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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 #1

Referee comment: This manuscript summarizes measurements of glyoxal, methylglyoxal and their precursor gases at two sites downwind of the remote temperate oceans.

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The paper concludes that 1) the two gases are present in low ppt concentrations, 2) the precursor gases are not sufficient to account for the measured glyoxal and methyl-glyoxal mixing ratios, and 3) the calculated vertical column densities of glyoxal and methylglyoxal are much lower than those retrieved by satellite. The paper is well written and should be published in ACP with minor revisions.

Referee comment: Page 21661 line 17.....make a significant contribution to aerosol number more biologically active summer months.

Author response: The reviewer suggests that this sentence should state that organics make a significant contribution to aerosol number during biologically productive periods, however, our intention was to state that organics make a significant contribution to aerosol mass, in line with the studies we cited by O'Dowd et al., 2004; Facchini et al., 2008a; Sciare et al., 2009; Ovadnevaite et al., 2011b).

To make this clearer, we have changed the sentence to "...organic carbon can make a significant contribution to the mass of submicrometer 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).

Referee Comment: Page 21661 Line 20. The organic matter is not necessarily from the SML. The bubbles likely pick up organic matter as they rise to the surface.

Author Response: Although organic matter is concentrated in the SML of the ocean, we acknowledge that organic matter is also transported via bubbles from bulk water to the ocean surface.

We have therefore changed this sentence to "This organic carbon may be primary organic matter, directly transferred from the bulk water and sea surface microlayer (SML) of the ocean to the atmosphere during bubble burst,...

Referee Comment: Page 21661 Line 22. It not an either or. Most likely it is both primary and secondary aerosol.

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Author Response: We agree. We have modified the paragraph (see below) to reflect the contribution of both primary and secondary organics.

"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)."

Referee Comment: Have you tested losses of glyoxal and methylglyoxal in your inlet lines and on the cartridge during the 24 hour sampling period?

Author Response: Losses in inlet lines:

During the SOAP voyage the inlet was tested for losses of methanol, dimethyl sulfide, isoprene and monoterpenes using a calibration standard diluted to low ppb level in humidified air. Negligible inlet losses of <2% were found. Losses of glyoxal and methylglyoxal were not specifically tested due to absence of an available gas standard, however losses of these dicarbonyls would most likely occur due to irreversible uptake into liquid water on the inside of the inlet. Due to the rapid flow rate of 10L/min and 3/8" tubing, no condensation was seen or would be expected in the inlet line under these conditions.

At Cape Grim the inlet was not tested for losses, however due to the rapid flow rate consistent with laminar flow design, and short length (3m) of $\frac{1}{4}$ " PFA tubing, losses are unlikely.

We conclude that it is therefore unlikely that significant losses of glyoxal and methylglyoxal occurred at either site, however we did not specifically test for losses of these species.

The following text has been added to Section 2.1.2 SOAP Voyage

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"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 gas calibration standard"

Losses on cartridges:

As stated in the manuscript, we checked for losses of glyoxal and methylglyoxal by spiking known quantities on to DNPH cartridges and checking for recoveries. While we did not explicitly test for losses during the 24 hour sampling period, other studies have determined collection efficiencies of > 93% for carbonyls on DNPH cartridges at flow rates similar to ours (Zhang et al., 1994; Slemr, 1991; Grutter et al., 2005). Also, in this study the total mass of aldehydes and ketones sampled was at most 7% of the cartridge capacity as stated by the manufacturer (and typically 1-4 %), which was further confirmed by a large DNPH peak evident in all the sample chromatograms. Therefore in light of reported collection efficiencies from previous studies, and the excess derivatising agent DNPH remaining on the cartridges after sampling, losses of dicarbonyls on cartridges is unlikely.

The following sentence has been added to Section 2.2.1 DNPH Cartridges and HPLC analysis

"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."

Referee Comment: I think you need to at least mention the possibility that glyoxal and methylglyoxal and/or their precursor gases and/or semi-volatile aerosols could enter the boundary layer via entrainment from the free troposphere.

Author Response: We agree and have added the following text to introduction:

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“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]”

Referee Comment: If the measured precursor gases can only account for 1-3% of the measured glyoxal and methylglyoxal mixing ratios, was is the needed carbon flux into the boundary layer to support the measured mixing ratios?

Author Response: The values stated here are an error from the Referee, as the 1-3 % stated by the reviewer here should be 1-3 ppt. As suggested by the Referee we have calculated the additional production rate of dicarbonyls in the boundary layer needed to support the mixing ratios and have added the following paragraph to the manuscript in Section 3.3.

“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. ”

To put these production rates into context in Section 3.3, as suggested by Referee 2, we have compared them with production rate estimates of OVOCs from oxidation of OA as reported by Kwan et al (2006) (see Author Response to Referee 2).

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

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