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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ship-based detection of glyoxal over the remote tropical Pacific Ocean" *by* R. Sinreich et al.

Anonymous Referee #2

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The paper by Sinreich et al. describes measurements of glyoxal (CHOCHO) in the remote Eastern Pacific. Since this study supports recent studies on satellite observations which have shown elevated levels of CHOCHO above water bodies, it is of high relevance for several research topics like VOC oxidation, SOA or CTM. In general, glyoxal observations are quite sparse and this data set has the potential to fill some of the gaps in our knowledge. The study comprises three major sections: 1) the description of the instrument itself, the analysis and the data filtering (sections 2 to 6, I would prefer to have subsections 2.1 to 2.5). 2) The description of the retrieved data (section 7). 3) The detailed discussion of possible sources for the observed glyoxal amounts (section 8). In general the paper is an interesting and scientific important piece of work and merits publication in ACP. The introduction as well as the discussion section are well written and reflect (with some minor exceptions) the current knowledge. However, I

have some serious concerns about the presentation of the data and its interpretation. These concerns are explained below.

First of all, I agree with referee #1 that the authors should avoid to claim that they did direct observations of glyoxal. They are describing remote-sensing data in the UV/Vis and that's never direct. Furthermore one should avoid terms like "inherently calibrated" or "unequivocally identifies" (p15079) to characterise the DOAS technique. If this would be the case the interpretation of DOAS data would be much easier. In particular for small absorbers there is always the risk that radiation processes not proper accounted for, induce false signals.

The spectral "proof" for the detection is given in Figure1. The authors have calculated a RMS of the residual of about 3.7e-4 which is 4 times smaller than the signal of glyoxal shown here. However, I prefer to define the residual as peak-to-peak and in this case this would lead to the same number as the glyoxal signal (1.5e-3). In fact only the main band of the glyoxal absorption cross section close to 455 nm is visible in the residual. In general the residual seems to have several systematic features. How does the residual looks like, when more than 30s are integrated? Just to clarify: I'm not challenging the detection of glyoxal in general but I'm really sceptical about the very optimistic assumptions in section 7 leading finally to 30% total error for the calculated VMR including the fitting error!

Figure 2: Here DSCDs for CHOCHO (2a) and O4 (2b) are shown for one single week only, from a total of ten weeks. What is the reason that only this week is shown? If there is a good reason, it would be helpful for the reader if the authors could stretch the x-axis in order to be able to identify more details. The diurnal variation of the glyoxal looks a bit strange. It is always u-shape for this week, independent of cloud coverage having highest values close to sunrise and sunset. This cannot be explained with changes in radiative transfer. In fact O4 shows a completely different behaviour. Could the authors comment on that? Is it possible to calculate mean diurnal variations for cloud/non-cloud scenarios for the whole data set? This information would be also

helpful for the discussion of possible sources of the glyoxal.

Values measured with an elevation angle of 25° should be a good proxy for the total vertical column of the trace gas, independent of the aerosol content in the atmosphere (dAMF $\sim$ 1). This has been shown by several other studies. For O4 this is the case (Figure 2b), but for CHOCHO (Fig 2a) in particular those values measured under clear sky conditions, are very close to zero and not in the range of a few 10e14 molec/cm2 as expected. Again, this is difficult to explain with changes in the light path. Comments?

The authors explain in detail the overlapping of DSCDs for different (but small) elevation angles. They are right that this is most probably due to aerosol extinction. But this is well-known and discussed in detail by many other studies (before Volkamer 2009b). But there is another possible explanation: the profile shape. If the trace gas layer is located a bit higher up in the troposphere or even in the boundary layer it leads to an overturning point for the DSCD similar to the aerosol effect. For that reason most state-of-the-art retrievals for MAXDOAS use as much information as possible (e.g. DSCDs for several elevation angles) to retrieve the trace gas information. It is not really clear for me, why the authors did not try to benefit from all their different observation modes.

Discussion: Since it is much simpler to retrieve tropospheric vertical columns instead of VMR from MAXDOAS observations, I would expect at least a simple comparison of MAXDOAS CHOCHO columns with satellite results. These results have originally triggered this study, or not? In contrast to the authors opinion most of the satellite retrievals are quite consistent (even those just published in ACPD for GOME2). The only exception might be the OMI data set, but this has never published.

Minor point: Instrumentation: For the correction of the pointing inclinometers are used. For which time period the standard deviation is calculated?

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