

Comment to “On the relative absorption strengths of water vapour in the blue wavelength range” by J. Lampel et al., *Atmos. Meas. Tech. Discuss.*, 8, 5895–5936, 2015

By Rainer Volkamer and Theodore Koenig

In the introduction the authors reference the importance of water vapor absorption to the DOAS retrieval of glyoxal. Citing Sinreich et al., 2010 they note that the optical density of water in the glyoxal DOAS fitting window is over ten times that of glyoxal itself. This point is well taken (under moist conditions typical of the boundary layer), however, the significance must be evaluated carefully in the context of whether water and glyoxal exhibit spectral cross-correlations such that this is relevant. The authors leave this question open asking whether the water absorption features are "potentially introducing cross-sensitivities". Again in Section 5, when discussing absorption band W4, the authors state it "could interfere with measurements of glyoxal". However, there is no mentioning of the fact that this matter has been the subject of targeted investigations as part of recent instrument inter-comparison exercises (Thalman et al., 2015; Volkamer et al., 2015). These and other findings (see below) inform the discussion about the relevance of H<sub>2</sub>O line parameters, and the related uncertainty for DOAS retrievals of glyoxal and IO (currently missing!) in unique ways, and need to be discussed.

Specifically, Thalman et al. (2015) present results from a comprehensive comparison of glyoxal, methyl glyoxal and NO<sub>2</sub> measurement techniques under simulated conditions. Nine instruments, and seven different measurement techniques were compared: broadband cavity enhanced absorption spectroscopy (BBCEAS), cavity-enhanced differential optical absorption spectroscopy (CE-DOAS), white-cell DOAS (W-DOAS), Fourier transform infrared spectroscopy (FTIR, two separate instruments), laser-induced phosphorescence (LIP), solid-phase micro extraction (SPME), and proton transfer reaction mass spectrometry (PTR-ToF-MS). Section 4.5 is dedicated to “Interference from H<sub>2</sub>O”, and states: “There is no obvious systematic behavior [...] that would suggest a specific H<sub>2</sub>O effect. The magnitude of intercepts was generally smaller than the LOD (compare Table 4), and the quality of correlations ( $0.80 < R^2 < 0.94$ ) did not show an obvious dependence on gas-phase H<sub>2</sub>O.” The text goes on to conclude “... that better knowledge of the water absorption cross sections at blue wavelengths is needed to eliminate residual absorption effects due to water’s bands. This has potential to help further improve the detection sensitivity by absorption techniques, and eliminate small potential for bias at ambient glyoxal concentrations”. In other words, no significant bias was observable, indicating that the residuals caused by missing H<sub>2</sub>O lines do not cross-correlate with glyoxal (bias smaller LOD = 15 pptv here for CE-DOAS, see Table 4).

Furthermore, Volkamer et al. (2015) show an inter comparison of glyoxal in the remote marine boundary layer. They compare the glyoxal measured by CE-DOAS (Coburn et al., 2014) with Ship MAX-DOAS (similar instrument to Sinreich et al., 2010) and Airborne MAX-DOAS at lower glyoxal (~ 35 pptv). The in situ and remote sensing instruments agree within small error bars when near surface concentrations are compared (Table 5, Fig. 8). Significant differences are however observed in the columns. When the Thalman et al. findings are scaled to the specific humidity conditions of this case study, the uncertainty due to possible bias from H<sub>2</sub>O lines can explain ~5 pptv uncertainty in the glyoxal concentration (Volkamer et al., 2015). This is consistent with the error of the CE-DOAS instrument used in this study (Coburn et al., 2014; see Table 5 in Volkamer et al., 2015). This evidence for small bias should be acknowledged.

Remote sensing techniques (as in situ CE-DOAS) suffer from similar spectral interferences of missing H<sub>2</sub>O lines. The combination of the results from Thalman et al. and Volkamer et al. suggests a small bias for glyoxal retrievals. Based on the available evidence, water absorption at blue wavelengths can be expected to impact the precision of current DOAS retrievals of glyoxal, but systematic studies under controlled conditions and in the real atmosphere have shown no evidence for such bias even at moderately high specific humidity. This should be made explicit.

The conclusion that "For the retrieval of glyoxal with its main spectral absorption features above 440 nm, a wavelength window which does not include water vapour absorption at 426 and 416 nm should be preferred when using these water vapour absorption cross-sections" is dubious, and needs to be clarified. In particular, what is the reason to "avoid H<sub>2</sub>O absorption" in light of the lack of evidence for spectral cross correlation? To the contrary, retrievals that avoid water absorption (e.g., at 442nm, see Mahajan et al., 2014) remove very meaningful constraints on H<sub>2</sub>O, AND "avoid" glyoxal absorption features that provide meaningful information to the glyoxal fit. There is no need for such avoidance as these glyoxal absorption features do not show a significant cross-correlation with H<sub>2</sub>O spectral features (Thalman et al., 2015). Avoiding H<sub>2</sub>O lines thus has the primary effect to increase the uncertainty due to missing H<sub>2</sub>O lines in spectral databases (see SI text of Volkamer et al., 2015 for further discussion). The claim made here is not supported by the available literature. It could be removed without loss to the objective to inform about H<sub>2</sub>O line parameters. However, a discussion along the above lines seems timely, and could also be added.

Furthermore, there is really no question about the presence of glyoxal over oceans. The observation that "no glyoxal dSCD is found to exceed  $5 \times 10^{14}$  molec cm<sup>-2</sup>" seems inconsistent with the available literature. The presence of glyoxal is supported from a variety of techniques, as was recently summarized in Volkamer et al. (2015): "Previous studies had measured ~ 80 pptv glyoxal over the Sargasso Sea by DNPH (2,4-Dinitrophenylhydrazine, Brady's reagent) derivatization/mass spectrometry detection (Zhou and Mopper, 1990), 40–80 pptv over the tEPO by SMAX-DOAS (Sinreich et al., 2010), 20–40 pptv during various cruises by SMAX-DOAS (Mahajan et al., 2014),  $32 \pm 6$  pptv (average northern hemispheric tropics) and  $47 \pm 9$  pptv (average southern hemispheric tropics) during the TORERO cruise by LED-CE-DOAS (Coburn et al., 2014), 24 pptv over the Southern Ocean and 7 pptv at Cape Grim by DNPH derivatization/high performance liquid chromatography detection (Lawson et al., 2015)." This fact should be firmly acknowledged. How are the differences explained?

There is essentially no detail given about the (lack of) glyoxal measurements over oceans, and the related retrievals and data interpretation. It should be acknowledged that other factors than H<sub>2</sub>O are at play here. For example, the findings that "more than 50 % of the glyoxal VCD is located above 2 km altitude" (Volkamer et al., 2015), may add to help resolving this. Volkamer et al. note that "Previous SMAX-DOAS measurements likely provide lower limits for the VCD because of uncertainties regarding SCD<sub>REF</sub> (see Table 5)." In fact, the authors note that "The highest glyoxal VMR is observed in the AMAX pro- file at 750 m altitude ( $45 \pm 7$  pptv)." There is no mentioning of this in the paper, and consequently the presented errors are lower limits. How does elevated glyoxal aloft affect the author's interpretation of their data? What is the SCD<sub>REF</sub> in the present study? And what is the effect on the error budget? Can these measurements be reconciled with previous measurements within revised error bars? If so, then why mention about the data at all? If not, assuming this is not an issue with the measurements, what is the evidence that H<sub>2</sub>O spectral parameters are actually at the core of this inconsistency? Clearly there are other factors at play here, and this needs to be acknowledged. The conundrum about the glyoxal

measurements raises questions about the author's measurements/data interpretation but it adds nothing to inform the topic of H<sub>2</sub>O spectral parameters, and their effect on glyoxal measurements.

Volkamer et al. further note that the choice of H<sub>2</sub>O cross section introduced ~ 13 % bias for glyoxal, and ~ 16 % bias for iodine monoxide, IO. There is currently no mentioning of the effect of H<sub>2</sub>O on IO in the present manuscript.

#### References:

Coburn, S., et al., *Atmos. Meas. Tech.* 7, 3579-3595, 2014. doi:10.5194/amt-7-3579-2014.

Lawson S.J., et al., *Atmos. Chem. Phys.* 15, 223–240, 2015. doi:10.5194/acp-15-223-2015.

Mahajan, A.S., et al., *J. Geophys. Res.-Atmos.* 119, 6160–6169, 2014. doi:10.1002/2013JD021388.

Sinreich, R. et al., *Atmos. Meas. Tech.* 10(23), 11359-11371, 2010. doi: 10.5194/acp-10-11359-2010.

Thalman, R. et al., *Atmos. Meas. Tech.* 8, 1835-1862, 2015. doi: 10.5194/amt-8-1835-2015.

Volkamer, R. et al., *Atmos. Meas. Tech.* 8, 2121-2148, 2015. doi:10.5194/amt-8-2121-2015.

Zhou, X. L. and Mopper, K., *Environ. Sci. Technol.* 24, 1864–1869, 1990.