(Numbers of equations, figures, lines and pages refer to the discussion manuscript, if not mentioned otherwise. **Authors' reponses are written in bold face**, the referees' text is shown in normal face.)

1 Referee #1

This paper investigates the consistency of different water vapour absorption cross- sections in the blue wavelength range (394-480 nm) calculated from recent updates of the HITRAN spectroscopic compilation. These investigations are performed through the retrieval of water vapour column density ratios for different spectral interval from Long-path and Multi-Axis DOAS measurements. A significant improvement of the DOAS evaluation is found when using the updated HITRAN data. However, the au- thors also showed that there are still problems with the relative strength of the different absorption bands in the 394-480 nm wavelength interval and their derived correction factors range from 0.5 to 1.9, which is highly significant. I recommend this paper for publication in AMT after addressing the following specific comments:

We would like to thank Referee #1 for the very helpful comments. The comments helped us to improve the manuscript, showed up some missing details and improved the overall manuscript.

1.1 Specific comments:

1. 1/Page 5899, line 24-26 and Page 5900, line 1-3: In both cases, I would add a sentence about the general objectives of these SOPRAN and HaloCaVe campaigns.

   We added a sentence describing the general objectives of the SOPRAN M91 and the HaloCaVe (which was also conducted within SOPRAN, the german branch of SOLAS) campaign.

2. 2/Page 5902, lines 8-10: I would add the list of elevation angles used by the MAX-DOAS instrument during this campaign.

   A list of elevation angles was added to the revised manuscript.

3. 3/Page 5904, lines 13-19: The authors should better justify their choice for the water vapour and aerosol profiles used for the radiative transfer calculations. Are these profiles representative of the conditions encountered during the campaign ? Why using constant profiles for the whole campaign period ?

   See below.

4. 4/Page 5904, lines 20-21: It is said that *The magnitude of the resulting water vapour dSCD obtained from the model agreed with the MAX-DOAS observations*. I find this sentence very vague. Is it valid for all elevation angles ? A figure showing the level of agreement between measured and calculated water vapour dSCD would help the reader.

   (Answer to 3+4) These simulations do not aim at obtaining concentration profiles and/or aerosol profiles, but they were used to estimate the effect, which differences in wavelength might have on the observed column densities. As the obtained corrections are significantly smaller ($\leq 7\%$) than the

observed differences in the relative absorption strengths of the water vapour absorption bands, an explicit inversion for each elevation angle sequence is not necessary. Also the correlation shown in the manuscript for W3 and W1 shows clearly the difference between observed and modelled absorptions, independent of the viewing geometry or possible influences of varying aerosol or water vapour concentration height profiles.

For the water vapour profile shape we already citet [Bleisch and Kampfer, 2012] and now we added [Wagner et al., 2013], who found scale heights around 2 km for the water vapour profile. The absolute humidity of air close to the sea surface was between 1.6-2.4% according to the meteorological data recorded onboard the research vessel. The AOD for the simulations was determined by using an inversion model for the O_4 dSCD. This is however not within the scope of this publication and will be addressed in future publications. The AOD is within the range of the values observed on R.V. Meteor during M77 in 2008 in the same region listed in the AERONET MAN database by [Smirnov et al., 2009], we added this as a reference. A change of the AOD to 0.1 or 0.3 did not significantly affect the simulation results. As now also published in [Fuhlbrügge et al., 2015], the relative humidity within the lowest-most kilometre is relatively constant (as is the virtual temperature). This is also the height of maximum sensitivity for MAX-DOAS observations and leads according to the Clausius-Clapeyron equation approximately to a scale height of 2km ([Wagner et al., 2013]). The impact of the exact shape of the water vapour concentration profile above 1 or even 2 km is typically negligible for the low elevation angles used here in the data analysis. A further indication, that the assumed water vapour concentration profile and the aerosol extinction profile are indeed sufficiently well representing the measurement circumstances is the fact that the correction improves the agreement of the MAX-DOAS and LP-DOAS data set.

5. 5/Page 5906-7, Section 4.1: Since there are a lot of Tables in the manuscript, maybe a figure could illustrate the comparison results between water vapour mixing ratios from LP-DOAS and meteorological stations.

   We added a corresponding graph to the revised manuscript: Figure 1

6. 6/Page 5908, lines 21-25: The water vapour absorptions appear to be present in the measurement data when using the Thalman and Volkamer O4 cross sections. Does it mean that the water vapour absorptions are less or not present when using other O4 cross sections like for instance Hermans et al. and Greenblatt et al. ? I think this point should be discussed in more detail.

   As this absorption structure seems to be present for all three available O_4 literature cross-sections, we re-phrased this statement to read: *Independent of the employed literature O_4 cross-section in our DOAS evaluation, the suspected water vapour absorption appear to be present in our measurement data, but the instability of the fit with respect to the used fit interval and large residual structures close to the possible water absorption indicate that there is still a significant mismatch between measurement and modeled absorption lines.*
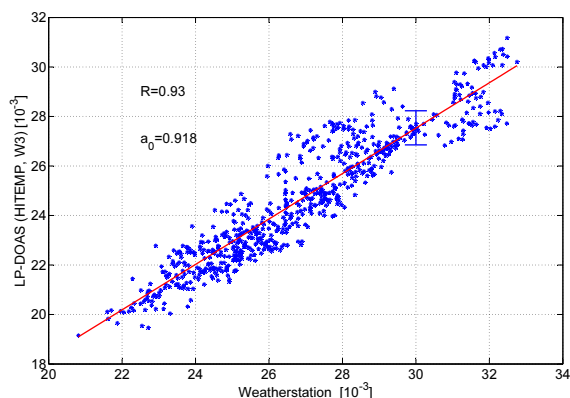
Figure 1: Comparison of LP-DOAS water vapour concentration with data from meteorological station on CVAO. At 0.03 the error bar shows the mean measurement error of the LP-DOAS measurements, estimated by twice the DOAS fit error. The standard deviation of the residual of the linear fit are 2.5 times as large as the fit error.

1.2 Technical corrections:

1. 1/page 5899, line 17: To be consistent with the other molecules, I would replace Formaldehyde by HCHO

   Formaldehyde was replaced by HCHO.

2. 2/Page 5900, line 1: Longpath should be replaced by Long-path. Should be also corrected at other places in the manuscript.

   Throughout the manuscript we use now 'Long-path'.

3. 3/Page 5911, line 20: given by 3 should be replaced by given Eq. (3)

   This is corrected.

2 Referee #2

Received and published: 18 August 2015

This paper investigates the effect of various water cross-sections on DOAS fitting at blue wavelengths. Cross-sections reflecting revisions to the HITRAN dataset are found to yield significantly improved DOAS fitting using both Long-Path and Multi-Axis instruments. The results further indicate that adjusting the relative strengths of different bands leads to even better agreement. The derived correction factors range from 0.5- 1.9 relative to the strongest band, suggesting changes to the cross-sections are large. I recommend the paper for publication, once the following comments are addressed:

We would like to thank Referee #2 for the very helpful comments and suggestions, which improved a lot the interpretation of the results presented in the manuscript.

2.1 Technical questions and major comments

1. 1) In the introduction, the authors address the fact that the weak water absorption features in the HITRAN and HITEMP databases are often based solely on theory, or on a limited number of validations at specific wavelengths. Where experimental data is available, it is sometimes used to scale bands whose shape is specified by theory, or else to adjust band positions. The former is similar to the method used by the authors to scale bands in the paper. While the latter relates to shape effects the paper addresses more obliquely. A comparison of the scaling factors arrived at in this paper with those used to generate the HITRAN and HITEMP cross-sections should be included. Since both BT2 and HITEMP are being considered and evaluated, the adjustments suggested by this paper should be put in this context.

   We are not aware of a publication explicitly listing the intensities of absorption lines used for one of the HITRAN/HITEMP line lists side by side with ab-initio line lists like BT2. A comparison of individual absorption lines from BT2 and experimental data from a larger wavelength interval (9250-26 000 cm^1) are shown in Fig. 2 of [Tolchenov et al., 2005] and shows also ratios of observed and calculated absorption lines from 0.2 to more than 2, especially for small intensities around 10^{-27} cm molec^{-1}. In HITEMP e.g. due to ambiguities in quantum assignments ([Rothman et al., 2010]) the energy of a certain absorption line from BT2 to be replaced by a measured intensity needs to be in agreement within a certain acceptable range. We did not try to reconstruct the HITEMP line list in order to compare the intensities of absorption lines in BT2 which were replaced by laboratory measurements. These replacements are done line-by-line, we are not aware of corrections of intensities of complete absorption bands of water vapour in the blue wavelength range.

   We added the number of absorption lines with intensities above 10^{-27} cm molec^{-1} at room temperature for the combined intervals W1 and W2: HITRAN2009: 20, HITEMP: 382 and BT2: 382. No systematic deviation of the absorption lines in HITEMP2009 and HITEMP is observed, but their ratios (BT2/HITEMP) are found between 0.5 and 3. HITRAN 2009 was used for the creation the HITEMP line list and is only based on observations. A comparison with HITRAN2009 absorption lines was not directly possible as at least half of the absorption lines within W1+W2 could not directly be associated with absorption lines listed in HITEMP or BT2.

2. 2) In Figure 1, the absorption spectrum shown is convoluted to an instrument function, however, the line indicating the "single line cutoff in HITEMP" is shown as it would apply to an unconvoluted line. This is potentially misleading. A line showing the maximum peak absorption of an isolated line convoluted to the instrument function would more accurately show which features HITEMP resolves.

   This is true, indeed, actually the unit of the cutoff is wrong in this plot. The actual cutoff depends on the number of absorption lines within the spectral resolution of 0.5 nm, therefore we removed the line in the revised manuscript. Figure 3
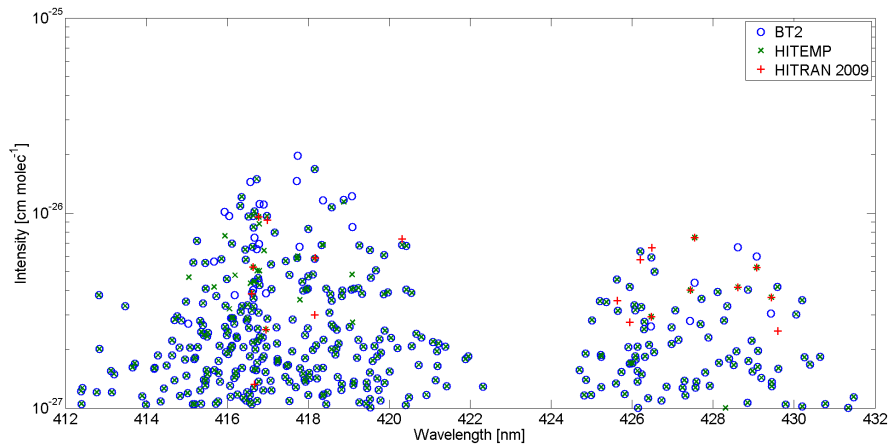
Figure 2: Line intensities for HITRAN 2009, HITEMP and BT2 for the intervals W1 and W2 with intensities above $10^{-27}\,\mathrm{cm\,molec^{-1}}$. HITRAN lists 20 lines, both other line lists 382.
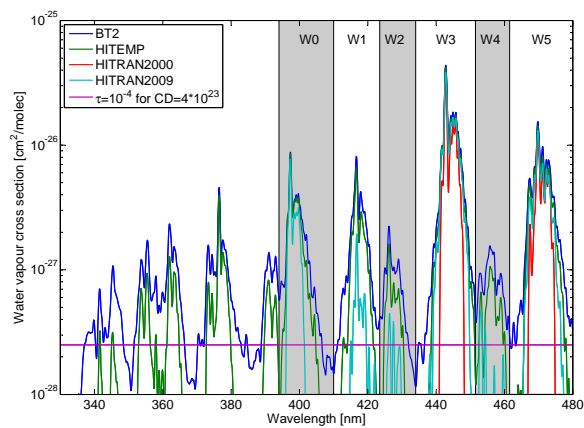

Figure 3: Updated overview figure

As in the UV below 380 nm there are no experimental validation measurements used in HITEMP, the difference between BT2 and HITEMP can be used in order to estimate the actual effect of the line cut-off. This typically amounts to more than 1×10^{-4} and up to 4×10^{-4} below 400 nm for a dSCD of 4×10^{23} molec cm^{-2}. We added this to the UV section of the manuscript (4.3).

3. 3) Some DOAS terms are referred to by redundant abbreviations, e.g. "S" = "SCD", "/delta S" = "dSCD". The former are generally found in equations while the latter dominate in the text. A single standard method of referring to these would increase clarity.

   We used in equations 'S', while we keep SCD in the text. Our use of S vs. SCD follows a (as we think) simple logic: SCD stands wherever we would write "slant column density" in the text, while S is the symbol for SCD when used in a formula or with direct relationship in the text. We think it is much better practice (in fact the overwhelming majority of publications follows this practice) using a single letter (e.g. S) in a formula instead of a strings of letters (e.g. SCD) since the latter could be confused with a product S*C*D.

4. 4) When discussing the vibrational Raman effects on the MAX-DOAS retrieval, N2 and O2 are mentioned, what of water vapor? Liquid water water is mentioned in section 4.3.1, why not here?

   The apparent optical density due to vibrational Raman scattering (VRS) of water vapour for typical volume mixing ratios is expected to result in an OD which is smaller than the OD of typical residual spectra, as discussed in [Lampel et al., 2015], where an upper limit of 5×10^{-5} is given. The absolute cross-section of VRS of water vapour is even 5-10 times larger than the ones of N_2 and O_2, however, as the mixing ratios of the order of several percent, the absolute effect is smaller than VRS of N_2 and O_2 which amounts to several 10^{-4} in the blue wavelength range. Also the scale height of water vapour is about 1/4 of the scale height of air. The spectral shift due to VRS of water vapour will lead an intensity offset and differential structures, which are largest in the region of the remapped Ca-Lines (393 and 396nm), which should appear at 459 and 463 nm ([Penney and Lapp, 1976, Murphy, 1978, Rizi et al., 2004]). Water vapour absorption listed in HITEMP and BT2 in W4 are at least 3 times larger than the possible contribution of VRS of water vapour. We added this estimate to the revised manuscript. We added the result for liquid water VRS to this paragraph.

5. 5) Page 5906, lines 18-20. After establishing an upper limit of 30ppt for glyoxal, its cross-section is removed from the analysis. Is this necessary? What is the effect of retaining the glyoxal cross-section in subsequent fits? Even if the trace gas optical depth is insignificant, it can still exert effects of interference and contribute to the residual.

   We included glyoxal once in the results of the analysis of the MAX-DOAS results in Table 5 in order to estimate the effect glyoxal could have on the

spectral retrieval, even though we did not observe it in significant amounts. The LP-DOAS measurements during HaloCaVe typically show larger residuals than the MAX-DOAS observations, which is why the effect of glyoxal included in the fit settings was only investigated for the MAX-DOAS observations.

6. 6) Page 5908, lines 13-25. The discrepancies between BT2 and HITEMP may also stem in part from corrections applied to obtain the latter from the former, see comment 1. I am confused as to what precisely the authors are saying here. What is the result when using other O4 cross-sections? There is fit instability, but with respect to what parameters? Residuals are large, but are the systematic in a way that suggests differences specifically as regards the water cross-section?

   In the HITEMP processing described in [Rothman et al., 2010] for water vapour absorption lines, the BT2 data was used as a starting point and basically copied (for states with $J \leq 50$), as there are no validation measurements below 390 nm available and no entries in HITRAN 2009 in this spectral range can be found. Afterwards the line-cutoff was applied. Therefore the line-cutoff is here the main reason for the discrepancy between the absorption listed in HITEMP and BT2 below 390 nm. The reduction was necessary, as the size of the BT2 line list restricted to $J \leq 50$ amounts to about 90GB in the HITRAN2004 format, which is not useful for most purposes. We took the BT2 line list and removed all lines with an intensity below the cutoff at room temperature - the resulting line list was below 370 nm identical to the HITEMP line list, above 370 nm differences started to appear, partly due to available experimental data (from HITRAN2009), partly due to the temperature dependence of the line intensities which we ignored, we calculated the cutoff at room temperature.

   The residual structures are independent of the used O_4 cross-section. As an example we used the [Thalman and Volkamer, 2013] cross-section, but the systematic residual structures were observed for all available O_4 absorption cross-sections. This now stated more clearly. Furthermore the fit was unstable with respect to the fit range, which is now added to the revised manuscript. As stated in p5908 line 3, the residual structures are systematic and elevation angle angle dependent, which suggests that these are caused by a tropospheric absorber. As stated in p5908 line 11-12, it was not possible to disentangle variations of H_2O and O_4 or other tropospheric absorbers due to the limited absolute water vapour content variation during the M91 cruise. This problem will be addressed in the future based on a MAX-DOAS data set covering a larger range of latitudes.

7. 7) The results show that the bands W0, W3, and W5 consistently scale relative to each other by factors not statistically different from 1. These represent bands from 3 different vibrational transitions. In contrast, the results within the 7v and 7v+d bands have significant relative scaling. This could be coincidence, or as the authors state in the discussion (Page 5913, lines 16-20) it could reflect the challenges of modeling intensities for these lines in models. Specifically it could indicate that the relative transition probability of different vibrational modes is not properly captured. The authors note

in particular that transitions involving the bending mode are especially troublesome. Meanwhile, discussion of the individual bands indicates that band-shape in particular has improved with the revision of HITRAN. The spectral databases include transition assignment, and partition function information. Discussion of the above hypothesis would be greatly improved if the authors comment on whether the latter observations regarding line shape are consistent? Do remaining residuals correspond to bending mode transitions? How do residuals scale within the polyad as the same dipole moments are leveraged by different state degeneracy?

(W3 is equal to one by definition, as we cannot measure these absorptions absolutely.) It is difficult to draw conclusions from the actual residuals, as all of these measurements were done in the field, and therefore other absorbers are present, which need to be compensated for and which might indeed compensate for residual structures from other absorbers as well. Therefore a relative 'correction' of the water vapour cross-section for the given spectral resolution is not possible and broader wavelength windows need to be analysed, as is done here.

The approach to look at different spectral intervals of the water vapour cross-section might have been not the best in order to quantify deviations related to the actual physical properties of the the respective absorption, but it was the way in which these were first observed at all and it provides information which is easily applicable to DOAS applications. We agree, that an approach based on underlying physical quantities could be more helpful to identify the reasons for these observations.

For example the W0 absorption is not purely 8ν (We now changed 'polyad' in Table 1,5,8 to 'dominating polyad'), but contains on its red flank also some $7\nu + \delta$ absorptions. As the $7\nu + \delta$ absorptions seem to be overestimated, this could have led to the apparent overestimation of the OD at around 402 nm as seen in Figure 2. Also in the W3 interval, which is dominated by the 7ν absorptions, also $6\nu + \delta$ absorptions are found. Therefore it could have been better to create cross-sections for each of the values of the respective quantum numbers and determine their relative strength. However, further investigations would be needed in order to clarify which of these could be useful to generate separated cross-sections. It is unclear if it would be $n = v_1 + v_2/2 + v_3$ (Def. from [Tennyson et al., 2001], probably motivated by absorption at longer wavelengths, were different polyads do not overlap?) or one of the v_i individually, or something completely different.

To clarify this, we separated the HITEMP database into bend modes and also into different polyads (compare Figure 4), $n\nu$ and $n\nu + \delta$ and fitted them separately to the MAX-DOAS data ($\nu_2 = 0 - 4$; n=$6\nu + \delta$,7ν,$7\nu + \delta$,8ν). These different separations did not result in improved residual spectra compared to the separation according to wavelengths. It shows however, that especially the absorptions with larger ν_2 seem to be overestimated in HITEMP (and thus also in BT2).

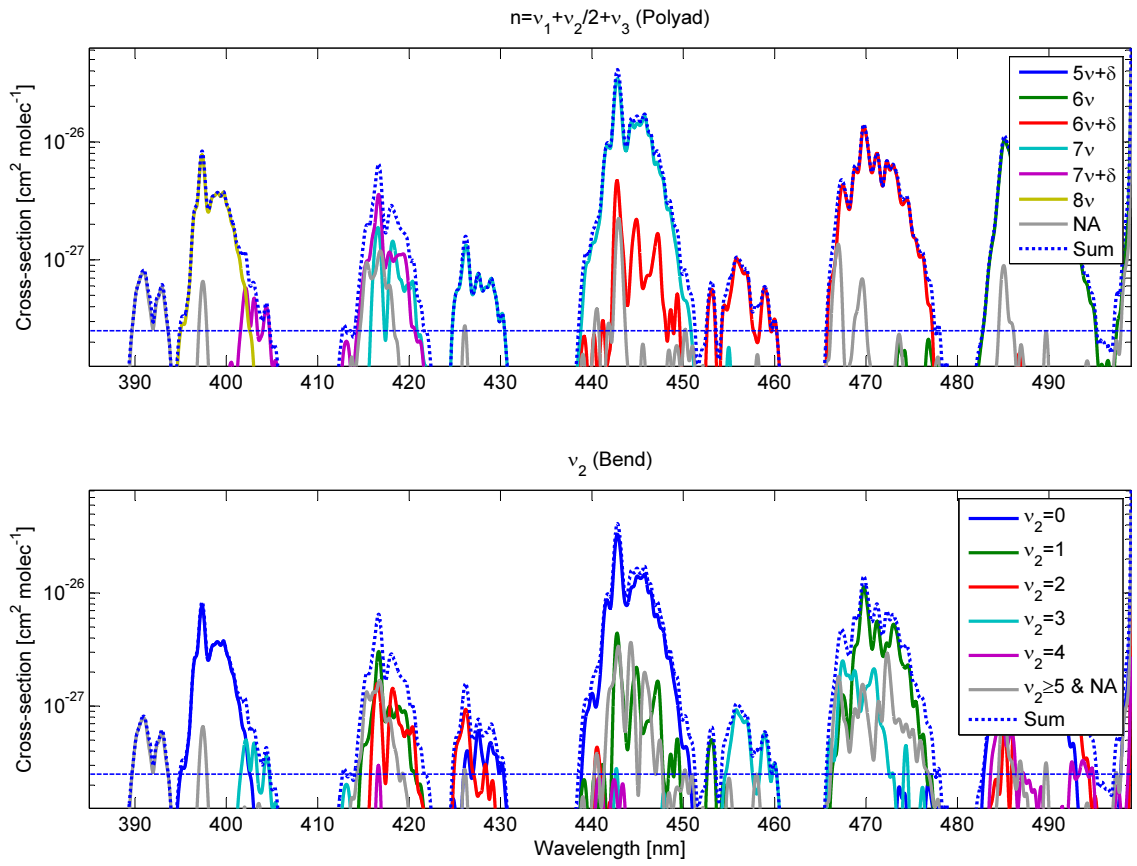**We added these observations as an additional subsection to the manuscript.**

Figure 4: Separation of HITEMP water vapour absorption lines according to polyad number and ν_2. Not assigned ('NA') are lines which are listed as $(\nu_1, \nu_2, \nu_3) = (-2, -2, -2)$ in HITEMP.

Table 1: Relative absorption strengths as listed above for the separated H_2O absorption cross-section according to the respective polyad shown in Figure 4. Below the same procedure was appplied to the HITEMP line list separated by values of the bend mode ν_2. As above the fit error is given in % at a dSCD of $4 \times 10^{23}\,\mathrm{molec\,cm^{-2}}$ of the 7ν and $\nu = 0$ absorptions, respectively. As the wavelength ranges are not as well defined as before, no corrections by the results of radiative transfer modelling listed in Table **??** were done.

Polyad	8ν	$7\nu + \delta$	7ν	$6\nu + \delta$	'NA'	
HITEMP	0.977(1)	0.283(1)	1	0.791(2)	1.045(2)	
Fit error [%]	5	19	1	8	10	
ν_2	0	1	2	3	4	≥ 5 and 'NA'
HITEMP	1	0.583(2)	0.427(3)	0.306(4)	[0.675(2)]	0.799(2)
Fit error [%]	0.6	6	12	23	42	35

2.2 Grammatical and minor technical corrections

1. 1) Page 5896, line 13. Change "from 0.5 and 1.9" to "from 0.5 to 1.9".

   This is changed.

2. 2) Page 5896, lines 21-22. Resolve number disagreement in "absorptions also needs"

   This is ressolved.

3. 3) Page 5897, line 10. Change "extend" to "extent"

   This is changed.

4. 4) Page 5897, line 21. Change "determining" to "determination"

   This is changed.

5. 5) Page 5898, line 8. Specify "Iodine monoxide" rather that "iodine oxide", this is inconsistent.

   This is changed.

6. 6) Page 5901, line 2. Change "also cross-sections can be subdivided" to "crosssections can also be subdivided"

   This is changed.

7. 7) Page 5901, line 11. Change "Each elevation" to "Each elevation angle". A list of elevation angles would be helpful to understanding which are considered "low".

   This is changed. A list of elevation angles is now included in the instrument description of the revised manuscript.

8. 8) Page 5902, lines 6-7. Change "largely cancel out" to "largely canceling out".

   This has been changed to '... stratospheric absorbers are largely cancelling out ...'.

9. 9) Page 5908, line 6. Change "currently no considered" to "currently not considered"

   This is changed.

10. 10) Page 5909, lines 1-2. Change "are exceeding" to "exceed"

    This is changed.

11. 11) Page 5913, line 26. Change "by 60 +- 10% too high" to "too high by 60 +- 10

    This is changed.

12. 12) Page 5914, line 9. Change "BT2 even by" to "BT2 by even"

    This is changed.

13. 13) Page 5914, lines 22-23. Which specific observations of glyoxal are being referred to? A citation may be helpful.

    We cite now [Mahajan et al., 2014] and estimate the resulting ODs: $dSCD_{Glyoxal} = 1 \times 10^{15}$ m corresponds to 6×10^{-4} at 455 nm, $dSCD_{H_2O} = 4 \times 10^{23}$ molec cm^{-2} to 4×10^{-4} for HITEMP at 456 nm.

14. 14) Page 5914, line 25. Change "can be also seen" to "can also be seen"

    This is changed.

15. 15) Page 5915, line 13. Change "argumentation" to "argument"

    This is changed.

3 Referees #3: R. Volkamer and T. Koenig

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, 58955936, 2015 By Rainer Volkamer and Theodore Koenig

We thank Rainer Volkamer and Theodore Koenig for their helpful comments. The comments helped us to improve the manuscript, showed up some missing details and improved the overall manuscript.

Before answering each of the points in detail, we want to mention that the aim of the manuscript is not to discuss glyoxal observations in the marine boundary layer, but rather to address systematic differences between observed water vapour absorption and available literature cross-sections. Glyoxal absorption had to be mentioned though, as they might interfere with water vapour absorption during the measurement campaign, especially as it took place in the eastern Pacific marine boundary layer. We did not intent to discuss glyoxal abundances in the marine boundary layer. We neither wanted to criticize previous MAX-DOAS observations, we just wanted to state that there is indeed the need for precise water vapour absorption cross-sections even for these small absorptions along light path lengths of several kilometre. Examples where it is needed are measurements of absorptions of glyoxal, IO and even NO2 in pristine areas(e.g. [Lee et al., 2010]). The fact that DOAS evaluations are often independent of additional residual structures of similar size is an advantage of the DOAS method, but understanding the differences between observations and measurements will in any case improve detection limits and allow further interpretations. Unaccounted absorptions will lead to different artefacts depending on instrumental properties

and details of the spectral retrieval process, therefore this often cannot be generalized.

1. 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_2O line parameters, and the related uncertainty for DOAS retrievals of glyoxal and IO (currently missing!) in unique ways, and need to be discussed.

2. Specifically, Thalman et al. (2015) present results from a comprehensive comparison of glyoxal, methyl glyoxal and NO2 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_2O, and states: There is no obvious systematic behavior [] that would suggest a specific H_2O 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_2O. 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 waters 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_2O lines do not cross-correlate with glyoxal (bias smaller LOD = 15 pptv here for CE-DOAS, see Table 4).

   (We added an estimation of the impact of the relative scaling on IO dSCDs) This is correct and is mentioned in the revised manuscript. This is only relevant to MAX-DOAS measurements when also considering the following publication, where MAX-DOAS and CE-DOAS yield agreeing glyoxal mixing ratios (including also a measured, glyoxal-free, water vapour absorption reference spectrum from [Sinreich et al., 2010]):

3. 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 H2O 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.

4. Remote sensing techniques (as in situ CE-DOAS) suffer from similar spectral interferences of missing H2O 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.

5. 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 H2O 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 H2O, 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 H2O spectral features (Thalman et al., 2015). Avoiding H2O lines thus has the primary effect to increase the uncertainty due to missing H2O 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 H2O 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 5x1014 molec cm-2 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, Bradys 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 ± 6 pptv (average northern hemispheric tropics) and 47 ± 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?

We observed the discrepancies for the absorptions around 416 and 426nm and therefore suggest not to use fit intervals including those, if including one of the other absorptions. This does not only apply to glyoxal and NO2 as mentioned in the manuscript, but needs to be considered in general. We

reformulated this sentence. The upper limit for LP-DOAS of 30pptv seems to be in agreement with the above mentioned literature. The MAX-DOAS measurements are in a similar concentration range. [Volkamer et al., 2015] and [Thalman et al., 2015] both avoided the spectral range from 420–430 nm, where glyoxal absorption can be found as well.

We do not support the idea that results of active DOAS methods can be directly transferred to passive MAX-DOAS observations. Radiative transfer for DOAS measurements using White-cells or cavity enhanced setups differ and the light sources typically show different spectral structures.

We do not discuss if one should include the large water vapour absorption at around 440nm to determine glyoxal dSCDs. However, there can be reasons to exclude this wavelength interval for MAX-DOAS observations:

(a) Small changes in the instrument slit function relative to the instrument function at a nearby HG emission line can amount to large residual ODs for the water vapour absorption. If the instrument function is determined from a Kurucz fit, the used model function might not fit the actual instrument slit function of the spectrometer. These points are especially valid for compact spectrometers, as also partly used in (Mahajan et al., 2014).

(b) Saturation effect due to changed RT: the effective light path length is modified within the stronger water vapour absorption band which can reach ODs of 0.2 in the blue spectral range for MAX-DOAS observations. This effect is typically not considered in the blue spectral range (or corrected by fitting residual spectra to the data).

(c) Saturation effect due to limited spectral resolution. This is in most publications not iteratively corrected for, but also only amounts to 1e-4 if the correction was done for 4e23 instead of 5e23 for a dSCD of 5e23.

Also for CE-DOAS the shortening of the light path within individual absorption lines result in a shorter lightpath.

Overall, a detection limit of 5e14 is corresponding to surface volume mixing ratios of, depending on the aerosol profile, around 20ppt. We do not see a strong disagreement with most of the above mentioned publications. It might be natural variability, as e.g. also other trace gases are found to be more abundant in the Peruvian upwelling itself (or the area probed during M91), compared to measurements west of 82°W, as e.g. IO (own measurements during M77 and [?]). The bulk of the measurements published in [Sinreich et al., 2010] were not as close to the coast as M91, the measurements by [Volkamer et al., 2015] were done in a different region, even north of the equator, which additionally also shows typically larger SST (sea surface temperature, 27°C according to MODIS) than the data presented here (SST: 14-22°C, e.g. [Fuhlbrügge et al., 2015]).

6. 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 H2O 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 SCDREF (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 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 authors interpretation of their data? What is the SCDREF 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 H2O 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 authors measurements/data interpretation but it adds nothing to inform the topic of H2O spectral parameters, and their effect on glyoxal measurements.

The exact glyoxal fit settings are indeed missing and are added to the revised manuscript. We don't actually care here about VMR, which is why a discussion about RTM of glyoxal concentrations and SCD$_{ref}$ is not found in the manuscript. As we did not find any measurements above the given detection limit, we did not do any RTM for glyoxal. We want to exclude a possible interference. In order to show that we are indeed independent of glyoxal absorption the MAX-DOAS analysis was already done also including the glyoxal XS in the first version of the manuscript and no significant differences for the individual water vapour absorption bands were found.

We added further information about the fit settings used to determine these values. Compared to the MAD-CAT intercomparison campaign we have here a larger spectral range and are not limited at 460 nm for the calculation of the Ring spectrum. Furthermore the result is independent of the used Ring correction spectrum (DOASIS ([Kraus, 2006]) or NDSC Ring by [Chance and Spurr, 1997]). We did furthermore study the dependence of the observed glyoxal dSCDs for the influence of VRS of air ([Lampel et al., 2015]), VRS of liquid water (e.g. [Peters et al., 2014], it caused often negative glyoxal values during other campaigns for measurements under full cloud cover and clear ocean water in the southern Atlantic), the above mentioned RTM effect, different water vapour cross-sections (HITEMP, HITRAN2009, BT2) and three different O$_4$ cross-sections. We did these tests for a fit interval from 432–460 nm. Additionally we tested a subset of these settings with different fit intervals, e.g. 418-460 nm, 448-460 nm and others.

7. Volkamer et al. further note that the choice of H2O cross section introduced 13% bias for glyoxal, and 16% bias for iodine monoxide, IO. There is currently no mentioning of the effect of H2O on IO in the present manuscript.

We added an estimate for the effect on IO, which is however small ($\leq 1 \times 10^{12}$ molec cm^{-2}), if the large absorption band at W3 is not included, as

it is often the case (e.g.[Großmann et al., 2013, Prados-Roman et al., 2015, Volkamer et al., 2015]). Most publications also avoid the main part of the W1 absorption band. The underestimation of the water vapour absorption by HITRAN2009 in W1 and W2 led however to unrealistic water vapour dSCDs in the IO fit range (pers. comm. K. Großmann, [Großmann et al., 2013]), which led to discussions about the validity of the IO measurements.

The upper limit for glyoxal is furthermore in agreement with MAX-DOAS measurements using the same instrument (but covering a slightly different wavelength range) during Cruise MSM18/3 on RV Maria S. Merian in the tropical Atlantic (short cruise report: [Körtzinger, 2011]).

8. References **(given in this comment)**:

- Coburn, S., et al., Atmos. Meas. Tech. 7, 3579-3595, 2014. doi:10.5194/amt-7-3579-2014. [Coburn et al., 2014]
- Lawson S.J., et al., Atmos. Chem. Phys. 15, 223240, 2015. doi:10.5194/acp-15-223-2015. [Lawson et al., 2015]
- Mahajan, A.S., et al., J. Geophys. Res.-Atmos. 119, 61606169, 2014. doi:10.1002/2013JD021388. [Mahajan et al., 2014]
- Sinreich, R. et al., Atmos. Meas. Tech. 10(23), 11359-11371, 2010. doi: 10.5194/acp-10-11359-2010. [Sinreich et al., 2010]
- Thalman, R. et al., Atmos. Meas. Tech. 8, 1835-1862, 2015. doi: 10.5194/amt-8-1835-2015. [Thalman et al., 2015]
- Volkamer, R. et al., Atmos. Meas. Tech. 8, 2121-2148, 2015. doi:10.5194/amt-8-2121-2015. [Volkamer et al., 2015]
- Zhou, X. L. and Mopper, K., Environ. Sci. Technol. 24, 18641869, 1990. [Zhou and Mopper, 1990]

References

[Bleisch and Kampfer, 2012] Bleisch, R. and Kampfer, N. (2012). Retrieval of tropospheric water vapour profiles by using spectra from a microwave spectro-radiometer at 22 GHz. In *Microwave Radiometry and Remote Sensing of the Environment (MicroRad), 2012 12th Specialist Meeting on*, pages 1–3. IEEE.

[Chance and Spurr, 1997] Chance, K. and Spurr, R. J. D. (1997). Ring effect studies; Rayleigh scattering, including molecular parameters for rotational Raman scattering and the Fraunhofer spectrum. *Appl. Opt.*, 36:5224–5230.

[Coburn et al., 2014] Coburn, S., Ortega, I., Thalman, R., Blomquist, B., Fairall, C. W., and Volkamer, R. (2014). Measurements of diurnal variations and eddy covariance (ec) fluxes of glyoxal in the tropical marine boundary layer: description of the fast led-ce-doas instrument. *Atmospheric Measurement Techniques*, 7(10):3579–3595.

[Fuhlbrügge et al., 2015] Fuhlbrügge, S., Quack, B., Atlas, E., Fiehn, A., Hepach, H., and Krüger, K. (2015). Meteorological constraints on oceanic halocarbons above the peruvian upwelling. *Atmospheric Chemistry and Physics Discussions*, 15(14):20597–20628.

[Großmann et al., 2013] Großmann, K., Frieß, U., Peters, E., Wittrock, F., Lampel, J., Yilmaz, S., Tschritter, J., Sommariva, R., von Glasow, R., Quack, B., Krüger, K., Pfeilsticker, K., and Platt, U. (2013). Iodine monoxide in the western pacific marine boundary layer. *Atmospheric Chemistry and Physics*, 13(6):3363–3378.

[Körtzinger, 2011] Körtzinger, A. (2011). Short cruise report rv maria s. merian cruise msm18-3.

[Kraus, 2006] Kraus, S. (2006). *DOASIS - A Framework Design for DOAS*. Dissertation, Heidelberg University.

[Lampel et al., 2015] Lampel, J., Frieß, U., and Platt, U. (2015). The impact of vibrational raman scattering of air on doas measurements of atmospheric trace gases. *Atmospheric Measurement Techniques Discussions*, 8(3):3423–3469.

[Lawson et al., 2015] Lawson, S. J., Selleck, P. W., Galbally, I. E., Keywood, M. D., Harvey, M. J., Lerot, C., Helmig, D., and Ristovski, Z. (2015). Seasonal in situ observations of glyoxal and methyl-glyoxal over the temperate oceans of the southern hemisphere. *Atmospheric Chemistry and Physics*, 15(1):223–240.

[Lee et al., 2010] Lee, J. D., McFiggans, G., Allan, J. D., Baker, A. R., Ball, S. M., Benton, A. K., Carpenter, L. J., Commane, R., Finley, B. D., Evans, M., Fuentes, E., Furneaux, K., Goddard, A., Good, N., Hamilton, J. F., Heard, D. E., Herrmann, H., Hollingsworth, A., Hopkins, J. R., Ingham, T., Irwin, M., Jones, C. E., Jones, R. L., Keene, W. C., Lawler, M. J., Lehmann, S., Lewis, A. C., Long, M. S., Mahajan, A., Methven, J., Moller, S. J., Müller, K., Müller, T., Niedermeier, N., O'Doherty, S., Oetjen, H., Plane, J. M. C., Pszenny, A. A. P., Read, K. A., Saiz-Lopez, A., Saltzman, E. S., Sander, R., von Glasow, R., Whalley, L., Wiedensohler, A., and Young, D. (2010). Reactive halogens in the marine boundary layer (RHaMBLe): the tropical north atlantic experiments. *Atmospheric Chemistry and Physics*, 10(3):1031–1055.

[Mahajan et al., 2014] Mahajan, A. S., Prados-Roman, C., Hay, T. D., Lampel, J., Pöhler, D., Großmann, K., Tschritter, J., Frieß, U., Platt, U., Johnston, P., Kreher, K., Wittrock, F., Burrows, J. P., Plane, J. M., and Saiz-Lopez, A. (2014). Glyoxal observations in the global marine boundary layer. *Journal of Geophysical Research: Atmospheres*, 119(10):6160–6169.

[Murphy, 1978] Murphy, W. F. (1978). The rovibrational Raman spectrum of water vapour v1 and v3. *Molecular Physics*, 36(3):727–732.

[Penney and Lapp, 1976] Penney, C. M. and Lapp, M. (1976). Raman-scattering cross sections for water vapor. *J. Opt. Soc. Am.*, 66(5):422–425.

[Peters et al., 2014] Peters, E., Wittrock, F., Richter, A., Alvarado, L. M. A., Rozanov, V. V., and Burrows, J. P. (2014). Liquid water absorption and scattering effects in doas retrievals over oceans. *Atmospheric Measurement Techniques*, 7(12):4203–4221.

[Prados-Roman et al., 2015] Prados-Roman, C., Cuevas, C. A., Hay, T., Fernandez, R. P., Mahajan, A. S., Royer, S.-J., Galí, M., Simó, R., Dachs, J., Großmann, K., Kinnison, D. E., Lamarque, J.-F., and Saiz-Lopez, A. (2015). Iodine oxide in the global marine boundary layer. *Atmospheric Chemistry and Physics*, 15(2):583–593.

[Rizi et al., 2004] Rizi, V., Iarlori, M., Rocci, G., and Visconti, G. (2004). Raman LIDAR observations of cloud liquid water. *Appl. Opt.*, 43(35):6440–6453.

[Rothman et al., 2010] Rothman, L., Gordon, I., Barber, R., Dothe, H., Gamache, R., Goldman, A., Perevalov, V., Tashkun, S., and Tennyson, J. (2010). HITEMP, the high-temperature molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 111(15):2139 – 2150. XVIth Symposium on High Resolution Molecular Spectroscopy (HighRus-2009).

[Sinreich et al., 2010] Sinreich, R., Coburn, S., Dix, B., and Volkamer, R. (2010). Ship-based detection of glyoxal over the remote tropical pacific ocean. *Atmospheric Chemistry and Physics*, 10(23):11359–11371.

[Smirnov et al., 2009] Smirnov, A., Holben, B. N., Slutsker, I., Giles, D. M., McClain, C. R., Eck, T. F., Sakerin, S. M., Macke, A., Croot, P., Zibordi, G., Quinn, P. K., Sciare, J., Kinne, S., Harvey, M., Smyth, T. J., Piketh, S., Zielinski, T., Proshutinsky, A., Goes, J. I., Nelson, N. B., Larouche, P., Radionov, V. F., Goloub, P., Krishna Moorthy, K., Matarrese, R., Robertson, E. J., and Jourdin, F.

(2009). Maritime aerosol network as a component of aerosol robotic network. *Journal of Geophysical Research: Atmospheres*, 114(D6).

[Tennyson et al., 2001] Tennyson, J., Zobov, N. F., Williamson, R., Polyansky, O. L., and Bernath, P. F. (2001). Experimental energy levels of the water molecule. *Journal of Physical and Chemical Reference Data*, 30(3):735–831.

[Thalman et al., 2015] Thalman, R., Baeza-Romero, M. T., Ball, S. M., Borrás, E., Daniels, M. J. S., Goodall, I. C. A., Henry, S. B., Karl, T., Keutsch, F. N., Kim, S., Mak, J., Monks, P. S., Muñoz, A., Orlando, J., Peppe, S., Rickard, A. R., Ródenas, M., Sánchez, P., Seco, R., Su, L., Tyndall, G., Vázquez, M., Vera, T., Waxman, E., and Volkamer, R. (2015). Instrument intercomparison of glyoxal, methyl glyoxal and no$_2$ under simulated atmospheric conditions. *Atmospheric Measurement Techniques*, 8(4):1835–1862.

[Thalman and Volkamer, 2013] Thalman, R. and Volkamer, R. (2013). Temperature dependent absorption cross-sections of O$_2$–O$_2$ collision pairs between 340 and 630 nm and at atmospherically relevant pressure. *Physical Chemistry Chemical Physics*, 15(37):15371–15381.

[Tolchenov et al., 2005] Tolchenov, R. N., Naumenko, O., Zobov, N. F., Shirin, S. V., Polyansky, O. L., Tennyson, J., Carleer, M., Coheur, P.-F., Fally, S., Jenouvrier, A., and Vandaele, A. C. (2005). Water vapour line assignments in the 925026 000 cm-1 frequency range. *Journal of Molecular Spectroscopy*, 233(1):68 – 76.

[Volkamer et al., 2015] Volkamer, R., Baidar, S., Campos, T. L., Coburn, S., DiGangi, J. P., Dix, B., Eloranta, E. W., Koenig, T. K., Morley, B., Ortega, I., Pierce, B. R., Reeves, M., Sinreich, R., Wang, S., Zondlo, M. A., and Romashkin, P. A. (2015). Aircraft measurements of bro, io, glyoxal, no$_2$, h$_2$o, o$_2$o$_2$ and aerosol extinction profiles in the tropics: comparison with aircraft-/ship-based in situ and lidar measurements. *Atmospheric Measurement Techniques*, 8(5):2121–2148.

[Wagner et al., 2013] Wagner, T., Andreae, M. O., Beirle, S., Dörner, S., Mies, K., and Shaiganfar, R. (2013). MAX-DOAS observations of the total atmospheric water vapour column and comparison with independent observations. *Atmospheric Measurement Techniques*, 6(1):131–149.

[Zhou and Mopper, 1990] Zhou, X. and Mopper, K. (1990). Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; implications for air-sea exchange. *Environmental science & technology*, 24(12):1864–1869.