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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal in situ observations of glyoxal and methylglyoxal over the temperate oceans of the Southern Hemisphere" *by* S. J. Lawson et al.

S. J. Lawson et al.

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We thank the Referee for their careful reading of the manuscript, and for their suggestions which have improved the manuscript. Our responses to each of the referee comments are given below, along with the resulting changes to the manuscript, where appropriate.

Anonymous Referee #2 The manuscript by Lawson et al. documents new measurements of glyoxal and methylglyoxal in two locations sampling temperate southern ocean conditions. There is currently a lack of understanding as to the origin of gly-

oxal and methylglyoxal over the ocean in many parts of the world, as observed from a small set of in situ measurements and also remote sensing data. The present work is timely in that these additional in situ measurements provide a valuable resource for determining the nature of the source of these compounds. While the analysis presented here doesn't by itself determine the missing source, or reconcile experiments with models, it is an original piece of work that will surely be useful in the overall story. The article is thus highly suitable for ACP. Overall, the manuscript was well written. I only have a few questions that constitute minor revisions.

Referee Comments / Questions: 21664/21665: Seems relevant to also mention that elevated glyoxal columns over the ocean appear to be correlated with chlorophyll.

Author Response: We agree and have added 'biologically active' to the following sentence to acknowledge the possible link between glyoxal columns and chlorophyll: 21664:18

"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."

Referee Comment: 21665.4: However, SCIAMACHY ocean columns seemed, on average, highest in the southern tropics / southern hemisphere. In fact, how are these sites situated relative to areas where high glyoxal concentrations were observed over oceans from the remote sensing studies? Were they in some of the peak areas, or were they in regions where values were below the satellite detection limit?

Author Response: We have modified 21664 line 15 to include discussion of regions where satellite glyoxal columns are close to detection limits:

"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

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evidence of the widespread presence and seasonal modulation of glyoxal over biologically active oceans, although in some regions, such as temperate SH oceans, the columns are close to satellite detection limits."

We have changed 21665 line 4 to be more specific about where in the SH Mahajan et al. found mixing ratios below the detection limits.

Sentence changed to: "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.

Referee Comment:21676: Is there any uncertainty introduced by using climatological OH and O3 values? If the source is episodic, such as correlating with phytoplankton blooms or some other temporary occurrence, would this climatological OH/O3 be representative?

Author Response: The OH and O3 values used, which were average values from Baseline air, would likely be quite consistent year to year. However, it is possible that a nearby phytoplankton bloom or some other activity may result in some difference between actual and assumed values. As the OH and O3 values were used only to calculate the lifetime of the precursor gases, the uncertainty introduced from using climatological values is expected to be minor. For example a $\pm$10% change in OH would change the calculated methylglyoxal yield explained from oxidation of precursors by a maximum of $\pm$3%, while a change of $\pm$5ppb in ozone would change the calculated methylglyoxal yield explained by maximum of $\pm$1%.

Referee Comment: Fig 4a: It's kind of hard to see the different line colors here since they are so thin and over a dark background.

Author Response: These plots (4a and 4b) have been modified to include thicker lines (see attached files)

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Referee Comment:Fig 4a/b / 21682.5: It seems to me that the obvious differences are the longitudes of the back trajectories. Also, it's not evident if there were any differences in the elevations,from one site to another or from day to day.

Author Response: As suggested we have modified the paragraph to acknowledge the different longitudes of the back trajectories between sites, and to discuss the differences in vertical back trajectories between sites:

"A major difference between the back trajectories of the two sites is the longitude, with Cape Grim back trajectories covering 50 °E - 140°E and the trajectories from the more easterly located Chatham Rise covering 90° E - 175°E. 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. "

Referee Comment:21678: Regarding contamination of the sampling by the ship's plume, the argument based on acetaldehyde makes sense. However, I don't quite see how they could be sampling CO2 from the ship exhaust (line 19), but not VOCs (13). Did these have separate inlets?

Author Response: Yes, VOCs and CO2 had separate inlets which were co-located. Details on the CO2 inlet are given on page 21763 line 14, and details on VOC inlet are given on page 21668, line 18.

Referee Comment:21681.6: "over the remote oceans" Or, over some remote oceans, as there is not much at Cape Grim. I'm not sure how much the results from just the two points measured here can be extrapolated to the rest of the world.

Author Response: This sentence concludes a paragraph which discusses all available glyoxal observations over the remote oceans from previous studies, not just the results

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from this study.

To make this clearer the sentence has been changed to:

“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.”

Referee Comment:21683: The differences in precipitation seem very significant, and I was surprised this wasn’t discussed earlier, given the importance of explaining differences between the two sites. It makes me wonder if there were other major differences in meteorological conditions, such as temperature, RH, background aerosol loading, insolation, etc.

Author Response: Meteorological data (air temperature, RH, rainfall) are already given for each site in the Methods section 2.1 under 2.1.1 Cape Grim Baseline Station (21668 lines 1-3) and 2.1.2 Surface Ocean Aerosol Production (SOAP) voyage (21669 lines 18-20). Differences in background aerosol loading between the two sites are already given in Table 1 (CN> 10nm). We believe that Section 3.2.3”Differences between dicarbonyl ratios at Cape Grim and Chatham Rise” is an appropriate part of the manuscript to discuss the differences in meteorology between sites, and the possible implications for the dicarbonyl mixing ratios.

Referee Comment: 21685.15: It might be more correct to say here that the fraction of the production that has been accounted for is largely driven by isoprene and monoterpenes, but perhaps since this is still only a small fraction of the total, with the driver of the remainder not yet know.

Author Response: We agree and have changed this sentence to:

“ Table 3. shows that the small proportion of glyoxal and methylglyoxal production accounted for is largely driven by isoprene and monoterpenes.”

Referee Comment: 21686.23: Could compare to / references estimates from Kwan et

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al. GRL 2006, regarding the organic aerosol source.

Author Response: As suggested we have compared the currently unaccounted carbon production from this study with the flux of carbon from organic aerosol estimated by Kwan et al (2006). Paragraph below has been added.

"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."

Referee Comment: 21687: Can the in situ data be shown on the same plot as the satellite data? It wasn't clear why they weren't shown together.

Author Response: As suggested Fig 5 has been modified so that the observations are shown on the same plot as the satellite data. The figure caption has also been modified:

"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)."

Referee Comment: More broadly, it seemed odd that the measurements were entirely described by a few values in Tables 1 and 2. Was there nothing that could be learned

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from time-series?

Author Response: The dicarbonyl measurements in this study were taken from 24 hour integrated samples. There were 34 samples taken at Cape Grim, and only 5 were comprised entirely of clean oceanic air. At Chatham Rise, six 24 hour samples were taken and 2 samples were comprised entirely of clean oceanic air. Hence most samples in this study contained air from multiple wind directions and were therefore impacted by a variety of terrestrial and marine sources. For this reason, any temporal variability or trend is likely to be dominated by variability in air masses and sources. A time series of clean oceanic 24 hour samples would be informative but there were insufficient clean oceanic samples do to this.

Referee Comment: 21687.27: Strictly speaking this isn't necessarily a "bias", since there isn't necessarily an error in the satellite VCD. It is possible there is just an inconsistency in determination of VCD from the surface vs the satellite.

Author Response: We agree, and have removed the word "bias". The sentence now reads:

"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 x 1014 molecules cm-2."

Referee Comment: 21688.17: Would you expect the satellite to be higher or lower than the 24 hr average?

Author Response: Without knowing the diurnal variation of glyoxal at these sites, this is impossible to determine.

Referee Comment: Corrections: 21660.20: Grim, suggesting âËŸAËĞT> Grim suggest 21660:26: Gloxyal surface observations âËŸAËĞT> Surface-level observations of glyoxal 21661.16: salt make âËŸAËĞT> salt, make 21661.25: extra space before period 21662.7: classed as SOA. (Rinaldi: : :). âËŸAËĞT> classified as, SOA (Rinaldi: :

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:). 21663.12: clouds is âËŸAËĞT> clouds,is 21664.3: However significant âËŸAËĞT> However, significant 21664.8: However there, âËŸAËĞT> However, there

Author Response: These corrections have been made as suggested

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 21659, 2014.

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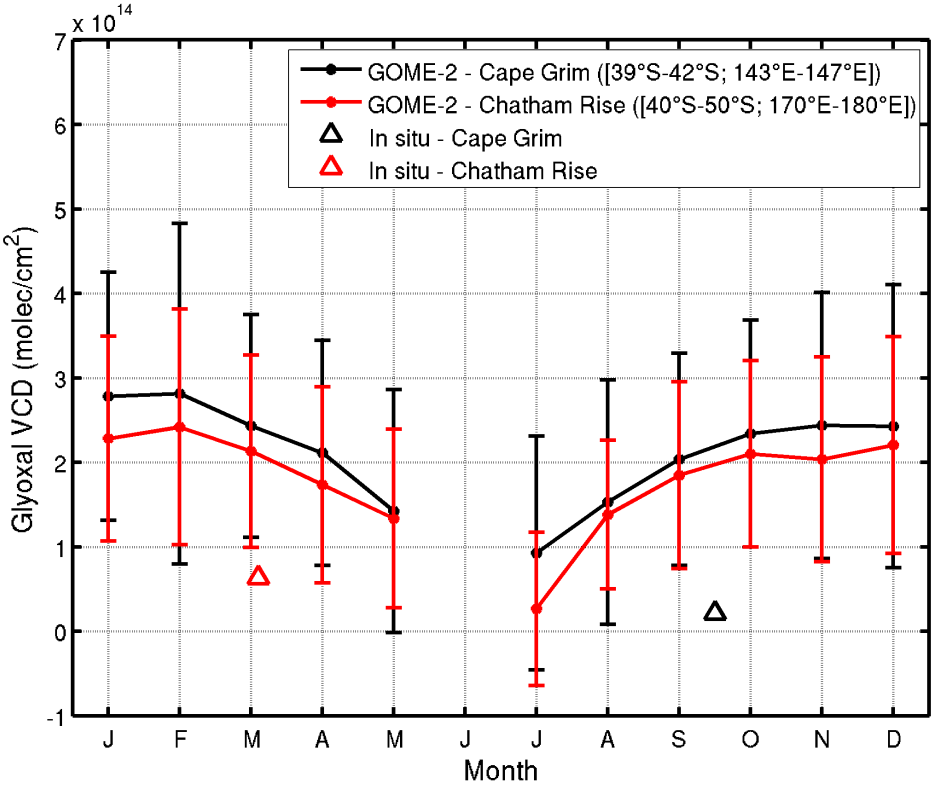

Fig. 1. Fig 5

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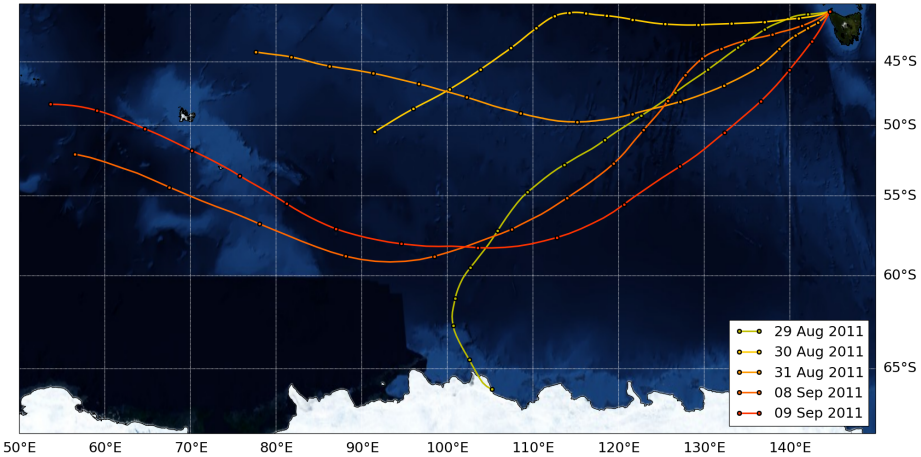

Fig. 2. Fig 4a

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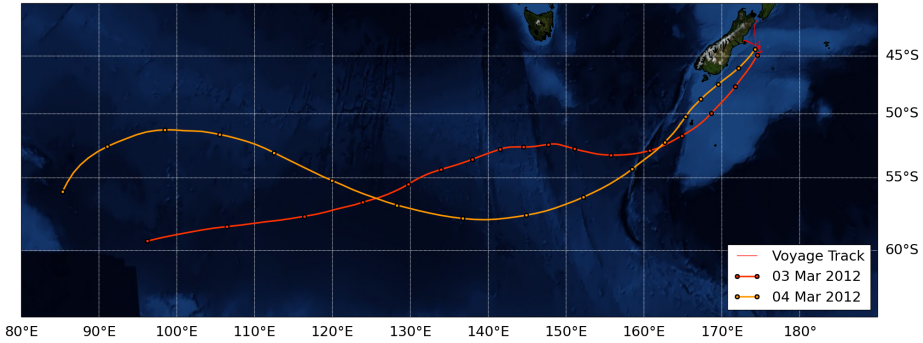

Fig. 3. Fig 4b

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