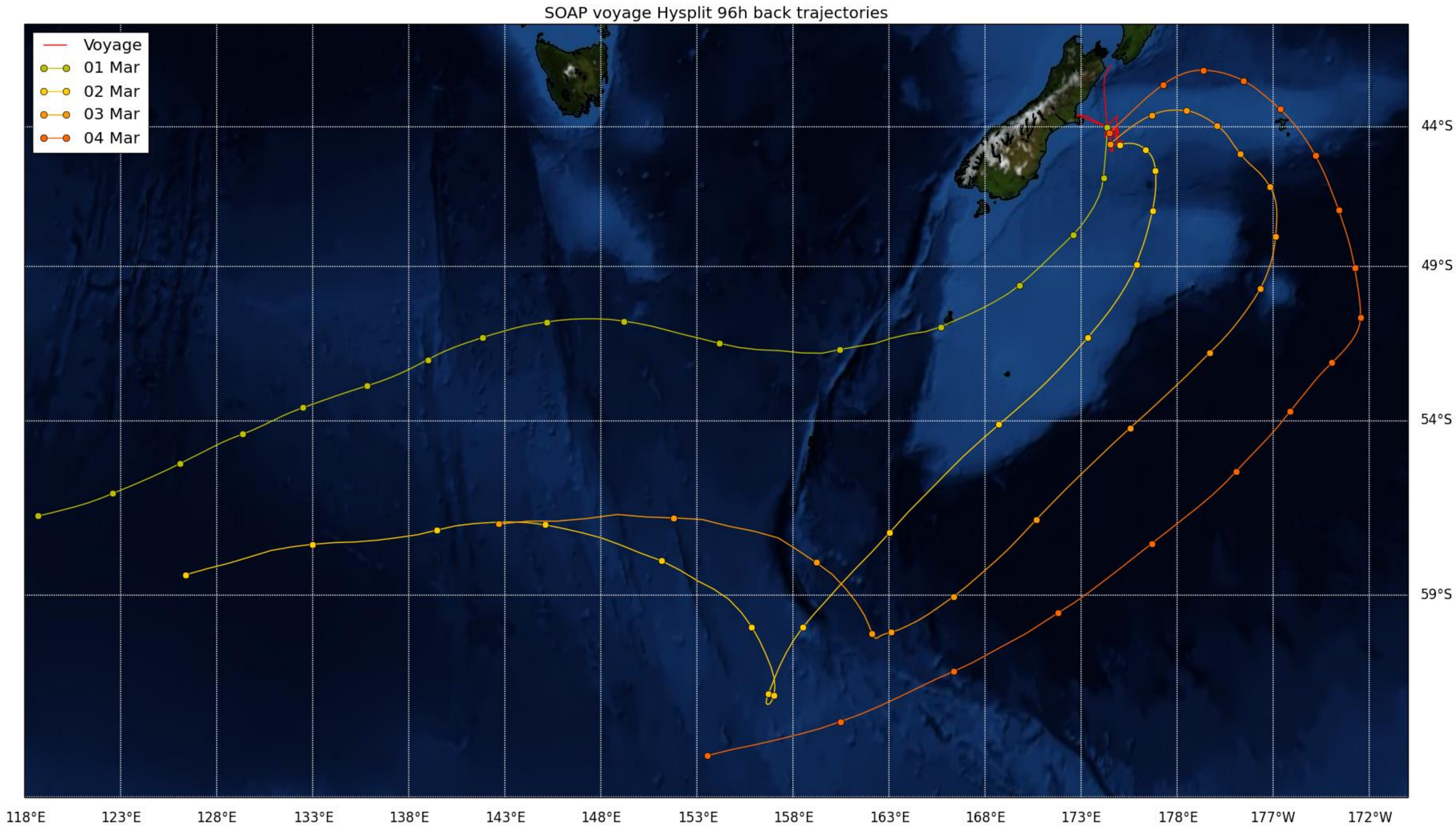








Back trajectories – SOAP baseline samples



Baseline concentrations (no land influence)

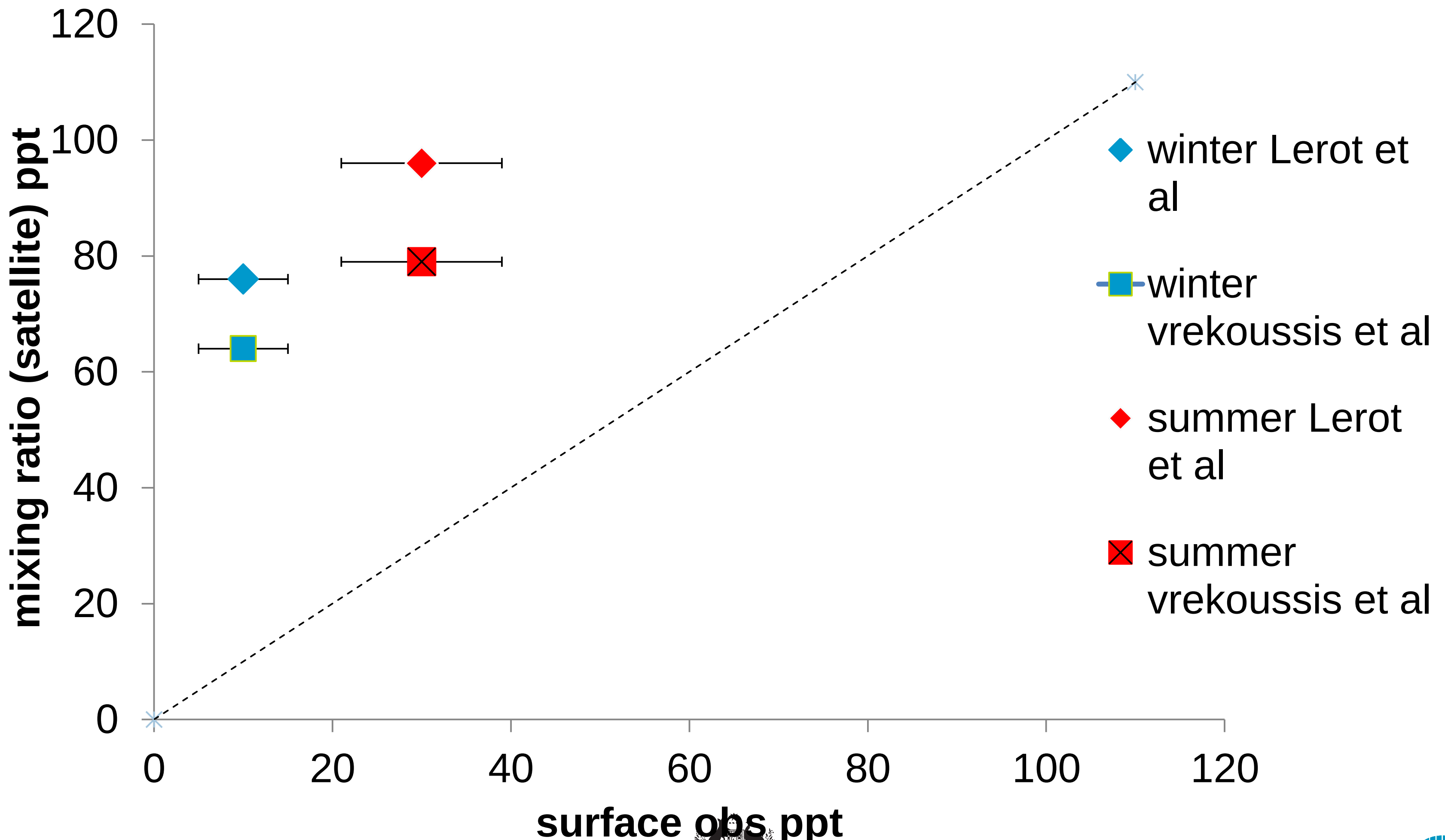
Site	Season	Glyoxal av (ppt) (std dev)	Methyl glyoxal av (ppt) (std dev)	CO_2 average (ppm) (std dev)	CN10 average (particles cm^{-3})	Radon ($mBq\ m^{-3}$)
Cape Grim n=5	Winter/Spring (Sep – Oct)	7 (2)	28 (11)	388.5 (0.02)	195 (30)	54 (11)
SOAP voyage n=4	Summer (Feb-Mar)	24 (5)	21 (7)	388.8 (1.6)	440 (1236)	n/a

Comparison with other studies

		Temperate ocean			Tropical ocean		
		Southern Ocean (Cape Grim) This work	South West Pacific (SOAP) This work	South West Pacific (SOAP) [a]	Eastern Tropical Pacific [b]	Tropical Pacific [c]	Caribbean Sea [d]
Glyoxal	Oceanic origin	7 ± 2	24 ± 5	-	43 ± 9 (SH) 32 ± 6 (NH)	63 ± 21	40*
	All data	10 ± 6	30 ± 12	22 ±?	-	-	-
Methyl glyoxal	Oceanic origin	28 ± 11	21 ± 7	-	-	-	10*
	All data	57 ± 32	27 ± 11	-	-	-	

[a] Majahan et al 2013
[b] Coburn et al 2014 submitted
[c] Sinreich et al 2010
[d] Zhou and Mopper 1990, *single sample

Comparison with satellite data



Assuming all glyoxal is within ~1 km boundary layer

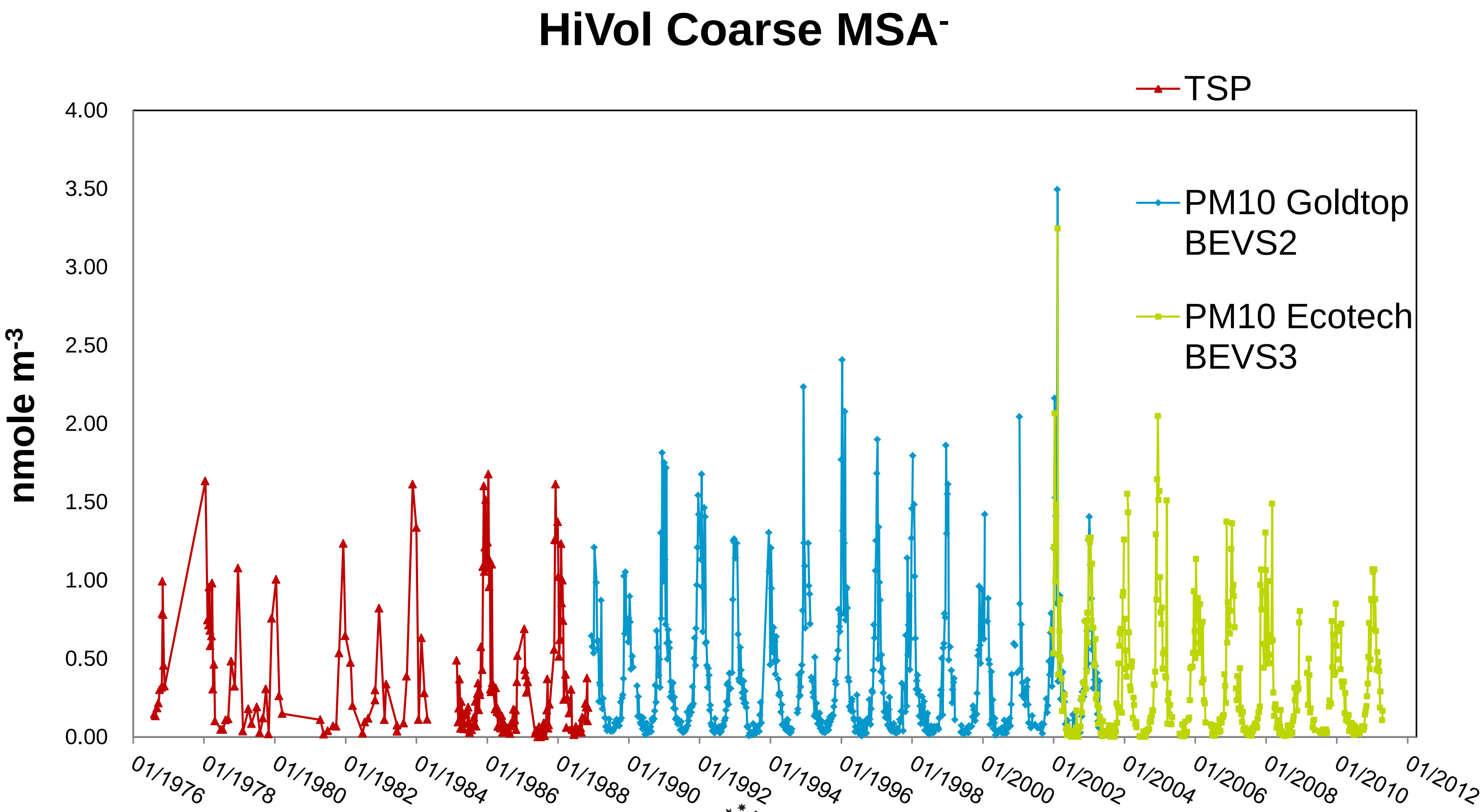
Dicarbonyl yields based on precursors

Precursor	precursor mixing ratios (ppt)		glyoxal yield (ppt)		methyl glyoxal yield (ppt)	
	SOAP	**Cape Grim**	**SOAP**	**Cape Grim**	**SOAP**	**Cape Grim**
acetylene	3[a]	39[a]	0.0	0.2	n/a	n/a
ethene	51[b]	31[b]	0.2	0.1	n/a	n/a
propene	17[b]	8[b]	n/a	n/a	0.0	0.0
propane	33[c]	35[c]	n/a	n/a	0.0	0.04
alkanes >c3^	52[c]	52[c]	n/a	n/a	0.0	0.04
Isoprene	17	21[d]	0.9	1.1	3.7	4.6
benzene	10	9[a]	0.0	0.0	n/a	n/a
Toluene	9	9*	0.1	0.1	0.1	0.1
xylenes sum	10	9*	0.3	0.2	0.4	0.3
monoterpenes	34	25[d]	0.9	0.7	1.4	1.0
acetone	125	118[e]	n/a	n/a	0.0	0.0
sum yield (ppt)			2.0	2.5	5.6	6.1
% explained			**10**	**25**	**27**	**32**

[a] Montzka Cape Grim HATS canisters
[b] Kivlington thesis
[c] Helmig NOAA Carbon Cycle Cape Grim canisters
[d] Lawson et al upper estimate Cape Grim
[e] Galbally et al upper estimate Cape Grim summer
*based on benzene
^ n4 and n5

	SOAP Chatham Rise Oceanic Bloom transects ppt	Cape Grim Oceanic
Formaldehyde	**259 - 749**	**342-1038**
acrolein	**12-24**	**nd**
propanal	**35-42**	**4-15**
butenal	**4-11**	**nd**
methacrolein	**coelution**	**7-10**
2-butanone	**coelution**	**nd**
benzaldehyde	**12-17**	**3-7**
pentanal	**8-13**	**2**
hexanal	**11-43**	**7-8**

Cape Grim - PM10- a 36 year record of MSA

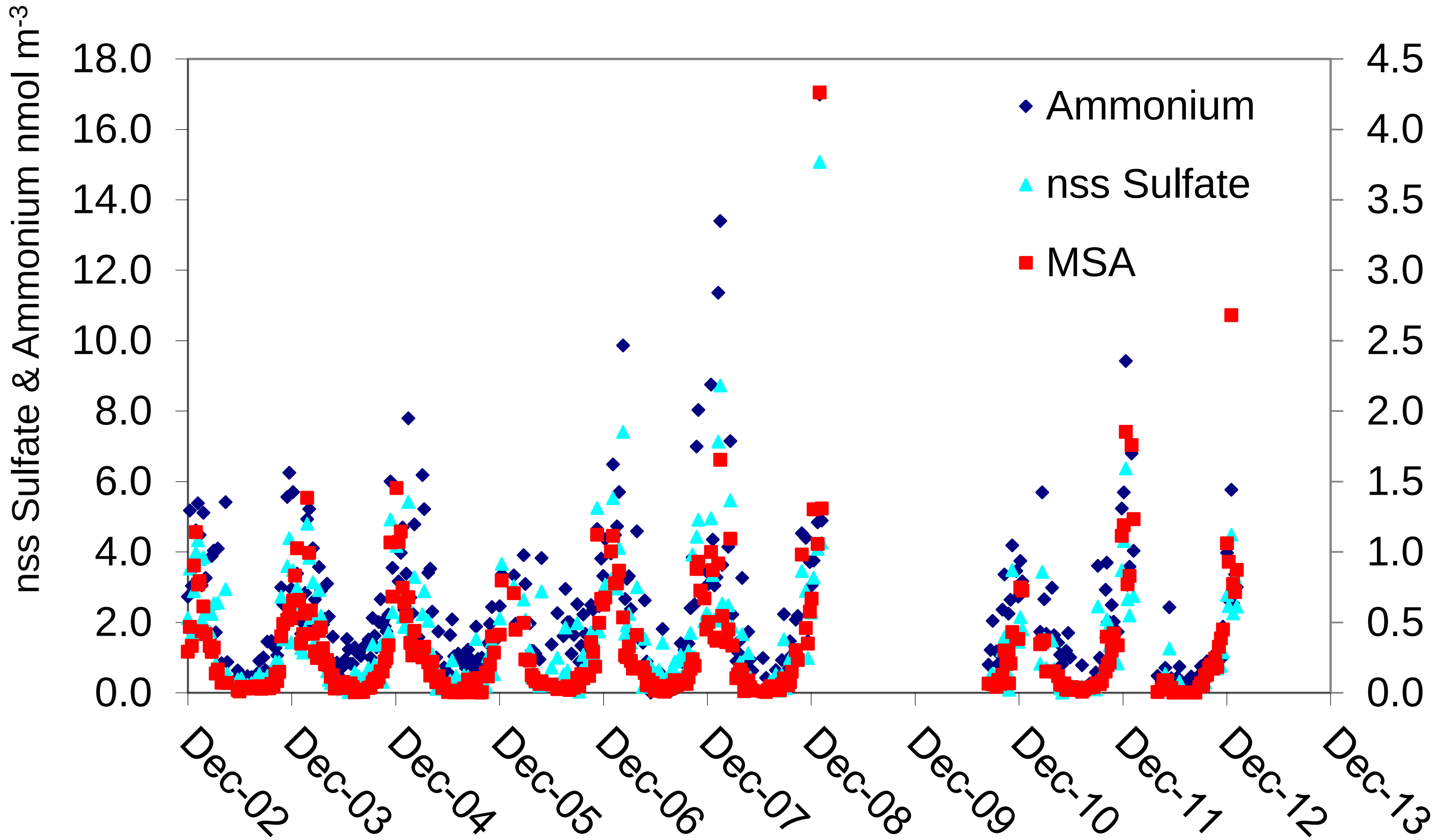


Australian Government
Bureau of Meteorology

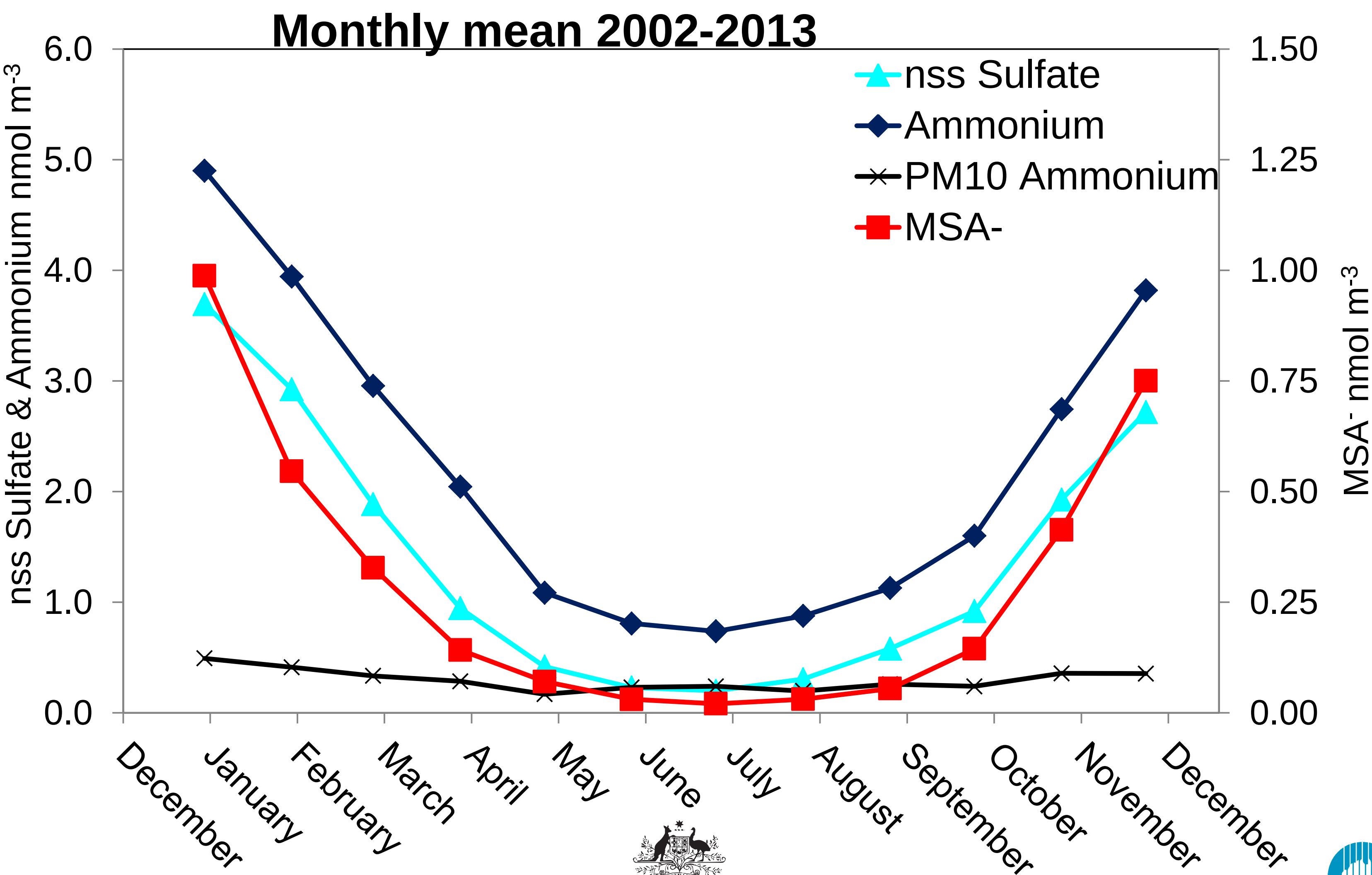
The Centre for Australian Weather and Climate Research
A partnership between CSIRO and the Bureau of Meteorology

CSIRO

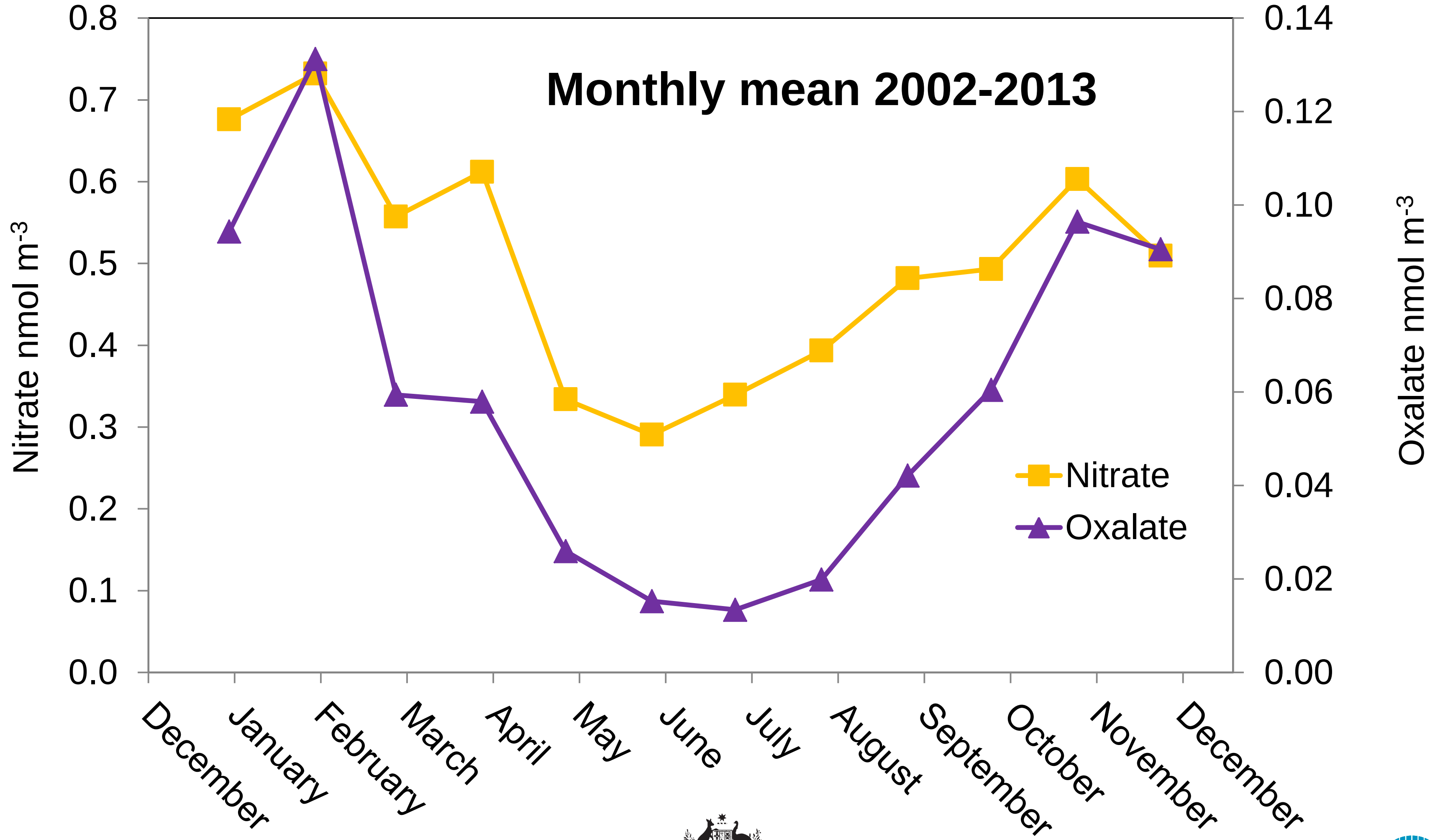
PM2.5 secondary species



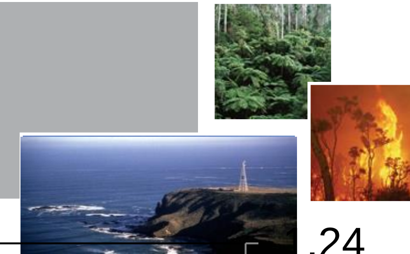
Seasonal cycles of secondary species

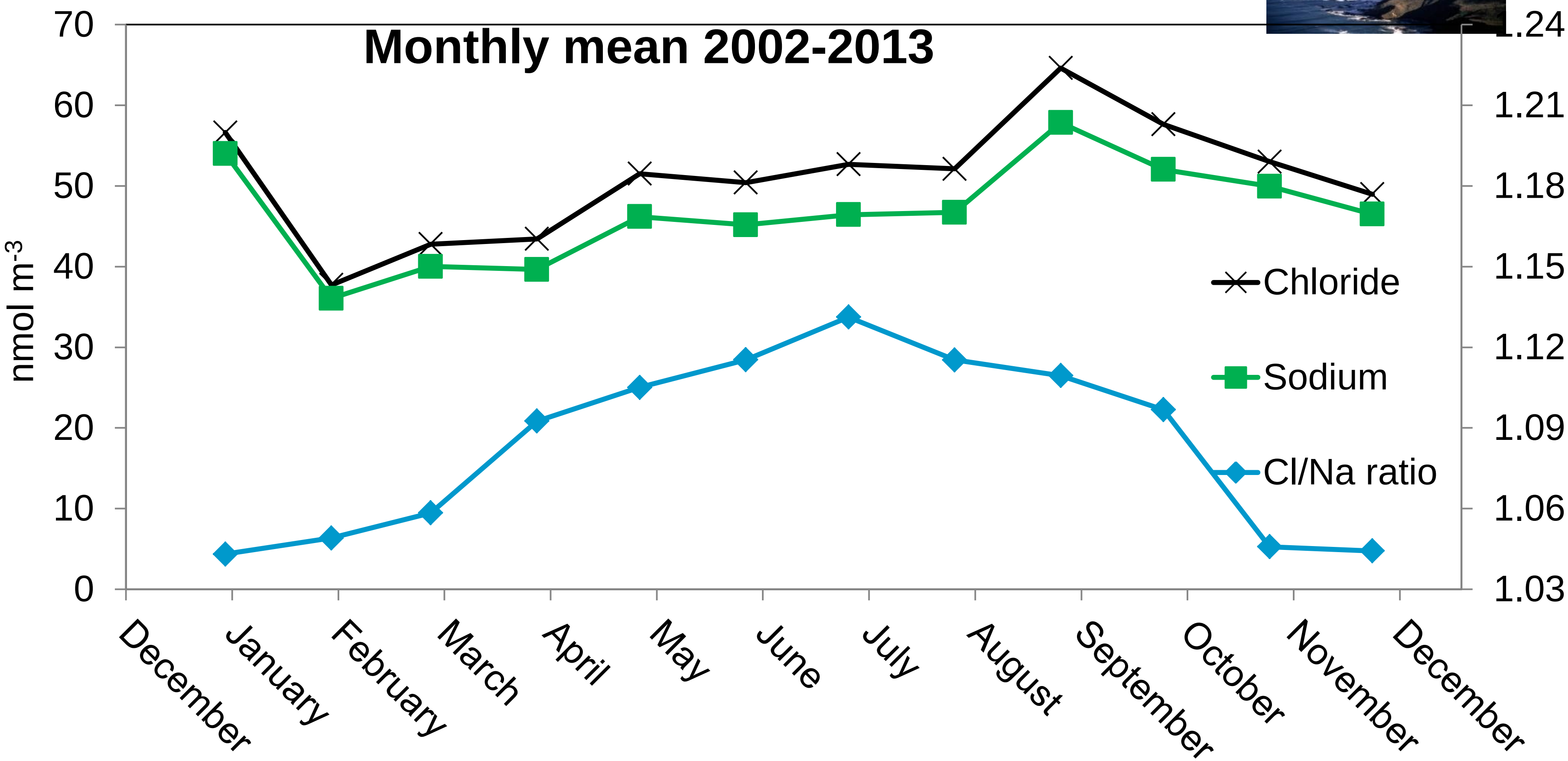


Seasonal cycles of secondary species



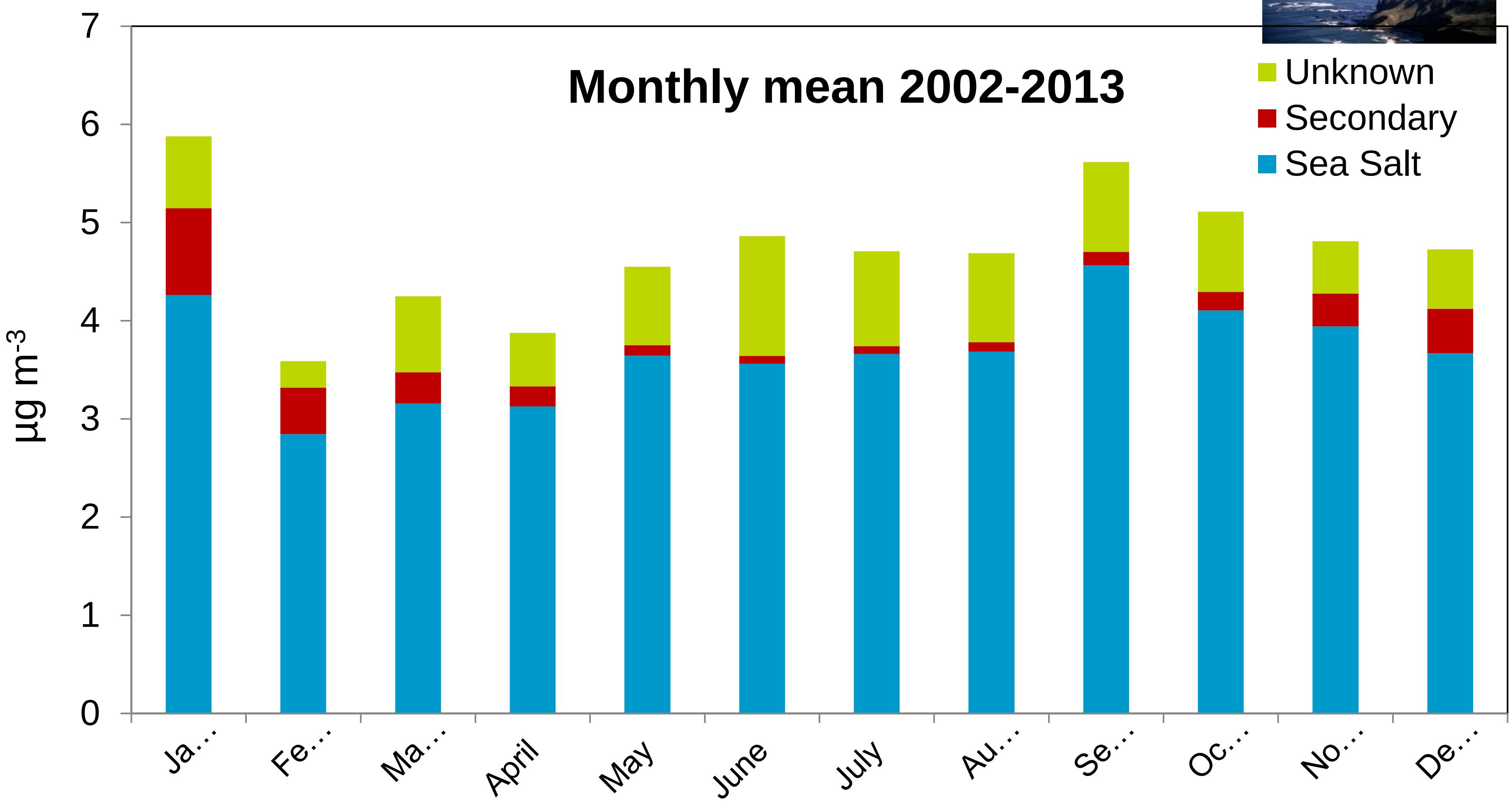
PM2.5 -Chloride loss in summer





- Winter Cl/Na ratio = seawater ratio
- Summer Cl/Na ratio << seawater ratio indicating chloride loss (displacement by sulfuric, nitric acid, photochemical reactions)

Unknown component of PM2.5

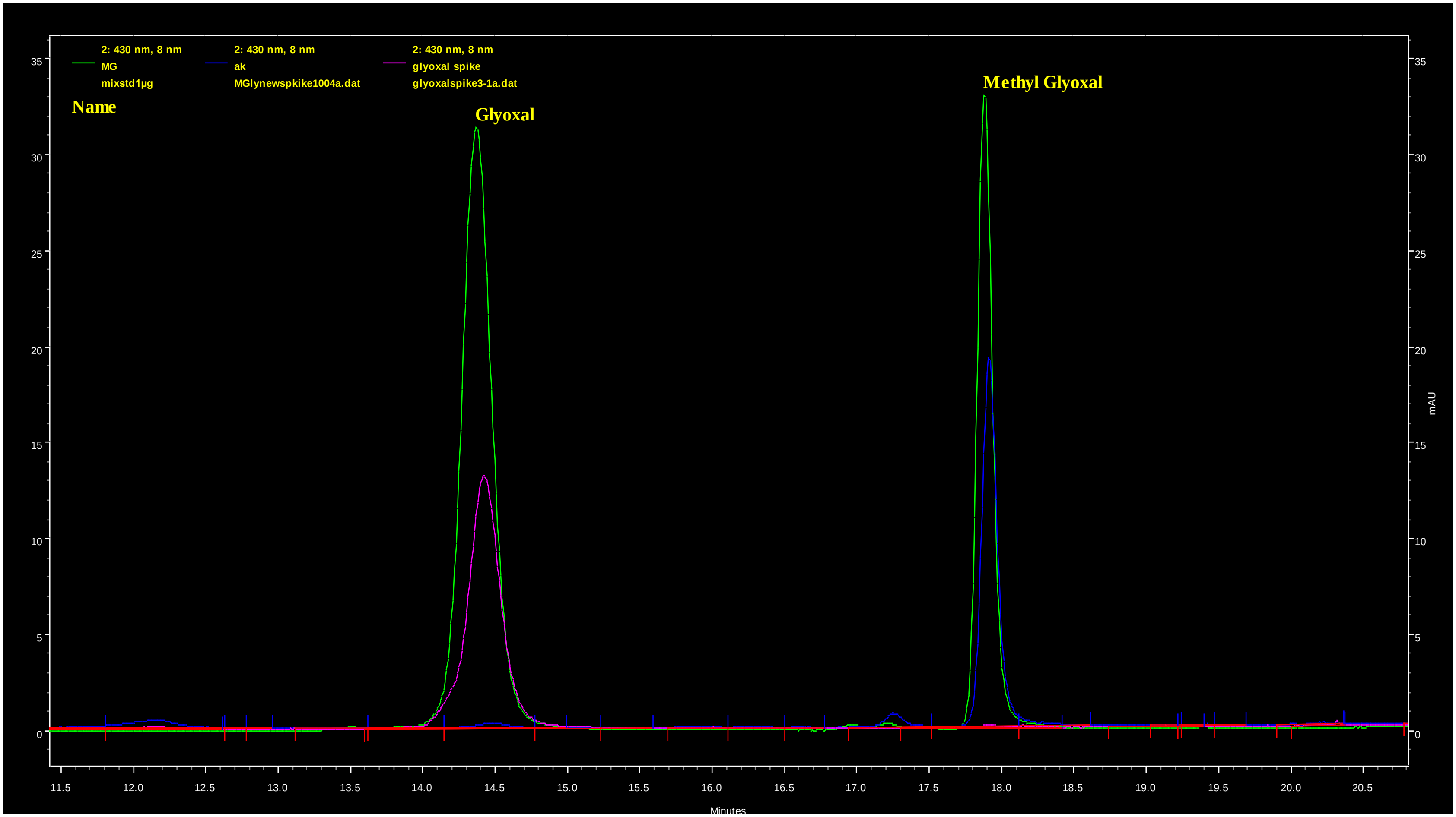


A proportion of the measured mass is not accounted for by water soluble species. This 10-20 % may be organics not detectable by ion chromatography

Australia's new Research Vessel - *RV Investigator*

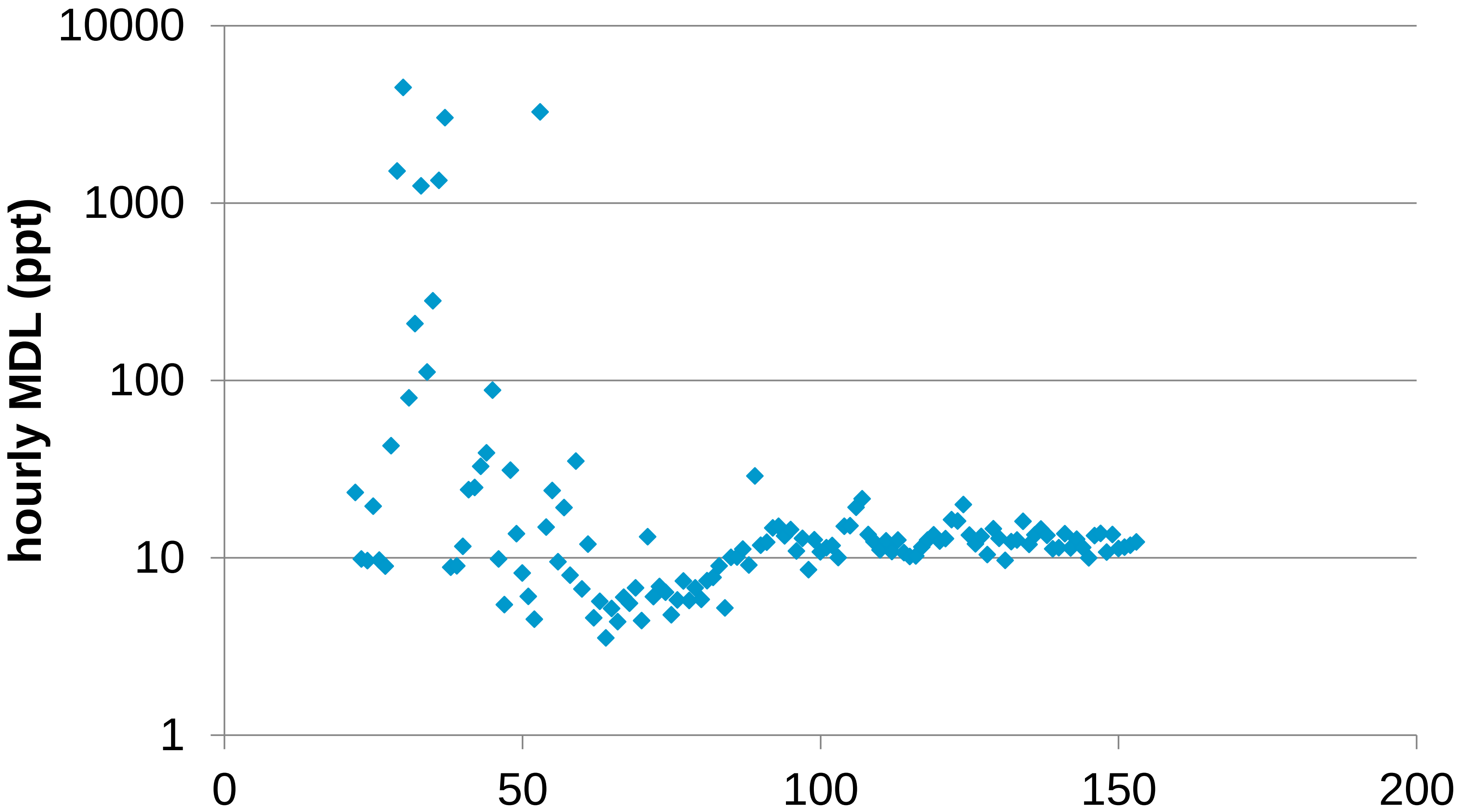
- 93m ship, accommodates 40 scientists, 300 days at sea per year
- Dedicated atmospheric composition laboratories onboard
- Australian atmospheric community -commissioning voyages in ~ late 2014
- Great Barrier Reef as a source of atmospheric aerosol in 2015-16 (biogeochemistry, dissolved VOCs, atmospheric VOCs and halogen oxides, halocarbons, aerosol composition and properties, cloud properties)

Dicarbonyl standards and spiked cartridges

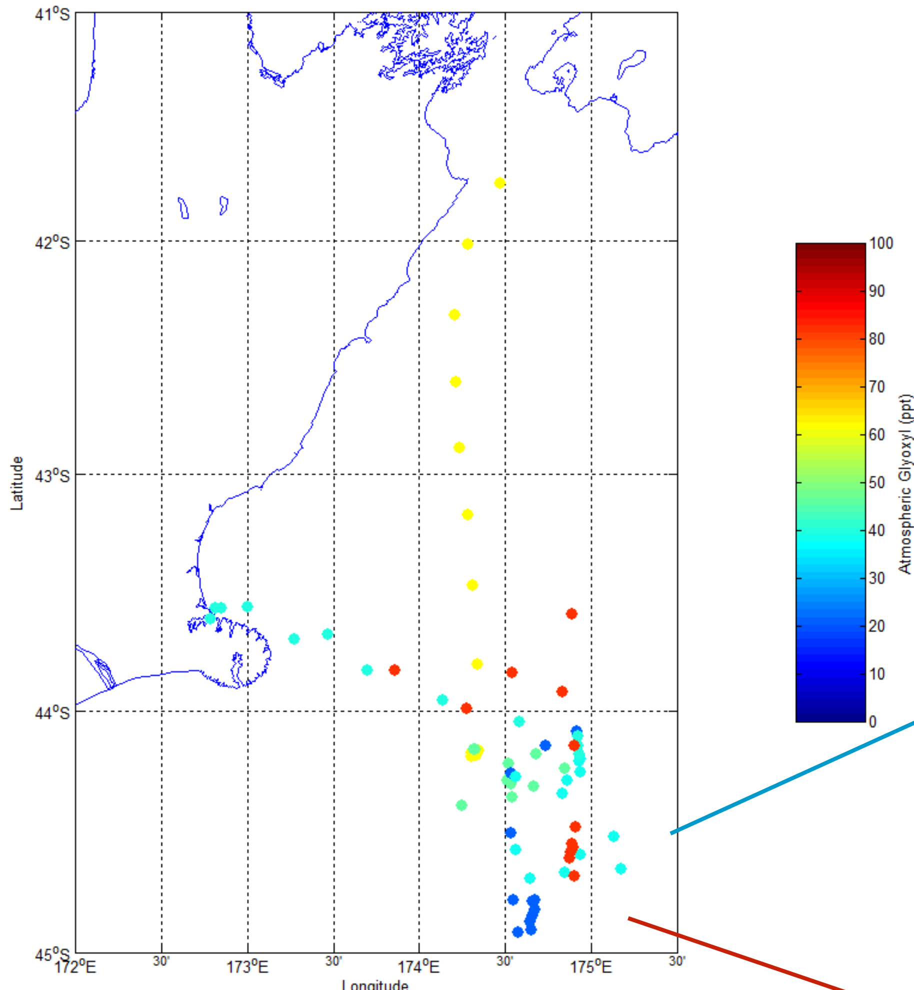


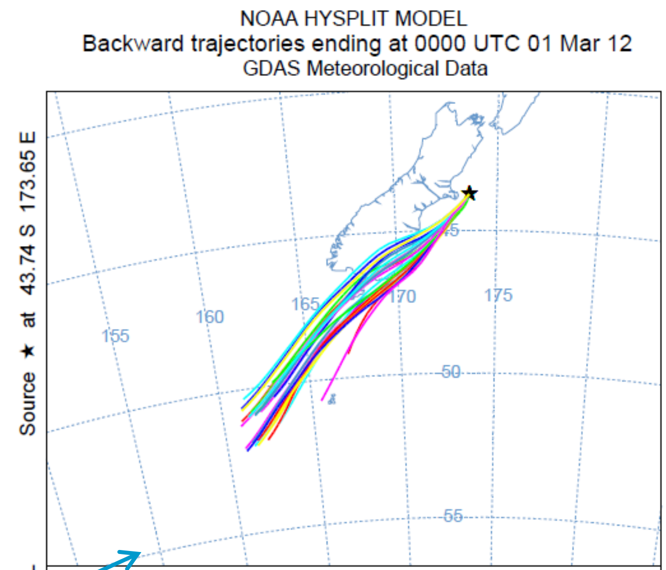
Green – standard
Blue and purple – spiked cartridges

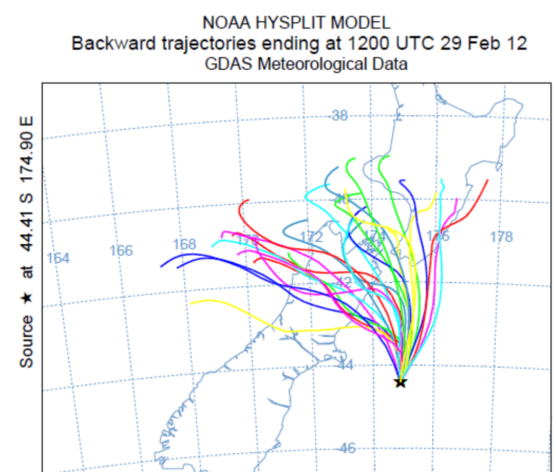
PTR-MS minimum detectable limit vs mass



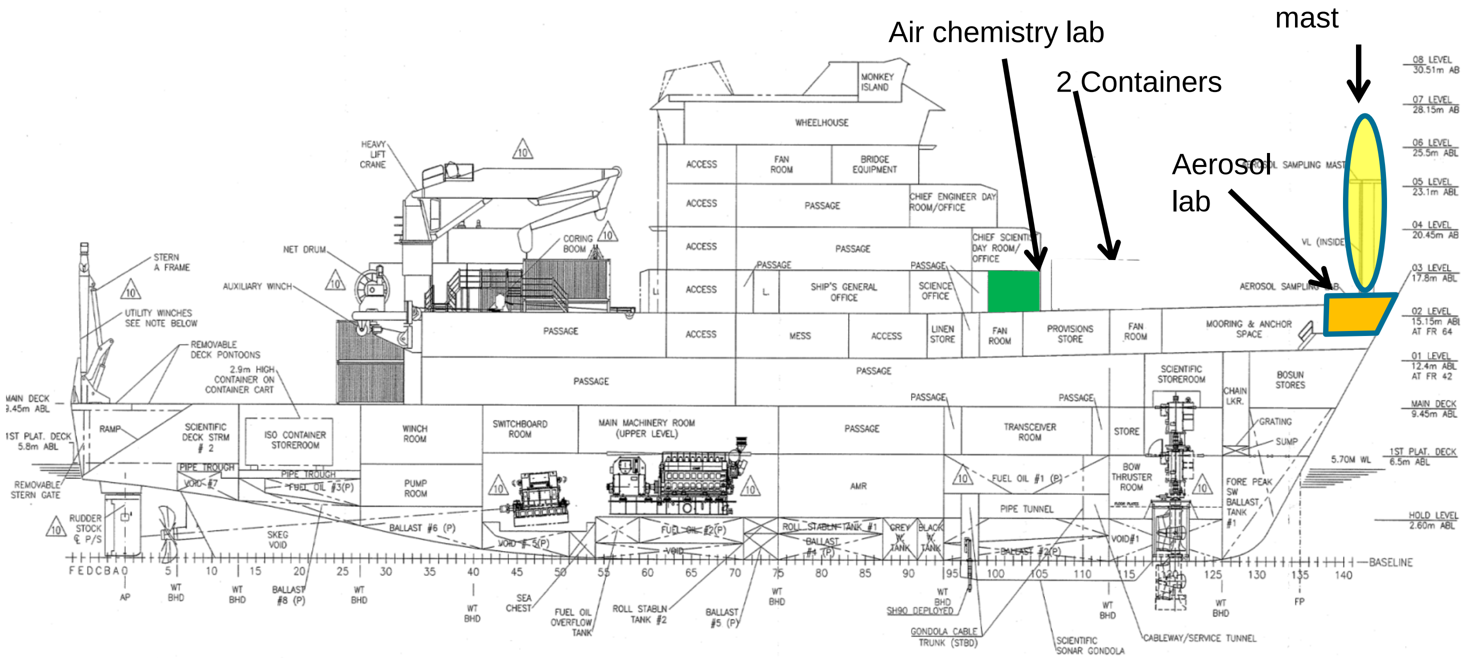
SOAP Voyage track – glyoxal







Atmospheric composition labs and specialist containers



- Weather radar
- Nephelometer
- Absorption photometer
- SMPS
- Sun photometer
- O_3 monitor
- NO_{xy} monitor
- CO_2/CH_4
- CO/N_2O
- Radon

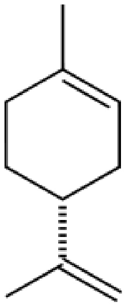
Future

- VOCs
- Others?

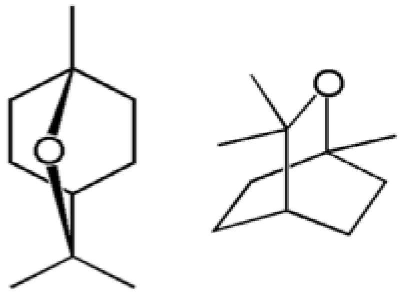
Australian Government
Bureau of Meteorology

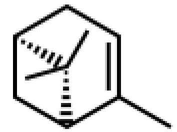
CSIRO

limonene



Eucalyptol

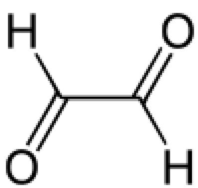




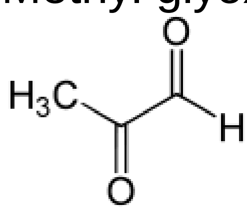
(+)-α-pinene

(−)-α-pinene

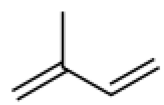
glyoxal



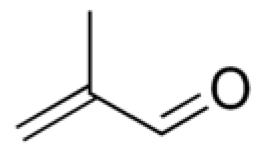
Methyl glyoxal



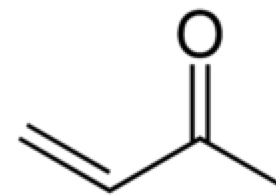
isoprene



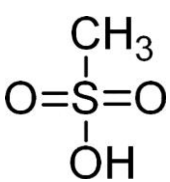
methacrolein



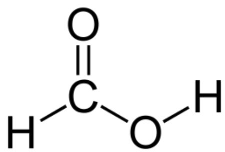
MVK



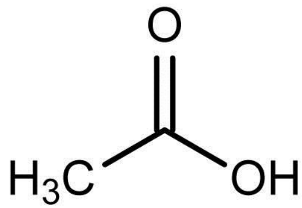
MSA



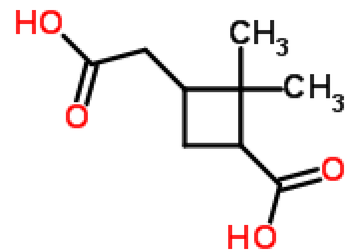
Slide of molecular structures



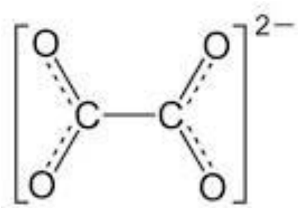
Formic acid



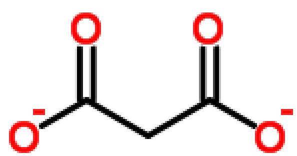
acetic acid



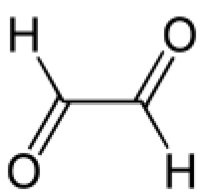
pinic acid



oxalate

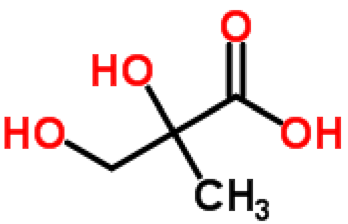


malonate

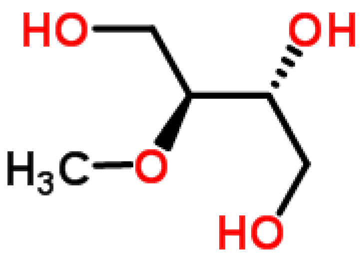


glyoxal

Isoprene SOA tracers

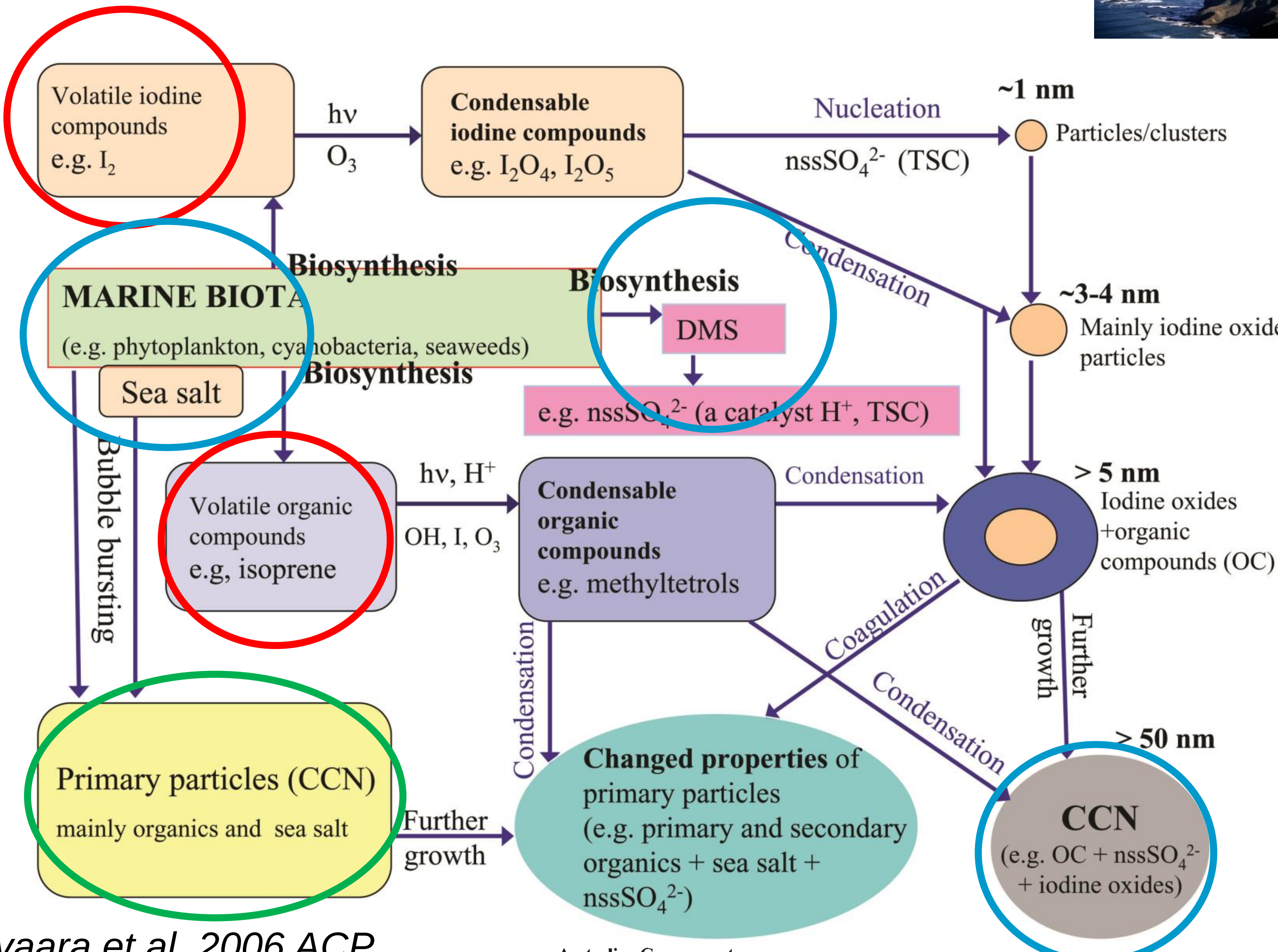


2-methyl glyceric acid



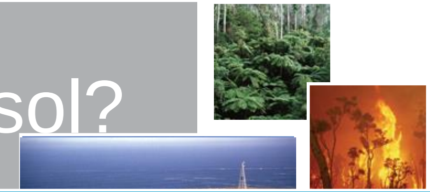
2-Methylerythritol

Complexities beyond CLAW – VOCs contributing to marine aerosol



Vaattovaara et al, 2006 ACP

Where has SOA been found in marine aerosol?



Location	SOA species	VOCs implicated
Mace Head (53ºN) Facchini et al 2008 Rinaldi et al 2010	MSA (methane sulphonic acid) Oxalate I_2O_5 and I_2O_4 Diethyl, dimethyl ammonium salts (amines + sulphate) Organosulphates (sulfate esters of hydroxyl carboxylic acids)	Dimethyl sulfide (DMS) Glyoxal Organic iodine compounds Amines
Amsterdam Island (37ºS) Sciare et al 2009 Claeys et al 2010	MSA Oxalate, malonate, succinate Organosulphates (sulfate esters of C9–C13 hydroxyl carboxylic acids)	DMS Glyoxal
Cape Verde (17ºN) Muller et al 2010 Muller et al 2009	MSA Oxalate, malonate, succinate Mono, diethyl, dimethyl ammonium salts (amines + sulphate)	DMS Glyoxal amines
Cape Grim (41ºS) Ayers et al 1986 Selleck et al 2013 (poster)	MSA, oxalate, formate	DMS Glyoxal
Cruise 70ºS to 85ºN (Ocean and Antarctic back trajectory) Hu et al 2013	Monoterpene SOA tracers (pinic acid) Isoprene SOA tracers (2-methyl glyceric acid, 2-methyl tetrols)	Isoprene monoterpenes