Seasonal in situ observations of glyoxal and methylglyoxal over the temperate oceans of the Southern Hemisphere

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Abstract

Dicarbonyls glyoxal and methylglyoxal have been measured with 2,4-dinitrophenylhydrazine (2,4-DNPH) cartridges and high performance liquid chromatography (HPLC), optimised for dicarbonyl detection, in clean marine air over the temperate Southern Hemisphere (SH) oceans. Measurements of a range of dicarbonyl precursors (volatile organic compounds, VOCs) were made in parallel. These are the first in situ measurements of glyoxal and methylglyoxal over the remote temperate oceans. Six 24 hour samples were collected in summer (Feb-Mar) over the Chatham Rise in the South West Pacific Ocean during the Surface Ocean Aerosol Production (SOAP) voyage in 2012, while 34 24 hour samples were collected at Cape Grim Baseline Air Pollution Station in late winter (Aug-Sep) 2011. Average glyoxal mixing ratios in clean marine air were 7 ppt at Cape Grim, and 23 ppt over Chatham Rise. Average methylglyoxal mixing ratios in clean marine air were 28 ppt at Cape Grim and 10 ppt over Chatham Rise. The mixing ratios of glyoxal at Cape Grim are the lowest observed over the remote oceans, while mixing ratios over Chatham Rise are in good agreement with other temperate and tropical observations, including concurrent MAX-DOAS observations. Methylglyoxal mixing ratios at both sites are comparable to the only other

marine methylglyoxal observations available over the tropical Northern Hemisphere (NH) ocean. Ratios of glyoxal : methylglyoxal > 1 over Chatham Rise but <1 at Cape Grim, suggest different formation and/or loss processes or rates dominate at each site. Dicarbonyl precursor VOCs, including isoprene and monoterpenes, are used to calculate an upper estimate yield of glyoxal and methylglyoxal in the remote marine boundary layer and explain at most 1-3 ppt of dicarbonyls observed, corresponding to 10% and 17% of the observed glyoxal and 29% and 10% of the methylglyoxal at Chatham Rise and Cape Grim, respectively, highlighting a significant but as yet unknown production mechanism. Surface – level glyoxal observations from both sites were converted to vertical columns and compared to average vertical column densities (VCDs) from GOME-2 satellite retrievals. Both satellite columns and in situ observations are higher in summer than winter, however satellite vertical column densities exceeded the surface observations by more than $1.5x10^{14}$ molecules cm^{-2} at both sites. This discrepancy may be due to the incorrect assumption that all glyoxal observed by satellite is within the boundary layer, or may be due to challenges retrieving low VCDs of glyoxal over the oceans due to interferences by liquid water absorption, or use of an inappropriate normalisation reference value in the retrieval algorithm. This study provides much needed data to verify the presence of these short lived gases over the remote ocean and provide further evidence of an as yet unidentified source of both glyoxal and also methylglyoxal over the remote oceans.

1 Introduction

Natural aerosols, including sea spray and secondary aerosols originating from marine dimethyl sulphide (DMS), have been shown to strongly affect the uncertainty of cloud radiative forcing in global climate models, highlighting a need to understand the composition and microphysical properties of marine aerosol in very pristine marine environments (Carslaw et al., 2013). While primary emissions, including wind-blown sea salt, make a large contribution to aerosol mass in the remote marine boundary layer (MBL), organic carbon can make a significant contribution to the mass of submicron marine aerosol in the more biologically active summer months (O'Dowd et al., 2004; Facchini et al., 2008a; Sciare et al., 2009; Ovadnevaite et al., 2011b). This organic carbon may be primary organic matter, including polymer microgels, viruses, bacteria, colloids and organic detritus, directly transferred from bulk water and the sea surface microlayer (SML) of the ocean to the atmosphere during bubble burst (Orellana et al., 2011; Facchini et al., 2008b). The organic carbon may also comprise secondary aerosol, formed from oxidation of gas phase ocean-

derived volatile organic compounds (VOCs) such as DMS, isoprene and monoterpenes (Shaw et al., 2010).

The organic component of marine aerosol is chemically complex and requires multiple state of the art techniques to elucidate (Fu et al., 2013; Fu et al., 2011; Decesari et al., 2011; Rinaldi et al., 2010; Claeys et al., 2010). A further challenge is the more recent blurring of distinction between primary and secondary organics, in which oxidative ageing and evaporation of semi volatile primary organic aerosol (POA) leads to production of gas phase, volatile, low molecular weight products, which may then go to form secondary organic aerosol (SOA) (Donahue et al., 2014). The resulting photochemically processed POA may have similar chemical properties to, and is sometimes loosely classified as SOA. (Rinaldi et al., 2010; Decesari et al., 2011; Ovadnevaite et al., 2011b). This interrelatedness of primary and secondary organics adds considerable complexity to understanding the formation and chemical processing of organic aerosols in the MBL.

The influence of organics on cloud condensation nuclei (CCN) activity of marine aerosol in general appears to be highly variable and investigations have mostly focused on primary organic aerosol (Ovadnevaite et al., 2011a; Meskhidze et al., 2011; Orellana et al., 2011; Westervelt et al., 2012; Topping et al., 2013). The contribution of DMS oxidation products to the CCN population over the remote Southern Ocean has been well established (Korhonen et al., 2008; Ayers and Gras, 1991), however an understanding of the contribution of other secondary aerosol species such as isoprene and monoterpene derived-SOA to the CCN activity of marine aerosol is still emerging. Meskhidze and Nenes et al. (2006) suggested a link between isoprene-derived SOA over a phytoplankton bloom site and cloud microphysical and radiative properties in the Southern Ocean, while Lana et al. (2012) found a correlation between modelled secondary sulphur and organic aerosols and variability of cloud microphysics derived from satellite observations over the remote mid and high latitude ocean.

The alpha dicarbonyl glyoxal (CHOCHO) is an important SOA aerosol precursor which in recent years has found to be widespread in the marine boundary layer (MBL), both via column measurements (Lerot et al., 2010; Vrekoussis et al., 2009; Mahajan et al., 2014; Wittrock et al., 2006) and in situ measurements (Coburn et al., 2014). The dominant source of glyoxal is oxidation of parent VOCs, with isoprene globally the most important precursor (explaining 47% of glyoxal formation) (Fu et al., 2008). Glyoxal has a global average lifetime of about 3 hours (Fu et al., 2008; Myriokefalitakis et al., 2008; Stavrakou et al.,

2009), and is highly water soluble and so can diffuse into aerosol or cloud water where it is converted to SOA through formation of low volatility products such as organic acids and oligimers (Ervens et al., 2011; Kampf et al., 2013; Sedehi et al., 2013; Lee et al., 2011; Lim et al., 2013). Alpha dicarbonyl methylglyoxal ($CHOCCH_3O$), a close relative of glyoxal, also forms low volatility products in the aqueous phase (Tan et al., 2012; Sedehi et al., 2013; Lim et al., 2013), has a short global lifetime of 1.6 hours and is produced by oxidation of gas phase parent compounds, predominantly isoprene (Fu et al., 2008). Destruction of both dicarbonyls is mainly via photolysis, followed by reaction with OH (Myriokefalitakis et al., 2008, Fu et al., 2008). The global sources of glyoxal and methylglyoxal are significant (45 Tg C a^{-1} and 140 Tg a^{-1} globally), and their SOA yield, which occurs mainly in clouds, is comparable in magnitude to SOA formation from other oxidation products of biogenic VOCs and aromatics (Fu et al., 2008). Major oxidation products of glyoxal and methylglyoxal at in-cloud relevant concentrations are oxalic and pyruvic acids (Lim et al., 2013).

There is considerable evidence that the dicarbonyls, and particularly glyoxal, makes an important contribution to the organic component of marine aerosol over the remote oceans. Both dicarbonyls have been found in marine aerosols over the Atlantic Ocean (van Pinxteren and Herrmann, 2013) and Pacific Oceans (Bikkina et al., 2014), with dicarbonyl mass positively correlated to organic acids (including oxalic acid) and ocean biological activity. Oxalic acid has been consistently found in pristine marine aerosol from remote sites including Amsterdam Island (Claeys et al., 2010), Mace Head (Rinaldi et al., 2010), Cape Verde (Muller et al., 2010) and Cape Grim (unpublished data), with highest concentrations during the biologically active summer months, coinciding with maximum concentrations of DMS oxidation products methanesulfonic acid (MSA) and non-sea-salt sulphate. Rinaldi et al. (2011) reported that oxalic acid in submicron marine aerosol from Mace Head and Amsterdam Island showed a similar seasonal cycle to SCIAMACHY glyoxal columns, and a chemical box model was able to explain the observed oxalate using the glyoxal columns.

However, significant unknowns remain. There are currently insufficient methylglyoxal observations to confirm its presence and importance to SOA formation over the remote oceans, and understanding the source of the observed glyoxal in the MBL has proven challenging. If the production of glyoxal is indeed due only to oxidation of precursor VOCs, calculating the expected yield of glyoxal should be straightforward in this relatively simple and well mixed chemical matrix over the remote ocean. However, there has been consistent suggestion that glyoxal concentrations in the MBL are in excess of the yields expected from

its precursors. Wittrock et al. (2006) reported enhanced concentrations of formaldehyde and glyoxal from SCIAMACHY satellite retrievals over tropical oceans, but were unable to reproduce observations using a global model. More detailed global modelling studies by Fu et al. (2008) and Myriokefalitakis et al. (2008) were also unable to reproduce SCIAMACHY glyoxal column retrievals over the tropical oceans, highlighting the possibility of unknown biogenic marine sources. Later satellite retrievals of glyoxal from SCIAMACHY (Vrekoussis et al., 2009), GOME-2 (Lerot et al., 2010) and recently from OMI (Miller et al., 2014) have provided further evidence of the widespread presence and seasonal modulation of glyoxal over biologically active oceans, although in some regions, such as the temperate SH oceans, the columns are close to satellite detection limits.

Glyoxal and methylglyoxal were first observed in the atmosphere and seawater in the Caribbean and Sargosso Seas as early as 1989 (Zhou and Mopper, 1990) where concentrations of glyoxal and methylglyoxal in seawater were 4 and 2 orders of magnitude too low to explain the atmospheric concentrations. MAX-DOAS retrievals observed hundreds of ppt glyoxal in the Gulf of Maine (Sinreich et al., 2007) and an average of 63 ppt glyoxal over the remote Tropical Pacific (Sinreich et al., 2010). The Sinreich et al. (2010) measurements were sufficiently far from land that the glyoxal observed was either from unrealistically high mixing ratios of long lived terrestrial precursors, or more likely a substantial unknown source possibly of marine origin, in support of earlier modelling and satellite studies. The widespread presence of glyoxal over the remote oceans was recently confirmed by Mahajan et al. (2014), who reported MAX-DOAS and long-path DOAS differential slant column densities from 10 field campaigns in both hemispheres in tropical and temperate regions. A global average value of about 25 ppt was reported with an upper limit of 40 ppt, however over the Southern Hemisphere oceans, particularly in sub tropical and temperate regions, glyoxal mixing ratios were mostly below instrument detection limits.

In 2014 an additional source of glyoxal in the MBL was identified in laboratory studies (Zhou et al., 2014), when oxidation of the sea surface microlayer (SML) led to emission of low molecular weight oxygenated compounds including glyoxal. However, the atmospheric yields of glyoxal were low, attributed to the fast irreversible hydrolysis of glyoxal which prevents transfer of glyoxal to the atmosphere. Van Pinxteren and Herrmann (2013) observed a glyoxal enrichment factor of 4 in SML compared to the bulk ocean, but the concentration observed was several orders of magnitude too low to explain mixing ratios of 10s of ppt typically seen in the MBL (Sinreich et al., 2010). The first eddy-covariance flux

measurements of glyoxal were recently made over the oceans, using an in situ Fast Light Emitting Diode Cavity Enhanced Differential Optical Absorption Spectroscopy (LED-CE-DOAS instrument) (Coburn et al., 2014). Negative flux (glyoxal transfer into the ocean) was observed in both hemispheres during the day, and a positive flux from the ocean in the SH at night. However, despite this first evidence of a direct oceanic source of glyoxal to the atmosphere, the positive flux at night could explain only 4 ppt of the glyoxal observed in the overlying atmosphere (some 30 % of the overnight increase), implying the contribution of another night-time production mechanism.

Despite these recent advances in our understanding of glyoxal production processes, our current inability to reconcile the presence of these short lived gases over the remote ocean suggests we have not identified a significant source of glyoxal. It is likely that this unidentified source also contributes to the glyoxal production in polluted terrestrial environments, but is masked by a large contribution from anthropogenic precursors such as acetylene. The production of glyoxal from photochemical processing of organic aerosol is a possible contributor (Vrekoussis et al., 2009; Stavrakou et al., 2009; Bates et al., 2012) though this remains unconfirmed. An additional source may be entrainment of glyoxal and its precursors from the free troposphere into the MBL, particularly in light of recent observations of non-negligible mixing ratios of glyoxal in the free troposphere (Volkamer, 2014).

A more in depth understanding is currently hindered by a lack of dicarbonyl observations in the MBL. While recent studies have contributed substantial additional observations of glyoxal over the remote oceans (Coburn et al., 2014; Mahajan et al., 2014), there have been no studies which have made parallel measurements of gas phase precursors, and so expected yields of glyoxal are only estimates. No in situ observations of glyoxal have been reported over temperate oceans of either hemisphere, and there is only one previous study reporting methylglyoxal observations over the world's oceans (in the tropical northern hemisphere, NH) (Zhou and Mopper, 1990). With the exception of the Caribbean and Sargasso Sea measurements (Zhou and Mopper, 1990), all column and in situ observations of glyoxal over the remote oceans have used optical measurement techniques (Mahajan et al., 2014; Sinreich et al., 2010; Sinreich et al., 2007; Coburn et al., 2014). Finally, given the challenges in retrieving low VCDs of glyoxal over the ocean from satellite observations (Lerot et al., 2010; Vrekoussis et al., 2009; Miller et al., 2014), more ground based measurements are required.

We provide much needed in situ glyoxal and methylglyoxal data from the very sparsely measured temperate oceans of the Southern Hemisphere. Observations have been made using

derivatisation of dicarbonyls on 2-4 DNPH cartridges and analysis with HPLC, which is an alternative measurement technique to the optical techniques used widely for oceanic glyoxal observations to date. Measurements have been made in two seasons, summer and winter, and auxiliary measurements, including carbon dioxide, radon and particles have been used to conclusively remove the possibility of any terrestrial influence on the dicarbonyl observations. This is the first study to concurrently measure a range of dicarbonyl precursors (VOCs), so that the yield of dicarbonyls from its gas phase precursors can be conclusively determined. Finally we provide the first methylglyoxal observations over the temperate remote ocean.

2 Methods

2.1 Sampling locations

Dicarbonyl in situ observations were made at the Cape Grim Baseline Air Pollution Station (CGBAPS) and during a voyage over the Chatham Rise in the South West Pacific Ocean during the Surface Ocean Aerosol Production (SOAP) study (see Fig. 1).

2.1.1 Cape Grim Baseline Air Pollution Station

The Cape Grim Baseline Air Pollution Station (BAPS) is located on the north-west tip of the island state of Tasmania, Australia, (40.683°S 144.689°E). CGBAPS is a World Meteorological Organisation (WMO) Global Atmosphere Watch (GAW) Global Station and hosts a wide variety of long term measurements including greenhouse gases, ozone depleting substances, aerosols, radon and reactive gases. The station is situated on a cliff 94m above sea level and when the wind blows from the south westerly 'Baseline' sector the air that arrives at the station has travelled over the Southern Ocean several days prior with no terrestrial influence (see Sec. 2.2.2.)

A total of 33 samples were collected from the 26 August – 29 September in 2011 (late winter-early spring). Each 24 hour sample consisted of approximately 2000L of air drawn through a 2,4-DNPH S10 Cartridge (Supelco) at a flow rate of 1.8L min^{-1}.

Ambient air was sampled down a 150mm diameter stainless steel inlet stack which extends 10m above the roof deck and is 104m above sea level. The flow rate of the intake was 235 L min^{-1} to ensure laminar flow was maintained. The DNPH cartridges were loaded in a

custom designed 'Sequencer' which allows up to 16 cartridges to be automatically sampled for a predefined time and sequence. The Sequencer drew air via a 3m length of ¼ inch PFA tubing which was extended into the centre of the stainless steel intake stack. Samples were collected in all wind directions and an ozone scrubber (KI impregnated filter) was placed in front of the cartridges. Chlorophyll-*a*, a measure of ocean biological activity, is low in the Southern Ocean in winter, with typical values of 0.1-0.2 mg m^{-3} (Bowie et al., 2011). Air temperatures throughout the sampling period ranged from 7ºC - 13ºC with an average of 10ºC and total rainfall during the sample period at the station was 90 mm. The average relative humidity was 78%.

Data collected from concurrent and continuous carbon dioxide, particle count and radon measurements at Cape Grim have been included in this work as indicators for clean marine air (see Sec. 2.2.2). VOC data from canister samples collected at Cape Grim for the NOAA Halocarbon (HATS) group and the Carbon Cycle Network have been used to calculate dicarbonyl yields (see Sec. 2.2.3)

2.1.2 Surface Ocean Aerosol Production (SOAP) voyage

The SOLAS-endorsed Surface Ocean Aerosol Production Study in 2012 investigated links between ocean biogeochemistry, air-sea exchange of trace gases and particles, and the composition of the overlying atmosphere (Landwehr et al., 2014). Measurements were made on board the RV Tangaroa over Chatham Rise, located over the biologically productive subtropical oceanic front. Six dicarbonyl samples were collected from the 29th Feb- 6th March 2012 (late summer). Each 24 hour sample consisted of approximately 1400L of air drawn through a 2,4 DNPH S10 Cartridge (Supelco) at a flow rate of 1.3 L min^{-1}. Cartridges were loaded in the "Sequencer' which drew air off a 25m 3/8 inch PFA inlet line with a flow rate of 10 L min^{-1}. Inlet losses were determined to be <2% for isoprene, monoterpenes, methanol and dimethyl sulphide however losses were not specifically tested for dicarbonyls due to the absence of a gaseous calibration standard. The sample inlet line pulled air from the crow's nest of the vessel above the bridge, some 28 m above sea level. To avoid ship exhaust from aft of the inlet being drawn into the PFA inlet line and sampled on to the cartridges, a baseline switch was developed and deployed using a CR3000 micrologger control system (Campbell Scientific, Logan UH). The switch used 1 Hz wind data from the vessel port/starboard pair of Wind Observer anemometers (Gill Instruments, Lymington, U.K.) and was configured to switch pumps off within 1 second of detecting non-baseline conditions.

The "baseline" was defined as: a five second running average relative windspeed > 3 ms^{-1} and 5 second vector averaged relative wind direction outside of the aft (135° to 225° relative degrees) wind-direction with meteorological convention of 0° at the bow. Five minute duration under accepted windspeed and direction was required before turning on. During experimentation and for much of the "steaming" transit legs, the vessel was oriented into the wind for as much of the time as possible in addition to dedicated periods of steaming into the wind. This resulted in a high frequency (~75%) of baseline conditions throughout the voyage.

During the voyage three distinct phytoplankton blooms were sampled, and dicarbonyl samples reported in this work were taken over the third bloom during the last 6 days of the voyage. Underway chlorophyll-*a* during this period ranged between 0.3-0.9 mg m^{-3} (10^{th}-90^{th} percentile) with median of 0.5 mg m^{-3} (calibrated against discrete data with data corresponding to sky irradiance >50W/m^{-2} removed, i.e. to exclude daytime data affected by photo-quenching). The bloom consisted of a mixed phytoplankton population of coccolithophores, small flagellates and dinoflagellates, and had a deep cold mixed layer characteristic of Sub-Antarctic waters. During the 6 days of sampling the vessel moved between 44.928ºS and 41.261ºS and 172.768ºE to 175.168ºE, including transiting to Lyttelton Port on the East Coast of the New Zealand South Island for several hours on the 1st March to exchange staff. However due to south westerly winds during this period and high wind speeds (average of 13 ms^{-1} and max of 29 ms^{-1}), air was predominantly of marine origin. Air temperatures during the sampling period ranged from 10ºC -18 ºC with an average of 13ºC and total rainfall during the 6 day sample period was 3.0 mm. The average relative humidity was 80% during the voyage.

Parallel measurements also made during the SOAP voyage which have been utilised in this work, include online VOCs via Proton Transfer Reaction Mass Spectrometry (PTR-MS) (see Sec. 2.2.3) and carbon dioxide and particle concentrations (Sec. 2.2.2).

2.2 In situ measurements

2.2.1 DNPH cartridges and HPLC analysis

During sampling, carbonyls and dicarbonyls were trapped on S10 Supelco cartridges, containing high purity silica adsorbent coated with 2,4-dinitrophenylhydrazine (2,4-DNPH), where they are converted to the hydrazone derivatives. Samples were refrigerated

immediately after sampling until analysis. The derivatives were extracted from the cartridge in 2.5 ml of acetonitrile and analysed by a High Performance Liquid Chromatography (HPLC) system consisting of a Dionex GP40 gradient pump, a Waters 717 autosampler, a Shimadzu System controller SCL-10A VP, a Shimadzu diode array detector (DAD) SPD-M10A VP, a Shimadzu Column Oven CTO-10AS VP and Shimadzu CLASS-VP chromatography software. The compound separation was performed with two Supelco Supelcosil LC-18 columns in series, 5 µm, 4.6 mm ID x 250 mm in length, Part No 58298. The chromatographic conditions include a flow rate of 1.6 ml min^{-1} and an injection volume of 25 µl, and the DAD was operated in the 220nm to 520nm wavelength range. The peaks were separated by gradient elution with an initial mobile phase of 64% acetonitrile and 36% deionised water for 10 minutes, then a linear gradient to 100% acetonitrile at 20 min, and column temperature of 30°C. The deionised water used for analysis was 18.2 MΩ.cm grade produced from a Millipore Milli-Q Advantage 10 system and HPLC grade acetonitrile was purchased from Merck.

Standards for glyoxal and methylglyoxal were prepared by making hydrazone crystals from glyoxal (40% wt in H_2O), methylglyoxal (40% wt in H_2O) and derivatisation reagent 2,4,DNPH (all from Sigma-Aldrich). The crystals were weighed and dissolved in acetonitrile to produce a stock standard for the glyoxal and methyglyoxal derivatives, which was used to make up a range of standards from 0.125 to 1.000 µg ml^{-1} which gave a linear response with a correlation coefficient of 0.999 for both derivatives.

The DAD enables the absorption spectra of each peak to be determined. The mono carbonyl DNPH derivatives all have a similar shaped absorption spectrum with a maximum absorption near 360nm. In contrast, the dicarbonyls glyoxal and methylglyoxal have absorption spectra which differ in shape to the monocarbonyls, and have a maximum absorption near 435nm (Fig. 2). The difference in the spectra highlights which peaks in the chromatograms are mono- or dicarbonyl DNPH derivatives and along with retention times allows identification of the glyoxal and methylglyoxal peaks. Quantifying the dicarbonyl DNPH derivatives at 435nm results in increased peak height and also has the added benefit of reducing the peak area of any co-eluting mono-carbonyl DNPH derivatives (Fig. 3). All samples, blanks and standards for glyoxal and methylglyoxal in this work were quantified using absorption at 435 nm which as discussed above is optimised for dicarbonyl detection.

Sample recovery was determined by spiking 1µg of glyoxal and methylglyoxal on to DNPH cartridges – recoveries were 96 ±0.3 % for glyoxal and 111 ±8 % for methylglyoxal. The

degree of derivatisation was examined in these spiked cartridges to ensure both carbonyl groups in the glyoxal and methylglyoxal molecules had reacted with the 2-4, DNPH (Wang et al., 2009;Olsen et al., 2007). Analysis of samples that had been extracted within the last 24 hours showed a second smaller peak indicating that ~ 5% of the glyoxal had reacted to form mono-derivatives rather than bis-derivatives (e.g. only one carbonyl group had reacted). However analysis of samples that were held for > 24 hours after extraction showed all of the mono derivative had been converted into the bis-derivative. As all samples were extracted then held for at least 24 hours before analysis, complete derivatisation to the bis-derivative is expected. For methylglyoxal there was no evidence of any mono-derivatives. The total mass of carbonyls and dicarbonyls sampled on the DNPH cartridges was at most 7% of the cartridge capacity, and collection efficiencies of >93% have been determined for carbonyls on DNPH cartridges at similar flow rates to those used here (Zhang et al., 1994;Slemr, 1991;Grutter et al., 2005). Hence no significant losses of dicarbonyls during sampling are expected.

The minimum detectable limit (MDL) for glyoxal and methylglyoxal were calculated from the standard deviation of field blanks collected during the study period based on the principles of ISO 6879 (ISO, 1995). Field blanks were opened and installed in the Sequencer sampling train for the same time period as samples. MDLs for a 24 hour sample were 1 ppt (glyoxal) and 1.7 ppt (methylglyoxal) during SOAP, and 0.6 ppt (glyoxal) and 0.9 ppt (methylglyoxal) at Cape Grim. Glyoxal and methylglyoxal mixing ratios were above MDLs in all 24 hour samples.

2.2.2 Supporting measurements for selection of clean marine periods

HYSPLIT (https://ready.arl.noaa.gov/HYSPLIT.php) 96 hour air-mass back trajectories (300m above sea level) were used as an additional means of identifying clean marine samples from Cape Grim and the Chatham Rise (see Figs. 4a and 4b). Specific surface measurements used to indicate clean marine air for each site are discussed below.

Cape Grim

Atmospheric radon-222, carbon dioxide and particle concentration data were used to select dicarbonyl samples with clean marine origin and no terrestrial influence.

Atmospheric radon-222 is a useful atmospheric tracer to determine the degree of contact between an air parcel and a terrestrial surface, due to the much larger flux of radon from

terrestrial surfaces compared with the ocean. Hourly atmospheric radon-222 measurements at Cape Grim are made on air taken from a 70 inlet (height above sea level 164 m) and using the dual-flow loop two filter method. See Zahorowski et al. (2013) for details of the measurement technique and application of radon data to identify clean marine air.

Carbon dioxide (CO_2) concentrations may be used to indicate whether an air mass is primarily of marine origin or has had recent contact with land. Terrestrial contact results in enhancement or draw down of CO_2 depending on the land use and anthropogenic sources. Continuous CO_2 measurements at Cape Grim are sampled via a 70m inlet and measured via a continuous, ultra precise CSIRO LOFLO NDIR system, described elsewhere (Steele et al., 2014). Hourly averaged CO_2 concentrations were used in this work.

Particle concentration may be used as an indicator of an air mass history, as recent contact with a terrestrial surface leads to particle concentrations enhanced above low concentrations typically found in marine air. Measurements of condensation (CN) nuclei greater than 10 nm in diameter (CN>10nm) are made at Cape Grim using a 3010 CPC TSI particle counter, sampling from the 10 m sample inlet described in Sec 2.1.1 (Gras, 2009). Hourly averaged particle concentration data was used in this work.

Baseline status at Cape Grim

Air is automatically classified as Baseline at Cape Grim (e.g. clean marine air) using a combination of wind direction (190º and 280º) and a seasonally adjusted particle concentration (CN>10nm) threshold based upon the previous five year's particle concentration data (Keywood, 2007). This Baseline status was used to identify clean marine samples.

SOAP Voyage

Carbon dioxide and particle concentrations (CN>10 nm) were used to identify dicarbonyl samples with a clean marine origin and no terrestrial influence during the voyage.

Carbon dioxide (CO_2) measurements were made continuously using a Picarro Cavity Ringdown laser (CRDS). The instrument was calibrated before and during the voyage using three reference calibration tanks. The CO_2 intake through 6 mm Decabon tubing, from alongside the crow's nest had a flow rate of 300 mL min^{-1}.

CN>10nm concentrations were measured with a 3010 CPC TSI particle counter. Antistatic (copper coil) polyurethane ducting was used as a common aerosol inlet, and sampled air from

the main radar tower at 21 m in height above sea level. The inlet was 10 cm in diameter, 30 m in length, with a flow rate of 800 L m^{-1}. The CPC intake was connected to the common aerosol inlet via ¼ inch stainless steel tubing. Inlet loss tests indicated particle loss rates were ~15% for total particle counts.

2.2.3 Measurements for dicarbonyl yield calculations

A High Sensitivity Proton Transfer Reaction-Mass Spectrometer (PTR-MS) (Ionicon Analytik) was used to measure VOCs in real time during the SOAP voyage. Details on PTR-MS measurements are given in Galbally et al. (2007) and some additional information is provided here.

The PTR-MS ran with inlet and drift tube temperature of 60ºC, 600V drift tube, ~2.2 mbar drift tube pressure, which equates to an energy field of 133 Td. The O_2+ signal was <1% of the primary ion H_3O^+ signal. The PTR-MS sampled from a 25 m PFA 3/8 inch inlet line, which had a continuous flow of 10 L min^{-1}, except during 'non baseline' periods when the inlet pump switched off and the PTR-MS sampled room air through a VOC scrubber. The Baseline status was logged on two separate programs and PCs and so room air measurements were removed from the data. The PTR-MS measured in scan mode in the range of m/z 21 – m/z 155 with a dwell time of 10 seconds per mass, allowing 3 full scans of the mass range per hour. Measurement of background signal resulting from interference ions and outgassing of materials was achieved by passing ambient air through Platinum coated glass wool catalyst at 350ºC for 30 minutes 4 times per day. An interpolated background signal was used for background correction. All species used in this work were calibrated daily by introducing a known flow of calibration gas to VOC-free ambient air which had previously passed through the catalyst. Calibrations and background measurements were carried out using an automated calibration system, see Galbally et al. (2007). Calibration gases used were ~ 1 ppm custom VOC mixture in nitrogen Apel Riemer (~1ppm acetone, benzene, toluene, m-xylene, a-pinene) and a custom gas mixture from Scott Specialty Gases (~ 1ppm isoprene and 1,8-cineole).

The MDL for a single 10 s measurement of a selected mass was determined using the principles of ISO6879 (ISO, 1995) i.e. 5% of the 10 s background measurements give a false positive reading. MDLs were as follows: m/z 59 (acetone) 17 ppt, m/z 69 (isoprene) 28 ppt, m/z 79 (benzene) 16 ppt, m/z 93 (toluene) 16 ppt, m/z 107 (sum xylenes) 19 ppt, m/z 137

(sum monoterpenes) 66 ppt. In contrast to the first week of the voyage, the mixing ratios of VOCs during the last 6 days of the voyage were low and subsequently many of the VOCs were below detection limit. The percentage of observations above MDL during this period are as follows m/z 59 – (95%), m/z 69- (14%), m/z 79- (15%), m/z 93- (14%), m/z 107 – (7%), m/z 137-(4%). Where the observation was lower than MDL, the half MDL value was substituted. Hence due to the high periods of time that VOCs were below MDLs, the reported concentrations used for yield calculation are strongly influenced by the MDL. Reported mixing ratios of dicarbonyl precursors and dicarbonyl yields calculated with PTR-MS data (Sec. 2.5) are therefore likely to be an upper limit.

VOC Flask data

VOCs measurements from flasks collected at Cape Grim in Baseline conditions were used to provide supplementary mixing ratios for species which were not targeted, or could not be measured with sufficient senstivity by PTR-MS at Cape Grim and during the SOAP voyage.

Stainless steel and glass flasks have been collected for and analysed by the National Oceanic Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) Halocarbons (HATS) group with Gas Chromatography (GC) techniques since the early 1990s (Montzka et al., 2014). In this work, benzene and acetylene mixing ratios (analysed with GC-mass spectrometry detection (Rhoderick et al., 2014;Pétron et al., 2012)) from August- September 2011 were utilised, as well as acetylene values in March 2011, as a proxy for mixing ratios during SOAP. Benzene values are calculated from an average of 6 pairs of flasks (2 glass and 4 stainless steel pairs) while acetylene values are from 3 pairs of stainless steel flasks in Aug-Sep 2011 and a single pair of stainless steel flasks in March 2011. There is low interannual variability in benzene and acetylene at Cape Grim, so the values used, which correspond to the same sample periods as dicarbonyls, were representative of typical values for these months.

Glass flasks collected in Baseline Air at Cape Grim for the NOAA Carbon Cycle Group are analyzed for VOCs by an automated gas chromatography system at the University of Colorado's Institute of Arctic and Alpine Research (INSTAAR) (Helmig et al., 2014; Helmig et al., 2009). Average propane, iso-butane, n-butane, iso-pentane, and n-pentane mixing raios were utilised from 5 pairs of glass flasks collected in Aug-Sep 2011 (filtered data). Flask data were also used to estimate alkane mixing ratios during the SOAP voyage

(average mixing ratios from flasks sampled in March between 2005-2014). The following number of flasks were used in calculating average values for March: propane (4 pairs and 2 single flasks), n-butane (9 pairs and 4 single flasks), iso-butane (10 pairs and 2 single flasks), n-pentane (7 pairs and 2 single flasks) and iso-pentane (10 pairs and 2 single flasks).

Additional VOC measurements from Cape Grim were utilised for the dicarbonyl yield calculations, including online PTR-MS measurements in clean air at Cape Grim in February (summer) 2006 (Galbally et al., 2007), online PTR-MS measurements in clean air in spring (November) 2007 (Lawson et al., 2011), in which data has been further filtered to include only Baseline hours (Sec. 2.2.2) and stainless steel canisters which were collected at Cape Grim between 1998 – 2000 and analysed at Aspendale with GC with flame ionisation detection (FID) (Kivlighon, 2001). Further details of how these data were utilised is provided in Sec. 3.3 and Table 3.

OH and ozone concentrations

Precursor (VOC) lifetimes at Chatham Rise and Cape Grim were calculated using estimated OH concentrations, and measured ozone mixing ratios from Cape Grim in March and August –September respectively.

[OH] was estimated from a simple steady state chemical model where:

$$O_3 \xrightarrow{J(O^1D)} O_2 + O(^1D) \quad (1)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (2)$$

OH is presumed to be removed overwhelmingly by reaction with carbon monoxide and methane (Sommariva et al., 2004). J(O^1D) is estimated from UV-B measurements for 2000 – 2005 inclusive (Wilson, 2014). All other chemical parameters are measured at Cape Grim (hourly averages) except for ozone where climatological values were used. The full temperature dependence of reaction rates was used.

Average measured ozone mixing ratios in Baseline air at Cape Grim were taken from Molloy et al. (2014).

3 Results and Discussion

3.1 In situ observations in clean marine air

3.1.1 Selection of clean marine samples

Five of the 33 samples from Cape Grim, and 2 of the 6 samples from Chatham Rise were identified as coming from a clean marine back trajectory air over the 24 hour sampling period. Mixing ratios of glyoxal and methylglyoxal at Cape Grim and Chatham Rise in clean marine air alongside supporting measurements are shown in Table 1. Air mass back trajectories (96 hour) for these clean marine samples are shown in Figs. 4a and 4b.

Samples were identified as being of clean marine origin in the following way. Samples from Cape Grim were initially identified as those for which > 90% of the sample hours were classified as Baseline according to the criteria described in Sec. 2.2.2. Between 92-97% of the sampling time was Baseline for the clean marine samples. Chatham Rise clean marine samples were initially identified using the HYSPLIT air mass back trajectories, and in situ measured wind direction. As an additional indicator of clean marine baseline air, concurrent measurements of in situ continuous CO_2, and CN > 10nm were calculated for Cape Grim and SOAP samples (see Table 1). Concurrent atmospheric radon-222 concentrations were also calculated for Cape Grim samples.

The pristine marine nature of these samples is clearly demonstrated by these supporting measurements. The particle concentration (CN>10nm) at Cape Grim during sampling of clean marine samples was 194 particles cm^{-3}, lower than the typical concentration of ~400 particles cm^{-3} in Baseline air in August/September (Gras, 2014). Particle concentrations corresponding to the Chatham Rise clean marine samples are also low (328 particles cm^{-3}) but with a large standard deviation of 1591 particles cm^{-3}. This is due to short-lived, major enhancements (up to 30,000 particles cm^{-3}) of CN, which correspond to measured enhancements in black carbon, identifying ship exhaust. This raises the possibility that there may have been a minor influence of ship exhaust on the VOC measurements, even though the VOC and aerosol inlets were not co-located. While glyoxal and methylglyoxal have been identified in medium duty diesel exhaust (Schauer et al., 1999), and so could be emitted by the ship's diesel engine, Schauer et al. (1999) showed that oxygenated VOCs such as acetaldehyde and acetone were present in mixing ratios 10-20 times higher than glyoxal. No

coincident spike in acetaldehyde or other VOCs were seen with the particle peaks – therefore it is unlikely that ship exhaust had any influence on the glyoxal or methylglyoxal measured.

Average CO_2 concentrations during clean marine samples were 388.84 (std dev 0.12) and 388.54 ppm (std dev 0.8) at Cape Grim and SOAP respectively, very close to Southern Ocean Baseline concentrations in August 2011 (388.51 ppm) and March 2012 (388.69 ppm) (http://www.csiro.au/greenhouse-gases/). The higher standard deviation from Chatham Rise was due to positive CO_2 excursions above background and is therefore likely also a minor impact of ship exhaust.

Finally the atmospheric radon-222 concentration of 43 mBq m^{-3} at Cape Grim is indicative of clean marine air. This value compares well to a median baseline sector value of 42 mBq m^{-3} and is much lower than the median non-baseline value of 378 mBq m^{-3} reported by Zahorowski et al (2013).

3.1.2 Dicarbonyl observations in clean marine air

The glyoxal mixing ratio at Cape Grim in winter is low (7 ± 2 ppt), and in contrast is higher over Chatham Rise in summer (23 ±8 ppt). The low standard deviations indicate consistency in glyoxal mixing ratios in clean marine air at both sites. The higher mixing ratios in summer compared to winter are in agreement with higher VCDs of glyoxal in summer compared to winter over the temperate SH oceans as observed by SCIAMACHY and GOME-2 (Vrekoussis et al., 2009; Lerot et al., 2010) (see Sec. 3.4 for further discussion of satellite comparison).

In contrast to glyoxal, the methylglyoxal mixing ratios in pristine marine air are higher at Cape Grim (28 ± 11ppt) compared to Chatham Rise (10 ± 10 ppt). The average ratio of glyoxal:methylglyoxal in clean marine air is ~4 over Chatham rise (range 1.7-5.9) while at Cape Grim the average ratio is 0.3 (range 0.2-0.4) Given that many of the gas phase precursors of methylglyoxal are also precursors of glyoxal this major difference in ratios at the two sites is striking, and is also seen when taking into account non-pristine marine samples. Possible reasons for this difference are discussed in Sec. 3.2.3 below.

3.2 Clean marine versus all data and comparison with other marine background observations

Cape Grim and Chatham Rise dicarbonyl observations from clean marine samples and for all samples are presented in Table 2. For comparison, other studies reporting mixing ratios of

glyoxal and methylglyoxal from remote temperate and tropical oceans are also presented. Where other studies have explicitly excluded possibility of terrestrial influence via back trajectories or other means, these values are listed as 'clean marine.' Where possibility of terrestrial influence has not been investigated, values are listed as 'all data', however values listed under 'all data' are not necessarily affected by air of terrestrial origin.

3.2.1 Glyoxal

Average mixing ratios of glyoxal at both Cape Grim and Chatham Rise are higher when averaging all samples (which include air from all wind directions and hence terrestrial sources), compared to clean marine samples. This is expected as the terrestrial environment is a major source of important biogenic dicarbonyl precursor gases isoprene and alpha-pinene, and is also a source of precursors from anthropogenic and biomass burning sources, including longer lived gases such as acetylene, benzene, acetone, alkanes and $>C_2$ alkenes which can travel long distances before being oxidised. Higher standard deviations in all samples compared to clean marine samples likely reflects a greater variation in concentrations of precursor gases resulting from differing wind directions. Interestingly, at Cape Grim, the average enhancement in glyoxal when including data from all wind direction is only 3 ppt, even though a further 28 samples have been included. This suggests terrestrial sources have a minimal contribution to glyoxal mixing ratios at Cape Grim in winter.

The glyoxal mixing ratio from Cape Grim of 7 ppt in clean marine conditions and 10 ppt in all conditions, is the lowest mixing ratio that has been reported over the world's oceans to date. This low mixing ratio is supported in part by the study by Mahajan et al. (2014), in which many of the observations over the temperate SH oceans were below detection limits. The glyoxal mixing ratio from Chatham Rise all data (30 ±12 ppt) compares well to the mixing ratio derived from MAX- DOAS measurements during the same voyage (23 ± 10 ppt) (Mahajan et al., 2014). Despite the techniques employing different approaches (in situ derivatised samples versus column measurement) this suggests good agreement between these techniques at these low mixing ratios. Recent inter-comparisons of dicarbonyl measurement techniques have examined the relationship between optical and derivatisation techniques, but with a focus on a wider range of mixing ratios than observed over the remote ocean (Thalman et al., 2014; Pang et al., 2014).

The glyoxal mixing ratios from Chatham Rise also compare well to those observed by Mahajan et al. (2014) over the North Pacific and Atlantic (25 ± 13 ppt) and tropical Pacific

and Atlantic (24 ± 12 ppt SH, 26 ± 15 ppt NH). It should be noted that these Mahajan et al. (2014) values were calculated only from data above the instrument detection limit and so contain a positive bias and are upper estimates. Chatham Rise mixing ratios are also similar to the Eastern Tropical Pacific NH average (32 ± 6 ppt) (Coburn et al., 2014) but somewhat lower than those observed in the SH Eastern Tropical Pacific (43 ± 9 ppt) (Coburn et al., 2014), and over the Tropical Pacific (63 ± 21 ppt) (Sinreich et al., 2010). The Caribbean Sea value of 80 ppt is the highest average mixing ratio reported over the oceans and substantially higher than mixing ratios observed in this study, although the variation of this value is not given (Zhou and Mopper, 1990). Overall, the synthesis of glyoxal observations from this and other studies provides compelling evidence for the widespread presence of glyoxal, in non-negligible mixing ratios, in the atmosphere over the remote oceans.

3.2.2 Methylglyoxal

Mixing ratios of methylglyoxal at Cape Grim and Chatham Rise are higher when considering all data, and have greater variation, reflecting substantial influence of terrestrial precursors. In particular, mixing ratios of methylglyoxal at Cape Grim in all samples are approximately twice the mixing ratios of clean marine samples. This significant enhancement at Cape Grim in all data is likely due to substantial terrestrial influence at Cape Grim when considering all wind directions. The station is bounded by farmland to the east and south-east, and mainland Australia, and the city of Melbourne is ~300km north across Bass Straight. The greater enhancement of methylglyoxal compared to glyoxal in all data from Cape Grim may be due to the much higher yield of methylglyoxal from isoprene and monoterpenes compared to glyoxal, and the rich source of methylglyoxal precursors from urban regions including alkenes and alkanes > C_2 (Fu et al., 2008).

The only other observations of methylglyoxal over the world's oceans come from the Caribbean Sea (Zhou and Mopper, 1990), with an approximate value of ~ 10 ppt which is somewhat lower than that observed at Cape Grim, but in agreement with Chatham Rise mixing ratios in this study.

3.2.3 Differences between dicarbonyl ratios at Cape Grim and Chatham Rise

The average ratio of glyoxal: methylglyoxal is 3.8 over Chatham Rise (range 1.7-5.9) in clean marine air and 2.3 in all samples (range 1.2-5.9). At Cape Grim the average ratio is 0.3 (range 0.2-0.4) in clean marine air and 0.2 in all samples (range 0.1-0.4). The dominance of

methylglyoxal at Cape Grim and glyoxal at Chatham Rise points to a major difference between sites and warrants further investigation.

The back trajectories of air in clean marine samples at both Cape Grim and Chatham Rise indicate that the air sampled at both sites originated from the Southern Ocean, from a latitude of 55 - 65ºS 96 hours prior (Fig. 4a and b). A major difference between the back trajectories of the two sites is the longitude, with Cape Grim back trajectories covering 50 ºE - 140ºE and the trajectories from the more easterly located Chatham Rise covering 90º E - 175ºE. The 3-D trajectory altitude (not shown), suggests that air from all clean oceanic samples at both sites travelled in the lower 750m of troposphere 24 hours prior, and which up to 48 hours prior had originated at a height of between 500-1500m (Chatham Rise) and 300-1200m (Cape Grim). No clear differences in vertical back trajectories between sites, or relationship between height and mixing ratios were evident.

Because glyoxal and methylglyoxal are so short lived, their observed mixing ratios are due to equilibrium between local production and loss. Therefore the difference in ratios between sites indicates a major difference or differences in production or loss rates.

If differences in ratios are due to differing rates of production of dicarbonyls, this could be due to a) varying concentrations of precursor gases, b) different emission rates of dicarbonyls from the SML, or c) other unconfirmed production mechanisms. Methylglyoxal and glyoxal have a number of overlapping gas phase precursors, and while there are precursors specific to each (e.g. acetylene, acetone and benzene for glyoxal and higher alkanes and alkenes for methylglyoxal) (Fu et al., 2008), in clean marine conditions precursor mixing ratios are unlikely to differ significantly between sites. The calculated yield of dicarbonyls from parallel or best estimate precursor mixing ratios at both sites is low (see Sec. 3.3) and so other production mechanisms must be dominating at these sites.

Emission of glyoxal from the SML has only very recently been reported for the first time (Zhou et al., 2014), and there is no evidence as yet of direct emission of methylglyoxal from the oceans. It is likely that methylglyoxal is emitted from the oceans: it has been measured alongside glyoxal in the SML in concentrations which are enhanced above the bulk water, indicating its production in the SML, (van Pinxteren and Herrmann, 2013; Zhou and Mopper, 1990). However, the relative abundance of methylglyoxal in the SML compared to glyoxal is highly uncertain, but the studies that have investigated this have found higher concentrations of glyoxal compared to methylglyoxal by a factor of 3 (van Pinxteren and Herrmann, 2013)

and 5 (Zhou and Mopper, 1990). Meanwhile, a laboratory study which detected glyoxal from oxidation of the SML did not find evidence for methylglyoxal production (Zhou et al., 2014). It is therefore possible that the ratio of glyoxal:methylglyoxal is higher at Chatham Rise compared to Cape Grim due to enhanced direct emission of glyoxal from biologically productive waters which were targeted over Chatham Rise, in contrast to Cape Grim which in winter samples air which has passed over waters of low biological productivity. The likelihood of SML as a major source of glyoxal is uncertain given the modest atmospheric yields of glyoxal in laboratory studies (Zhou et al., 2014) and modest positive fluxes of glyoxal from the tropical ocean (Coburn et al., 2014). However emission of dicarbonyls from the temperate oceans has not been studied and so the temperate SML, as a source of dicarbonyls particularly in biologically active regions such as Chatham Rise, cannot be discounted.

It is also possible that the difference in dicarbonyl ratios between the two sites is due in part to differences in loss rates between glyoxal and methylglyoxal. The major sink for both dicarbonyls is photolysis which is unlikely to explain the difference in observed ratios. Other sinks include oxidation by OH, irreversible uptake into cloud droplets and particles followed by conversion to SOA, or wet or dry deposition (Fu et al., 2008). Satellite imagery shows both sites had partial cloud cover during the sampling periods, however a major difference was the amount of rainfall that occurred at Cape Grim (90 mm over 33 days) compared to during dicarbonyl sampling on over Chatham Rise (3 mm over 6 days). Specifically during sampling of the Cape Grim clean marine samples, 1-7 mm of rain fell each day, (sum 14.0 mm for 5 samples), while during clean marine Chatham Rise samples 0-0.4mm fell each day (sum 0.57mm for 2 samples). It is possible that due to the higher Henry's law constant of glyoxal compared to methylglyoxal (Kroll et al., 2005; Zhou and Mopper, 1990; Betterton and Hoffmann, 1988), glyoxal was more efficiently removed from the atmosphere via wet deposition at Cape Grim due to its more rapid uptake into aqueous particles. While wet deposition is a globally minor sink, it is likely to be important at night in the absence of other major sinks (Fu et al., 2008). However, the reason for this difference cannot conclusively be determined. The only other observations of glyoxal and methyglyoxal over the open ocean for comparison are in the tropics (Zhou and Mopper, 1990) and show an average glyoxal mixing ratio far in excess of methylglyoxal mixing ratio. This is in direct contrast to Cape Grim, and in partial agreement with the Chatham Rise results. Production and loss processes at each site could be explored with chemical modelling.

3.3 Calculation of expected glyoxal, methylglyoxal yields from measured VOC precursors in clean marine air

Expected yields of glyoxal and methylglyoxal were calculated, based, where possible, on parallel precursor VOC measurements over Chatham Rise and Cape Grim (Table 3). Where a concurrent measurement of a precursor was not available, an estimate was made. All estimated precursor mixing ratios are identified, and the source of the estimate is given in Table 3. Where no observations of the precursor at the site were available (e.g. toluene and xylene in winter at Cape Grim), but observations of a similar compound class were available (e.g. benzene) the mixing ratio of benzene was used as a reliable upper estimate for shorter-lived toluene and xylenes. Where no observations of the precursor were available, and no measurements of compounds from a similar class were available, mixing ratios were based on the same precursor species at a different site (e.g. summer Cape Grim acetylene, alkene and alkane observations were used for Chatham Rise). In other cases, in-situ observations from the site in the same season were used, but based on measurements several years prior (e.g. Cape Grim ethene and propene). Where observations from the specific season were not available, e.g. winter isoprene, acetone and monoterpenes at Cape Grim, a spring or summer value was used, which for isoprene and monoterpenes are likely to be an upper estimate. Three dicarbonyl precursors, glycoaldehyde, methyl butenol and hydroxyacetone, were excluded from the calculation as all are emitted from terrestrial processes (biomass burning and biogenic emission) and are short-lived, so are unlikely to contribute to dicarbonyl production over the remote ocean.

The expected mixing ratios of dicarbonyls that could be explained by oxidation of each precursor were calculated according to the following equation:

$$MR_{dicarbonyl} = \frac{MR_{precursor} \times Y_{dicarbonyl}}{\tau_{precursor}} \times \tau_{dicarbonyl} \quad (3)$$

Where $MR_{dicarbonyl}$ is mixing ratio of dicarbonyl, $MR_{precursor}$ is mixing ratio of precursor, $Y_{dicarbonyl}$ = yield of dicarbonyl, τ_{prec} = lifetime of precursor and $\tau_{dicarbonyl}$ = lifetime of dicarbonyl.

Global annual mean molar yields of glyoxal and methylglyoxal from precursor gases were taken from Fu et al. (2008). Lifetimes of all precursors were calculated based on average daytime concentrations of [OH] of 8.7×10^5 molecules cm^{-3} at Chatham Rise in March and 3.7×10^5 molecules cm^{-3} at Cape Grim in August-September, except for monoterpenes (proxy

for alpha-pinene), isoprene and propene lifetimes which were based on the [OH] stated above and [ozone] of 4.9×10^{11} molecules cm^{-3} at Chatham Rise and 8.0×10^{11} molecules cm^{-3} at Cape Grim (see Sect 2.2.3). Global average lifetimes of glyoxal (2.9 hours) and methylglyoxal (1.6 hours) were used (Fu et al., 2008).

Table 3. shows that the small proportion of glyoxal and methylglyoxal production accounted for is largely driven by isoprene and monoterpenes. The precursors can explain at most 1-3 ppt of glyoxal and methylglyoxal at these two sites, which equates to only 17% and 10% of glyoxal and 10% and 29% of methylglyoxal over Cape Grim and Chatham Rise, respectively. By dividing the difference between the measured and calculated mixing ratios by the average global lifetime of glyoxal and methylglyoxal, the production rate in the boundary layer required to reconcile the measured and calculated dicarbonyl mixing ratios can be determined. For glyoxal, the additional production rate required is 48 ppt/day (97 ppt C/day) and 172 ppt/day (343 ppt C/day) while for methylglyoxal the additional production rate required is 378 ppt/day (1135 ppt C/day) and 106 ppt/day (318 ppt C/day) at Cape Grim and Chatham Rise.

As mentioned in Sec. 2.2.3, the isoprene and monoterpene mixing ratios over Chatham Rise were below the instrument detection much of the time, and substitution of half MDLs may result in an upper estimate of mixing ratios for these species. Regardless, this is the first study which has used concurrent measurements of these important precursors to constrain the yields of glyoxal and methylglyoxal. As parallel isoprene and monoterpene mixing ratios were not available at Cape Grim the yield calculation used summer and spring isoprene and monoterpene mixing ratios which are likely to result in an upper estimate of dicarbonyl mixing ratios resulting from precursor oxidation. Conversely using the global average lifetimes of glyoxal and methylglyoxal is likely to lead to an underestimate of the mixing ratio of dicarbonyls at Cape Grim, as actual dicarbonyl lifetimes in winter at Cape Grim are likely to be longer than the global average. The calculation also does not take into account diurnal variation in production and loss rates. However, Coburn et al. (2014) showed that while glyoxal over the Eastern Tropical Pacific varied by approximately 15 ppt (~30%) between night and day, it did not decrease below 30 ppt at night (average both hemispheres). The approach used here should therefore give a good approximation of the 24 hour dicarbonyl mixing ratio expected from oxidation of precursors. The absence of photolytic destruction and OH oxidation of dicarbonyls at night (the dominant known sinks), coupled with an absence of dicarbonyl production through OH oxidation of precursors at night (the

dominant known source) likely contributes to the relatively constant mixing ratios between day and night.

The low proportion of dicarbonyl mixing ratios that can be explained by oxidation of precursors calculated here supports previous claims that there is unlikely to be sufficient levels of VOC precursors over the remote oceans to explain the non-negligible levels of glyoxal observed (Coburn et al., 2014; Sinreich et al., 2010). For the first time, we show that the same applies to methylglyoxal over the ocean.

The large proportion of glyoxal and methylglyoxal which cannot be explained by the precursor mixing ratios confirms the importance of other production mechanisms. As discussed previously, it is unclear whether positive SML fluxes are sufficiently large to explain the unaccounted for portion of these gases at Cape Grim and Chatham Rise. Kwan et al (2006) estimated that OH oxidation of organic aerosol (OA) may result in a production rate of up to 70 ppt C/day of OVOCs in the FT and a production rate of up to ~500 ppt C/day OVOCs in the lower continental troposphere in the summertime. The combined boundary layer production rate of glyoxal and methylglyoxal at Chatham Rise needed to reconcile the measured and calculated mixing ratios is 661 ppt C/day, in reasonable agreement with the Kwan et al (2006) estimate, while the Cape Grim glyoxal and methylglyoxal flux (1232 ppt C/day) is a factor of 2-3 times higher. Whilst the Kwan et al (2006) estimates contained significant uncertainties, and used continental measurements, they do suggest that oxidation of OA may make a non-negligible contribution to the dicarbonyl mixing ratios.

Another possible production mechanism is oxidation of as yet unidentified gas phase precursors.

3.4 Comparison of glyoxal surface observations with satellite vertical columns

In situ glyoxal mixing ratios from Cape Grim and Chatham Rise were converted into vertical column densities (VCDs) and compared with glyoxal VCDs from GOME-2 on Metop–A.

Mixing ratios were converted to VCDs assuming that all glyoxal observed was well mixed within the boundary layer, and assuming standard conditions throughout the boundary layer of temperature (25ºC) and pressure (1 atm). Boundary layer heights of 850m were used for both Chatham Rise (average of daytime and nocturnal radiosonde flights) and an average modelled value for Cape Grim in all wind directions (unpublished data, see Zahorowski et al.

2013 for model details). Chatham Rise surface observations were compared to an average GOME-2 column for March 2012 in the region 40-º50 S and 170-180ºE, while Cape Grim surface observations were compared to GOME-2 columns taken from August-September 2011 in the region 39-42ºS and 143-147ºE.

In the Austral summer, GOME-2 glyoxal columns over the temperate oceans in the SH are low, but somewhat higher than other remote regions, while in winter the columns are among the lowest observed globally (Lerot et al., 2010). There is low inter-annual variability in the GOME-2 glyoxal VCDs at both the regions encompassing Cape Grim and Chatham Rise, but a clear seasonal cycle, with a maximum VCD in the summer months (Dec- Feb) and a minimum in the autumn-winter months (May-August). The 2007-2012 average seasonal variability of GOME-2 glyoxal VCDs from the sites above is shown in Figure 5. In June, VCDs cannot be calculated due to insufficient satellite sensitivity resulting from observation geometry (low angle of the sun).

Cape Grim VCDs calculated from in situ observations are 2.1×10^{13} molecules cm^{-2} (standard error of mean 2.1×10^{12}), while Chatham Rise calculated VCDs are 6.3×10^{13} molecules cm^{-2} (standard error of mean 1.0×10^{13}). In comparison, satellite retrieved VCDs are 1.8×10^{14} molecules cm^{-2} for the Cape Grim region and 2.4×10^{14} molecules cm^{-2} for the Chatham Rise region (both with an uncertainty of $\pm 1.3 \times 10^{14}$ molecules cm^{-2}) (Figure 5). While both satellite columns and in situ columns observe higher VCD over Chatham Rise in summer than Cape Grim in winter, the satellite VCDs exceed in situ VCDs at both sites by $>1.5 \times 10^{14}$ molecules cm^{-2}. There are several possible factors that may be contributing to the higher satellite VCD. The first reason may be due to the assumption that all of the glyoxal observed by the satellites is in the boundary layer. Aircraft measurements made as part of the TORERO campaign (Tropical Ocean Troposphere Exchange of Reactive Halogens and OVOCs), have confirmed the widespread presence of glyoxal in the free troposphere (Volkamer, 2014). If glyoxal is also present in the free troposphere over the temperate SH oceans, the satellite, which is sensitive to the entire troposphere, would indeed observe glyoxal VCD larger than VCD calculated from in situ measurements, which represent only the boundary layer. If glyoxal is widespread in the free troposphere this clearly has important implications for the interpretation of satellite column data. Another reason may be due to the significant challenges in retrieving low VCDs of glyoxal over the oceans, due to interferences by liquid water absorption, discussed elsewhere (Vrekoussis et al., 2009; Lerot et al., 2010). Also, the satellite glyoxal retrieval algorithm includes a normalization procedure comparing

actual retrieved columns to a reference value taken in a reference sector. As discussed in Miller et al. (2014), this reference value might be too large. Another possible reason is that the satellite VCDs are measured only once per day during the satellite overpass at 9:45am, whereas the in situ observations reported here are 24 hour averages. If there is a diurnal variation in glyoxal mixing ratios at these sites, as was shown over the Tropical Pacific Ocean (Coburn et al., 2014), the satellite VCD may not be representative of the 24 hour average.

Difficulty reconciling satellite VCDs and in situ observations over the ocean has recently been noted elsewhere, including the tendency of satellite VCDs to exceed in situ measurements, particularly in regions with low VCDs which are at the limits of satellite sensitivity (Coburn et al., 2014; Mahajan et al., 2014). Further comparisons between in situ and satellite observations over the oceans are needed, including characterisation of the vertical distribution of glyoxal.

4 Conclusions

This work confirms the presence of short lived dicarbonyl glyoxal over the remote temperate oceans, even in winter in very pristine air over biologically unproductive waters. We provide the first observations of methylglyoxal over temperate oceans and confirm its presence alongside glyoxal. These observations support the likely widespread contribution from these dicarbonyls to SOA formation over the ocean.

Glyoxal mixing ratios at Cape Grim in winter are the lowest measured over the ocean, while glyoxal at Chatham Rise is similar to other temperate mixing ratios, and similar to or at the lower end of tropical observations. Methylglyoxal observations at Cape Grim and Chatham Rise are comparable to the only other observations available (tropical Northern Hemisphere ocean).

Chatham Rise glyoxal observations from this study agree well with observations made via MAX-DOAS on the same voyage, suggesting a good agreement between the technique used in this work (DNPH derivatisation with HPLC analysis optimised for dicarbonyl detection) and the optical technique.

Different ratios of glyoxal: methylglyoxal were observed at the two locations, with an average ratio in clean marine air of ~4 over Chatham Rise (range 1.7-5.9) and 0.3 at Cape Grim (range 0.2-0.4). The reasons for this are unexplained but may be due to a larger positive flux of glyoxal from biologically active waters over Chatham Rise, and/or to preferential loss

of glyoxal over methylglyoxal by wet deposition at Cape Grim. Chemical modelling is suggested to better constrain the productions and loss mechanisms.

Expected yields of glyoxal and methylglyoxal were calculated based on parallel measurements of precursor VOCs, including isoprene and monoterpenes. At most, 1-3 ppt of the glyoxal and methylglyoxal observed in clean marine air can be explained from oxidation of these precursors, confirming a significant contribution from another source over the ocean. While the SML has recently been confirmed as a direct source of glyoxal both in the field and in laboratory studies, it seems unlikely this positive flux is a sufficiently large to explain the atmospheric concentrations observed. Other possible, but unconfirmed sources may include oxidation of as-yet unidentified gas precursors, or atmospheric oxidation of organic aerosol.

Glyoxal observations were converted to VCDs and compared with GOME-2 satellite VCDs. While in situ and satellite observations both observe a higher glyoxal VCD in summer, the satellite VCD exceeds the surface observations by more than 1.5×10^{14} molecules cm^{-2}. Recent observations of glyoxal in the free troposphere suggest that this discrepancy is least in part due to the incorrect assumption that all glyoxal observed over the ocean by satellites is in the MBL. Other reasons for the discrepancy may be due to challenges in retrieving low VCDs of glyoxal over the oceans, including accounting for interference by liquid water absorption and selection of an appropriate normalisation reference value in the retrieval algorithm. Further comparisons are needed, including characterisation of the vertical distribution of glyoxal.

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1 Tab01

2

Site	Season	Glyoxal (ppt)	Methylglyoxal (ppt)	CO_2 (ppm)	CN>10nm (particles cm^{-3})	Radon (mBq m^{-3})	% Baseline hours
Cape Grim n=5	Winter/Spring (Aug-Sep)	7 ± 2	28 ± 11	388.84 ± 0.12	194 ± 110	43± 14	95
SOAP voyage n=2	Summer (Feb-Mar)	23 ± 8	10 ± 10	388.54 ± 0.82	328 ± 1591	n/a	n/a

1 Tab02

2

		Temperate ocean				Tropical ocean			
		Southern Ocean (Cape Grim) This work	South West Pacific (Chatham Rise) This work	South West Pacific (Chatham Rise)[a]	North Pacific & Atlantic[a]	Tropical Pacific & Atlantic[a]	Eastern Tropical Pacific[b]	Tropical Pacific[c]	Caribbean and Sargasso Sea[d]
Glyoxal	Clean marine origin	7 ± 2	23 ± 8	-	-	-	43 ± 9 (SH) 32 ± 6 (NH)	63 ± 21	-
	All data	10 ± 6	30 ± 12	23 ± 10	25 ± 13	24 ± 12 (SH) 26 ± 15 (NH)	-	-	80
Methyl-glyoxal	Clean marine origin	28 ± 11	10 ± 10	-	-	-	-	-	-
	All data	57 ± 32	19 ± 14	-	-	-	-	-	~10

3

1 Tab03

Precursor	precursor mixing ratios (ppt)		glyoxal yield (ppt)		methylglyoxal yield (ppt)	
	Chatham Rise	Cape Grim	Chatham Rise	Cape Grim	Chatham Rise	Cape Grim
acetylene	3[a]	39[a]	0.02	0.08	n/a	n/a
ethene	51[b]	31[b]	0.22	0.06	n/a	n/a
propene	17[b]	8[b]	n/a	n/a	0.04	0.03
propane	33[c]	35[c]	n/a	n/a	0.02	0.02
alkanes $>C_3$ ^	54	52[c]	n/a	n/a	0.02	0.02
isoprene	14	14[d]	0.85	0.43	1.89	1.97
benzene	8	9[a]	0.02	0.01	n/a	n/a
toluene	9	9[*]	0.08	0.03	0.03	0.03
xylenes sum	10	9[*]	0.27	0.10	0.22	0.19
monoterpenes	32	17[e]	0.83	0.44	0.69	0.48
acetone	89	118[d]	n/a	n/a	0.01	0.02
sum yield (ppt)			2.3	1.2	2.9	2.8
% explained			**10**	**17**	**29**	**10**

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Table 1. Mixing ratios of glyoxal and methylglyoxal in clean marine air at Cape Grim and Chatham Rise, with supporting measurements of carbon dioxide, condensation nuclei (CN) >10nm and atmospheric radon-222. Values are average ± std dev. n = number of 24 hour samples.

Table 2. Glyoxal and methylglyoxal compared to dicarbonyl measurements from other remote oceanic sites. Data is listed as clean marine origin where study explicitly excludes terrestrial influence. All concs are in ppt. Values are mean ± std dev SH= Southern Hemisphere, NH= Northern Hemisphere. [a] Mahajan et al. 2014 (only data above MDL has been included in average) [b] Coburn et al. 2014 [c] Sinreich et al. 2010 [d]Zhou and Mopper 1990

Table 3. Calculated dicarbonyl yields based on precursor data from Cape Grim and Chatham Rise. Yields and dicarbonyl lifetimes based on Fu et al. (2008). Where supplementary (e.g. non-parallel) measurements were used these are denoted as follows: [a]Cape Grim flasks (NOAA HATS analysis) [b]Kivlighon 2001 [c]Cape Grim flasks (INSTAAR analysis) [d]Galbally et al. 2007 (upper estimate Cape Grim summer) [e]Lawson et al. 2011 (Cape Grim Baseline spring data, see text for explanation) [^] sum of C_4 and C_5 [*]upper estimate based on benzene

Figure 1. Cape Grim and Chatham Rise sampling locations

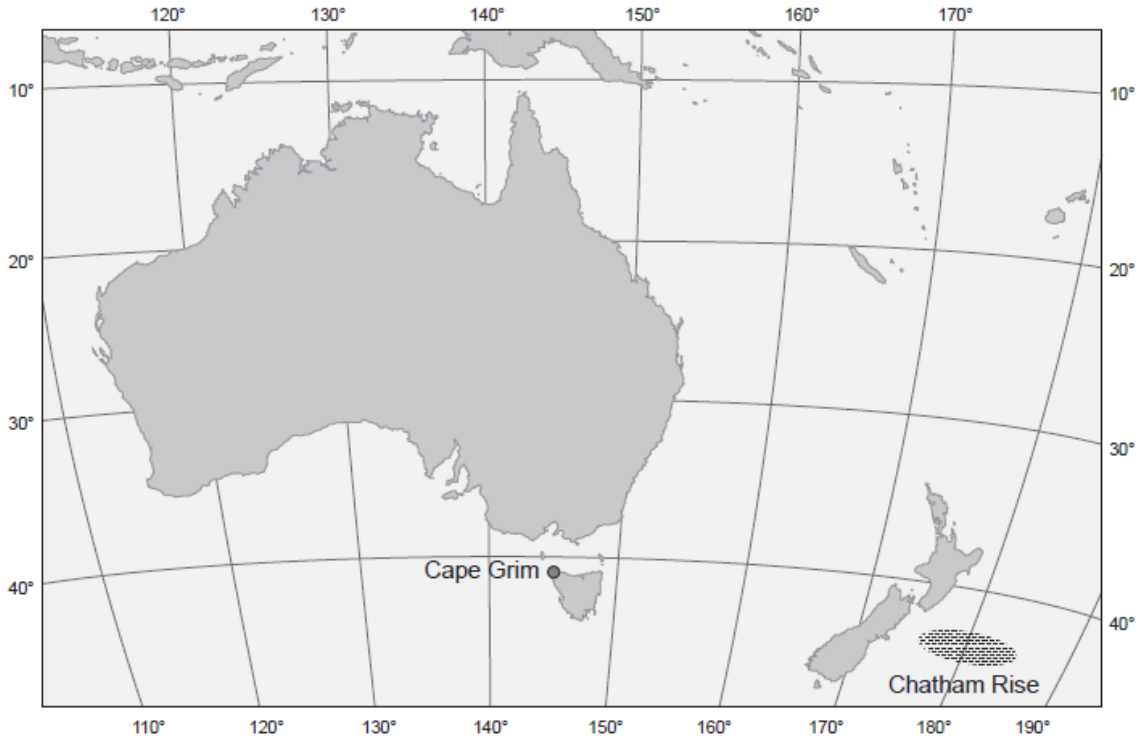


Figure 2. Absortion spectra for monocarbonyl formaldehyde (green) and dicarbonyls glyoxal (blue line) and methylglyoxal (red line)

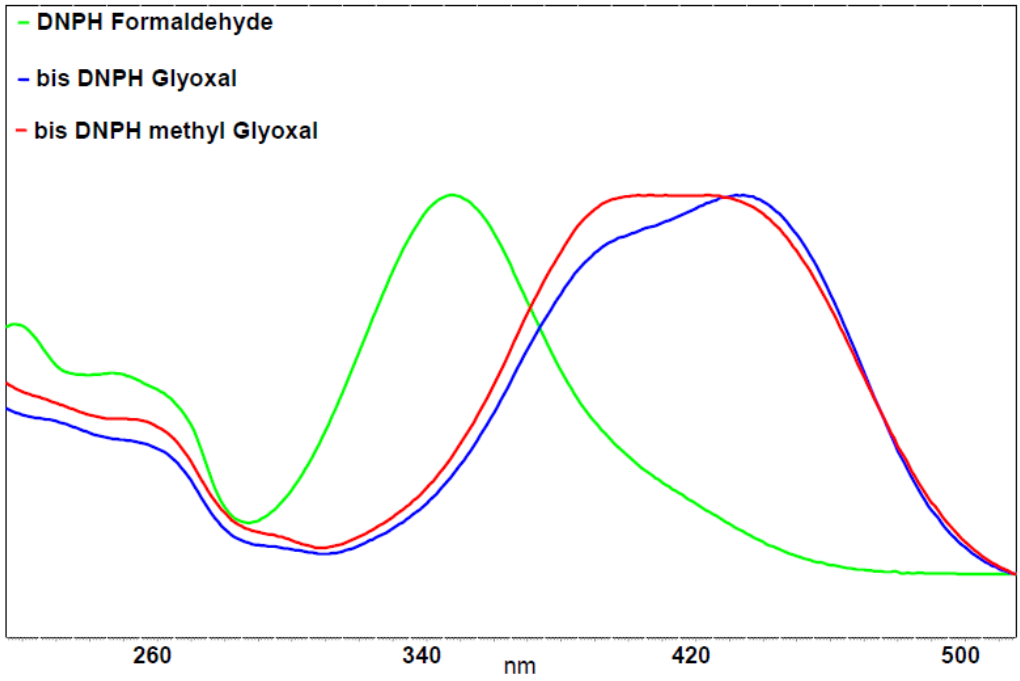
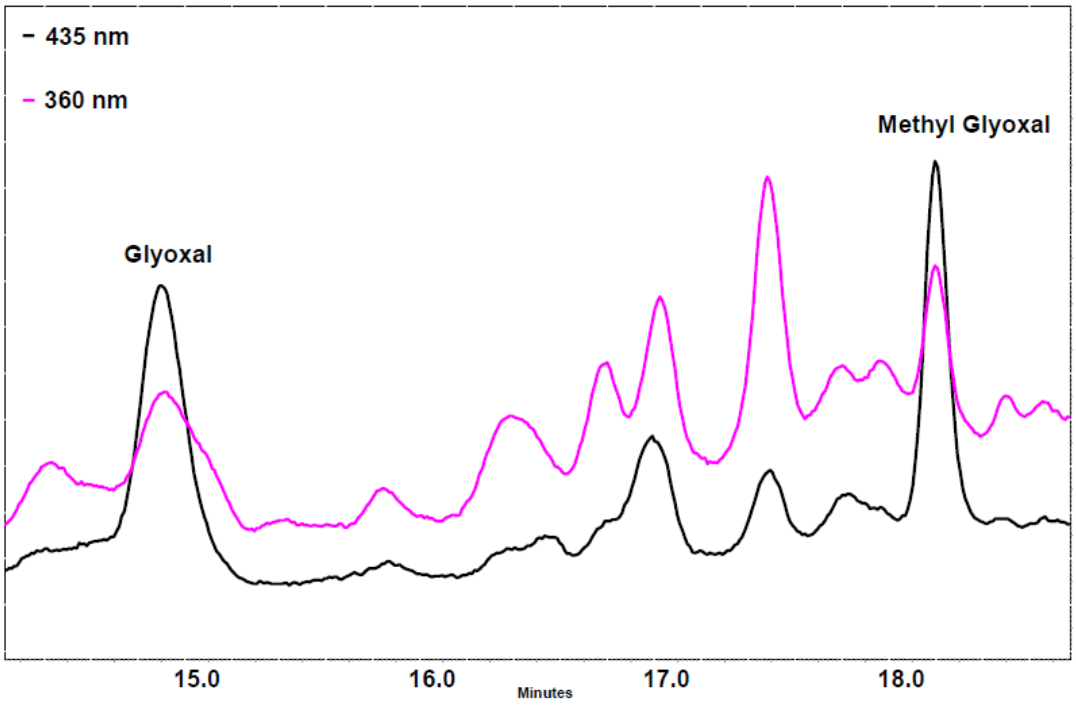


Figure 3. Example of sample chromatogram from Chatham Rise using absorption at 360nm (pink line) and 435nm (black line).



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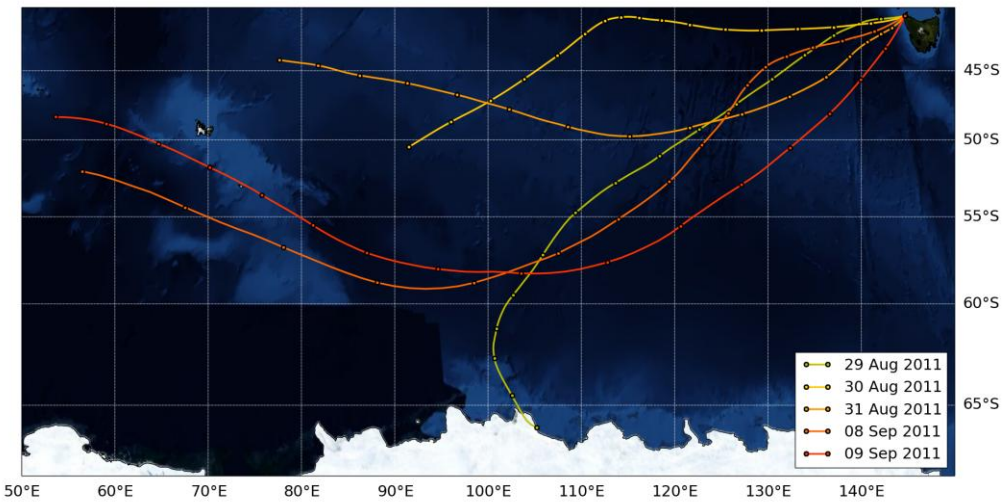
2 Figure 4a. HYSPLIT 96 hour back trajectory for the 5 clean marine samples from Cape Grim



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4 Figure 4b. HYSPLIT 96 hour back trajectory for the 2 clean marine samples from the SOAP

5 Voyage (Chatham Rise)

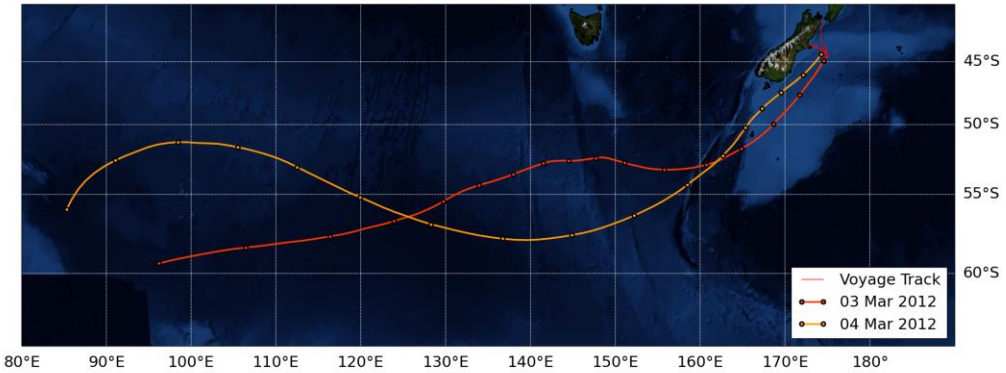
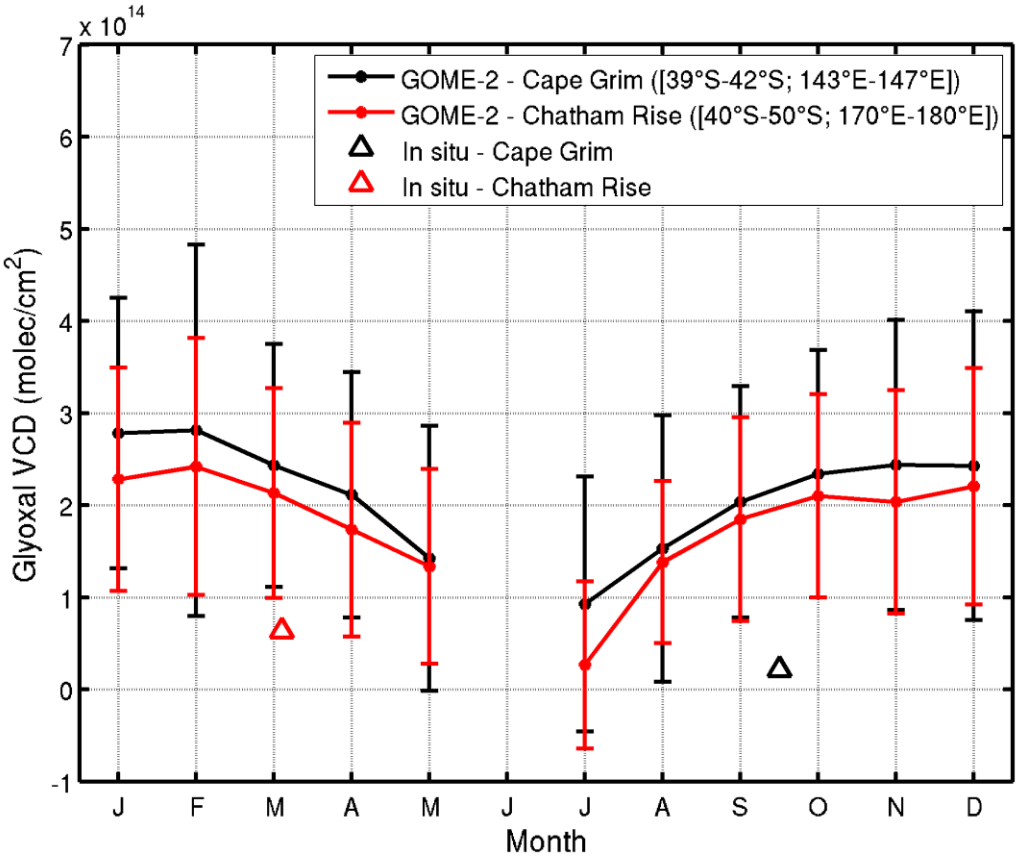


Figure 5. Seasonal glyoxal VCDs retrieved from GOME-2 and calculated from surface based observations at Cape Grim and Chatham Rise. GOME-2 values are for all data averaged between 2007-2012, for regions encompassing Cape Grim and Chatham Rise. Error bars for surface-based VCDs are insignificant on this scale and are not shown (see text for details).



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