

Answers to Anonymous Referee 2:

The subject of the paper is appropriate to AMT. The paper is well organized. Some improvement of English may be required. The paper contains original material that includes the derivation of the residual liquid water spectrum that mostly contains low-frequency structure of water vibrational Raman scattering (VRS). The use of this spectrum in NO₂ measurements over the ocean with DOAS techniques reduces the DOAS fit residuals as compared with other DOAS techniques. Results of the study can potentially improve DOAS measurements of trace gases over the ocean.

We would like to thank the reviewer for this general positive comment and for the detailed and helpful suggestions.

General comments

1. The authors make use of a pure water absorption spectrum (Pope and Fry, Appl. Opt. 1997) as a reference spectrum for DOAS applied to observations over the ocean. Pure water absorption is not a major absorbing component of seawater in the spectral range of interest (400-500 nm). Phytoplankton pigment (different types of chlorophyll and carotenoids) absorption is substantial in this spectral range – see the following basic references:

A. Morel and S. Maritorena, Bio-optical properties of oceanic waters: A reappraisal, JGR, 106, 7163-7180, 2001.

A. Bricaud et al., Variations of light absorption by suspended particles with chlorophyll concentrations in oceanic (case 1) waters: Analysis and implications for bio-optical models, JGR, 103, 31033-31-044, 1998.

This fact is clearly confirmed by Fig. 1 and 8 which are quite similar to chlorophyll maps derived from SeaWiFS/MODIS observations. These figures make evident that the length of underwater light path is primarily determined by phytoplankton pigment absorption but not by pure water absorption as the authors assume in their study. The H₂Ores spectrum is therefore contaminated by chlorophyll and other phytoplankton pigment absorption spectra. The authors should investigate results of including a chlorophyll absorption spectrum in their DOAS fit.

The referee addresses an important point. However, there might be a misunderstanding as we did not assume that the light path in the ocean is determined by liquid water absorption rather than by chlorophyll.

Our measurements are affected by photons leaving the ocean water, and the smaller the absorption by chlorophyll is, the larger is their contribution to the observed signal. In this sense we are dealing with a problem which occurs where there is little absorption by chlorophyll. Therefore, we are convinced that our work describes an improvement of the compensation of liquid water effects and not of chlorophyll absorption. To clarify things we include here 4 figures:

Fig. B1: This is Fig. 1 from our manuscript describing the fit factor of liquid water absorption if the cross-section is included in a DOAS fit from space

Fig. B2: This plot is taken from Bracher et al. 2009 (see reference below) who included the cross-section of diatoms in a DOAS fit. The SeaWiFS products look in principle similar.

“Bracher, A., Vountas, M., Dinter, T., Burrows, J. P., Röttgers, R., and Peeken, I.: Quantitative observation of cyanobacteria and diatoms from space using PhytoDOAS on SCIAMACHY data, Biogeosciences, 6, 751–764, doi:10.5194/bg-6-751-2009, 2009.”

Fig. B3: RMS of Fit1, i.e. if not compensating liquid water (August 2007 average)

Fig. B4: RMS of Fit3, i.e. if compensating for liquid water (August 2007 average)

Comparing Figs. B1 and B2 shows that the amount of liquid water absorption is always large where chlorophyll is not present (or only in small amounts). The reason is of course that – if chlorophyll is present – it dominates the color of water and reduces the average light path length under water. We only mentioned this shortly in the manuscript, which we change in the revised version.

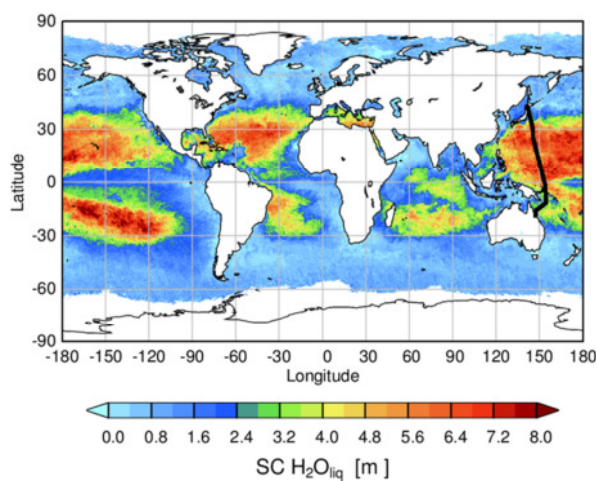


Fig. B1: Liquid water absorption (Fig. 1 from our study)

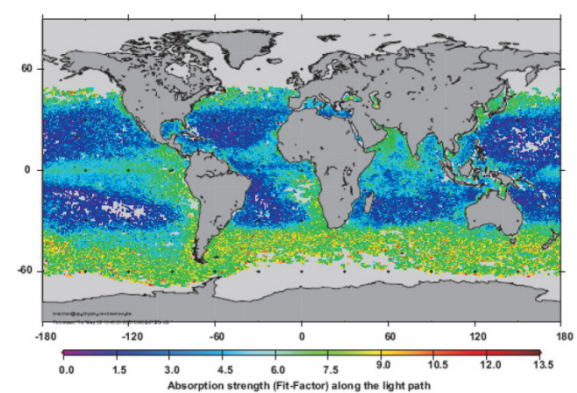


Fig. B2: Picture taken from Bracher et al. (2009): Diatom fit factor from PhytoDOAS fit

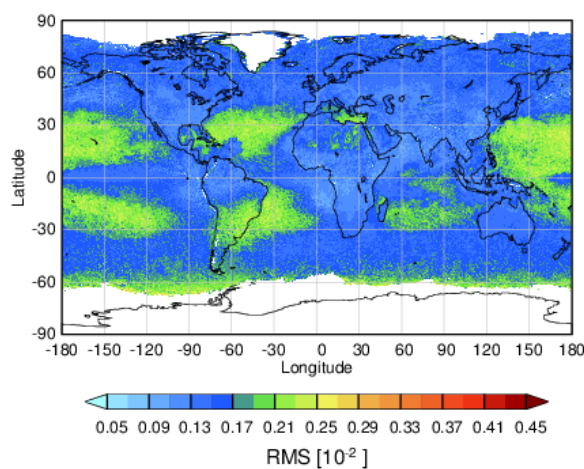


Fig.B3: RMS in Fit1 (without liquid water)

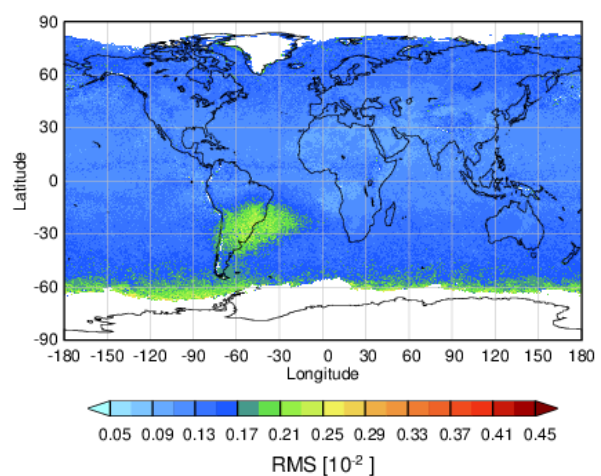


Fig. B4: RMS in Fit3 (with liquid water and H_2O_{res})

The cruise track indicated in Fig. B1 shows that the TransBrom campaign was carried out almost entirely in a region of very clear water and low chlorophyll concentration (with the exception of the beginning of the campaign close to Japan which we didn't include in our analysis). Thus, the spectra can be supposed to contain strong liquid water effects and low chlorophyll contamination. A direct evidence for this was given in Fig. 2 in our manuscript showing $\ln(I_0/I)$ in comparison to the liquid water absorption coefficient. The similarity was almost perfect proving that liquid water absorption was the dominant effect in our measurements (in agreement with the pictures above).

Fig. B3 shows the RMS of our DOAS fit of atmospheric NO_2 (425-497 nm) if we do not include the liquid water absorption spectrum. The RMS is high (a) at high southern latitudes because in August there is not a lot of light, (b) in the region of the South Atlantic Anomaly (SAA) where the Van Allen belt has a dip and radiation affects the satellite sensor, (c) over parts of the Sahara where Richter et. al (2011) could improve the fit by applying a broad-band sand structure (as mentioned in the manuscript), and (d) over clear ocean regions where liquid water absorption is seen to a large extent because chlorophyll is almost not present. Thus, the DOAS fit of atmospheric NO_2 suffers from uncompensated liquid water structures, but chlorophyll is obviously not a problem as the RMS is not increased at locations where the chlorophyll concentration is high.

Fig. B4 shows the RMS of Fit3 applying liquid water absorption and the $\text{H}_2\text{O}_{\text{res}}$ spectrum. Increased values at high latitudes and in the SAA remain while the increased values over the ocean vanish supporting the conclusion that our DOAS fit was influenced (the RMS was increased) by liquid water effects which are compensated in Fit3. (Note that even the broad-band sand structures over the Sahara are compensated by liquid water absorption and the $\text{H}_2\text{O}_{\text{res}}$ spectrum – by chance – but no change is observed between Figs.B3 and B4 at locations where chlorophyll is present).

Apart from that we directly compared our $\text{H}_2\text{O}_{\text{res}}$ spectrum with the absorption of chlorophyll (see your comment to P.5046, L.13 below) and found almost no correlation. Finally, the locations where the $\text{H}_2\text{O}_{\text{res}}$ spectrum is found are those of low chlorophyll concentrations.

In the revised manuscript, we

- Clearly state that phytoplankton pigment absorption can dominate the color of the water
- Include a subsection mentioning the importance of bio-optical properties and including the two basic references mentioned by the referee
- Clearly state that TransBrom was carried out where chlorophyll is low and subsequently liquid water absorption is the dominant effect (as demonstrated by Fig. 2 in our study)
- Clarify as demonstrated above that our fit quality suffers from uncompensated liquid water effects but not from unaccounted for chlorophyll absorption.
- State that we cannot strictly rule out that the retrieved spectrum is partly due to any phytoplankton pigment absorption (although this is unlikely for the reasons mentioned above)

2. Inherent optical properties (IOPs) of seawaters that determine the light penetration depth are not characterized along the ship track. This is a significant flaw of measurements because changes in IOPs can affect both retrievals and fit residuals.

We agree that IOPs can affect our retrievals. During TransBrom, there were HPLC measurements from which one could in principal calculate back to IOPs. The following plot

(Fig. B5) is the chlorophyll-a concentration as measured during TransBrom (T. Dinter, IUP Bremen, personal communication) in comparison to satellite chlorophyll-a. In general, the agreement is quite good. The numbers demonstrate again that TransBrom was carried out in a region of low chlorophyll concentration.

However, there might be a misunderstanding again. We are not performing a detailed study about (bio-)optical properties of ocean water and even less we are in competition with extensive studies about this topic (like Morel & Maritorena 2001 etc.). The objective of our study is the improvement of DOAS fits over water surfaces and the starting point is the observation that over very clear water surfaces the problems of DOAS fits are largest (see our answer to the first point).

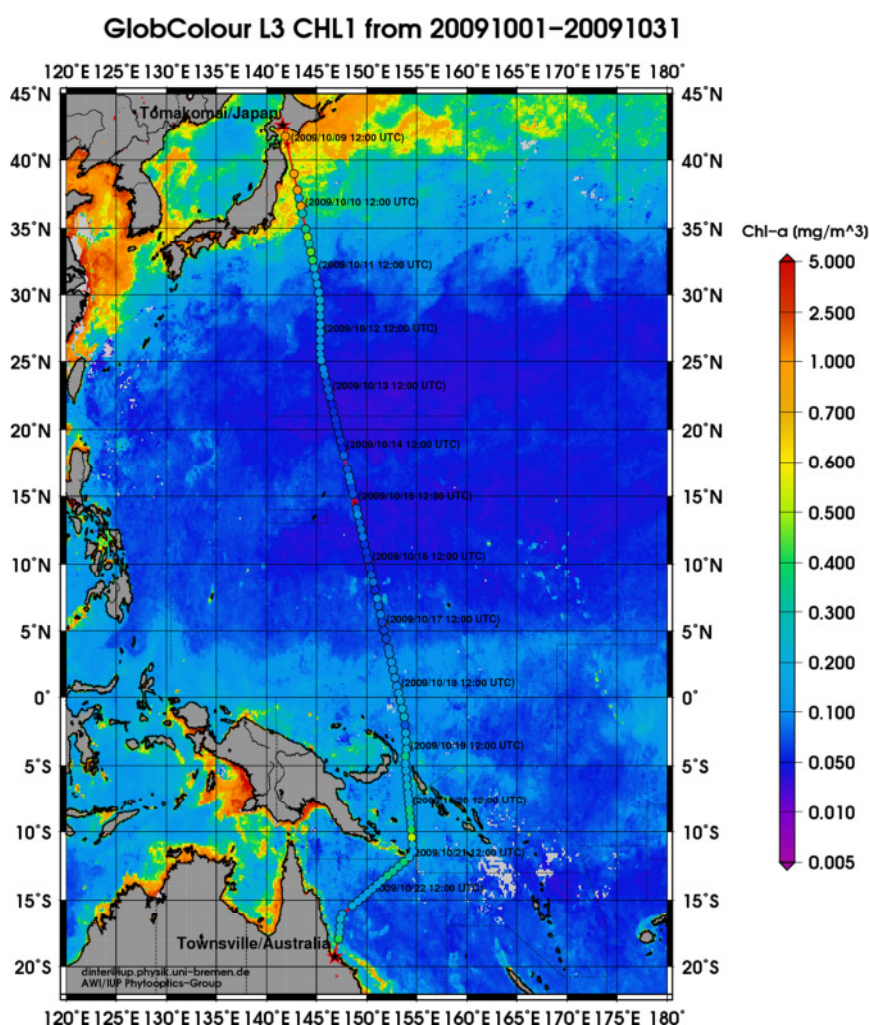


Fig. B5: Chl-a concentration measured during TransBrom (background: GlobColour). (Many thanks to T. Dinter, IUP Bremen, for providing this plot).

3. The largest reduction of the DOAS fit residuals is obviously demonstrated for negative values of the elevation angle of an instrument. The fit residuals are reduced by 4-20% only for near horizon observations which are supposed to be of primary interest. The authors should explain why they need to use negative values of the elevation angle in their actual measurements of NO₂ (Fig. 7).

The negative angles were used to study and demonstrate obvious spectral effects of liquid water in the atmospheric NO₂ DOAS fits. We clarified this in the text.

As the referee correctly states, small elevation angles above the horizon are the most important ones for DOAS applications. As our instruments have a field of view typically in the range of 1°, they partly see the surface for elevations < 1°. In addition, also at higher elevation angles photons can be detected which have penetrated the water surface and travelled some distance in the water before being scattered back into the atmosphere and eventually into the line of sight.

Furthermore, nadir satellite as well as air-borne observations point directly to the ground, i.e. over oceans directly towards the water surface. Thus, our findings are of interest for those measurements, which we state in the summary of the revised manuscript.

4. As usual, DOAS techniques are applied to weakly absorbing trace gases, i.e. optical depth of the trace gas should be small. Fig. 2 shows the retrieved optical depth of water as large as 3.5. The authors should investigate possible errors of their DOAS techniques involved with such large optical depths.

We agree that the optical depth of the liquid water absorption is large for DOAS standards and in fact, it can be the largest signal not only in our ocean pointing MAX-DOAS measurements but also in nadir satellite observations over clear ocean regions.

The assumption of small optical depth in DOAS applications is needed for two reasons:

1. Because the separation of light path calculation and spectral fit relies on the assumption, that the light path length is not affected by the amount of absorber present
2. Because for molecules with strongly structured absorption spectra the spectral signature changes if absorption is large

Here, we are not interested in determining the exact amount of water molecules (determined by the underwater light path) and therefore are not concerned with (1). As the absorption spectrum of liquid water has very little spectral structure, (2) is also not a problem in this case. We therefore do not think that the large optical depth creates errors in our analysis.

In response to the reviewer's comment, we have added a brief discussion of this point to the revised manuscript (last paragraph in Sect. 3.6).

In summary, the manuscript should be substantially revised with due attention to the attached comments before considering the paper for publication.

Specific comments

P.5029, L.6. As usual, the term "yellow substance" refers to colored dissolved organic matter (CDOM).

We included the term CDOM.

P.5030, L.3. You may want to add a reference to the paper

A.P. Vasilkov, J. Joiner, J. Gleason, and P.K. Bhartia, Ocean Raman scattering in satellite backscatter UV measurements, *Geophysical Research Letters*, Vol. 29, No. 17, 1837, doi:10.1029/2001GL014933, 2002, that was the first one that discussed ocean VRS effects in satellite observations.

Thank you very much for that suggestion, we included the publication (the doi for this document is 10.1029/2002GL014955).

P.5030, L.7. Pure water absorption is also important in UV attenuation because it significantly increases with wavelength decreasing (see the reference above).

Thanks again for that comment, we included it.

P.5031, L.23. Please provide a reference to your statement “salinity may have further influence on the absorption spectrum”. I never heard about marine salt absorption in the spectral range of your interest (400 – 500 nm).

Here we only speculated why liquid water (without chlorophyll) could differ from the laboratory measurements of pure water and standard conditions. For example, the refractive index of water depends on salinity. However, we removed this point.

Section 2. A discussion of the physics of pure water absorption may be too long particularly taking into the account that the phytoplankton pigment absorption is not discussed at all.

As clarified above we focused on clear water & low chlorophyll scenarios. However, we agree that there was a lack of discussion of bio-optical properties of water and therefore included a subsection comprising chlorophyll absorption mentioning the basic publications suggested in the first reviewer’s comment.

P.5033, L. 17&18. Kattawar et al. say that the strongest Raman lines are typically 50 cm⁻¹ from the frequency of the incident light. It is not equivalent to your statement “wavelength shift of up to 50 cm⁻¹”. A simple calculation shows that the wavelength shift for the strongest lines is equal to 1 nm at 450 nm. That is not “several Angstrom” as you state.

We calculated (Eq. 1) 0.8 nm = 8 Angstrom for an initial wavelength of 400 nm. The same estimation yields 1 nm shift for 450 nm initial wavelength, which is 10 Angstrom and in agreement with the referee’s number. We rephrased this sentence in the revised manuscript.

P.5036, L.1. The statement of constant water concentration is valid for pure water only. If you account for phytoplankton pigment absorption this statement is no longer valid because phytoplankton concentration depends on depth.

Agreed. We included the restriction on pure liquid water in the revised manuscript.

P. 5037, L.12. Eq. 4 is trivial and can be shortened.

Shortened as suggested.

Section 3.4. Fig. 1 discussion. How can you explain that there is so significant difference in underwater light paths derived from OMI measurements (7 m) and MAX-DOAS measurements (up to 50 m)? You say that such large light path was achieved when the instrument was “pointing directly into the water”, i.e. similar to nadir observations by OMI.

The light path derived from the measurements is not the average light path of a photon in the ocean but the average light path that the ensemble of photons registered by the instrument has spent under water.

The MAX-DOAS instrument is at the ground and the difference between I and I_0 in the optical depth for our measurements is determined by photons which have been in the water. In contrast, OMI measures the intensity at top of the atmosphere which consists to

a large extent of photons scattered in the atmosphere. Thus, only a small fraction of the photons measured by OMI have been under water in contrast to the situation for our MAX-DOAS measurements.

Section 3.6. When defining the color index, you have to control atmospheric conditions. If radiance from a single cloud is reflected from the clear ocean surface into the instrument field of view, the color index can be less than one and the observation can be misclassified as being for white caps.

We assume that direct sunlight is the major source of photons under water. However, even if diffuse light was more important, the CI method wouldn't misclassify a photon because it would still be assigned to the category of incident light (a misclassification would occur if the photon was first under water, came out, hit a cloud, were again reflected at the water surface into the instrument's line of sight – this is supposed to be unlikely).

P.5044, L.19. What inherent optical properties (IOPs) of seawater were used for SCIATRAN modeling of the VRS cross-sections? IOPs include optical properties of pure water, phytoplankton pigment absorption, and CDOM absorption. The VRS depends on IOPs at both excitation wavelength and emission wavelength. That's why it is important to specify the IOPs used for calculations.

SCIATRAN used the liquid water absorption spectrum from Pope & Fry (1997). For phytoplankton, the cross-section of Prieur & Sathyendranath (1981) is used. CDOM is then abstracted from this using Morel & Maritorena (2001) (page 7178, equations 16-18; for Chl in Eq. 16 a value of 0.1 mg/m³ was applied).

In the revised manuscript, we will include a subsection briefly describing the SCIATRAN computation.

Pope, R. M. and Fry, E. S.: Absorption spectrum (380–700nm) of purewater II Integrating cavity measurements, Appl.Optics, 36, 8710–8723, 1997.

Prieur, L., and Sathyendranath, S.: An optical classification of coastal and oceanic waters based on the specific spectral absorption curves of phytoplankton pigments, dissolved organic matter, and other particulate materials, Limnology and Oceanography, Vol. 26, No. 4, 671-689, 1981.

Morel, A., and Maritorena, S.: Bio-optical properties of oceanic waters: A reappraisal, JGR, 106, 7163-7180, 2001.

P.5045, L.20. "... averaged for each DOAs fit ..." What does it mean? Does it mean that the residuals were averaged over the entire ship track?

Yes, with the exception of the very beginning of the campaign (9 October 2009) where no measurements were performed due to a storm. So there is a lack of measurements in the Japanese coastal waters. We clarified that in Sect. 4.4 as well as Sect. 3.4.

P.5046, L.13. "... so far unaccounted spectral structure of natural liquid water ...". Please specify what unaccounted spectral structure you observe in the residual spectrum.

This is again a misunderstanding. We are not claiming that we have investigated a new and so far unknown effect. Instead, we pointed out that liquid water absorption cross-sections

(which are currently available in the literature) are potentially not good enough for use in DOAS measurements (mainly because of their spectral resolution). We changed “... so far unaccounted spectral structures...” in “... correcting for insufficiently removed spectral structures of liquid water absorption and broad-band VRS structures”.

P.5046, L.13. How did you verify that the H_2O_{res} spectrum is different from the differential structure of absorption by phytoplankton pigments such as chlorophyll -a, -b, -c and carotenoids?

This is a good question having two answers:

1. If the H_2O_{res} was due to chlorophyll absorption it should have been retrieved in a region of larger chlorophyll content. In addition, when using it in a satellite DOAS fit, it should be found in regions where larger chlorophyll concentrations occur. Both is not the case. Instead, H_2O_{res} is found where almost no chlorophyll is present but - because there is low chlorophyll - liquid water absorption is large. Thus, the obvious consequence is that the H_2O_{res} spectrum is linked to liquid water absorption.

2. We directly compared the H_2O_{res} spectrum to phytoplankton absorption. In the following 2 plots are shown. Left: Comparison between the differential (3rd order polynomial subtracted) phytoplankton spectrum from Prieur & Sathyendranath (1981) and our H_2O_{res} spectrum. The only feature that shows similarity is the increase around 460 nm which is in the case of H_2O_{res} for sure caused by VRS and not chlorophyll. Right: Correlation plot of the lines. The correlation is calculated to be 0.17. In the revised manuscript we provide this value.

However, we agree that we cannot strictly rule out that any bio-optical water property contribute to the H_2O_{res} spectrum. We now state this clearly in the conclusions of the revised manuscript (but also mention that this is unlikely for the reasons given above).

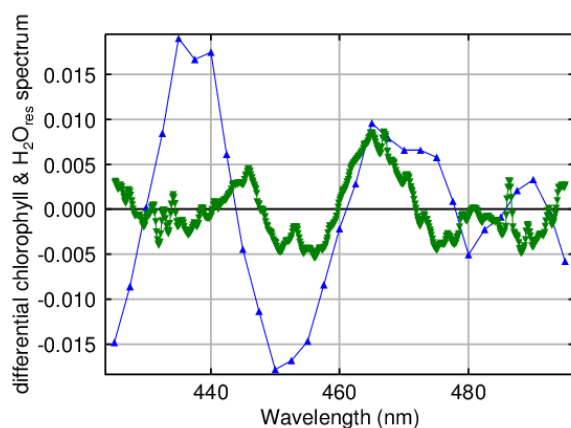


Fig. B6: H_2O_{res} spectrum (green) in comparison to differential chlorophyll spectrum

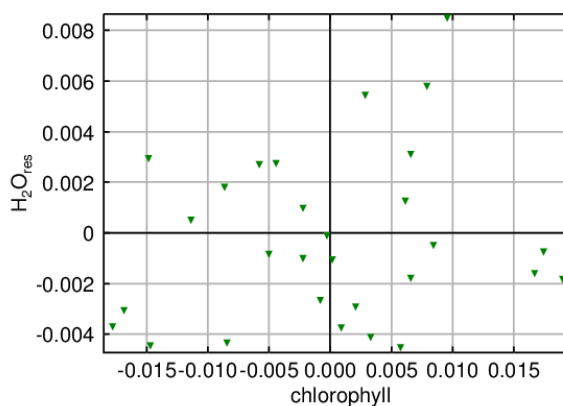


Fig. B7: Correlation plot between the lines in Fig. B6

P.5047, L.9. Does the simulated VRS spectrum depend on observational geometry?

If the observational geometry changes, the relative contributions of photons scattered in the atmosphere, at the surface and in the ocean changes and thus also the VRS effect changes (see our answer to the comment of Referee 1 concerning 5030.7).

In the DOAS fit, VRS is considered as a pseudo-absorber, i.e. a VRS spectrum calculated for a specific geometry is used and a VRS slant column is fitted. This implies that a linear

behavior is assumed (the absorption spectrum is scaled). This is of course only true in first approximation since VRS consists of wavelength shifts. However, we found that using VRS spectra calculated for a “wrong scenario” leads only to an RMS increase below the limit of typical DOAS fit RMS. This study can be found in:

Peters, E.: Improved MAX-DOAS Measurements and Retrievals focused on the Marine Boundary Layer, Ph.D. thesis, University of Bremen, available at: <http://elib.suub.uni-bremen.de/peid=D00103447>, 2013.

P.5047, L.22. Please explain the dependence of water slant columns on the solar zenith angle.

The slant columns of liquid water in our measurements depend on the purity of the water, the instrument’s pointing direction, the solar zenith angle (SZA) and the sun azimuth angle (SAA). We calculated for each measurement on 14 October the SZA and the SAA and plotted them in the following vs the liquid water slant columns shown in Fig. 6 ($I = -3^\circ$ Elevation, I_0 = zenith measurement).

The intuitive assumption that the SZA plays an important role for the liquid water slant column (as we assume that direct sunlight is the most important contribution) is confirmed in Fig. B10. In general, large liquid water slant columns are associated with small SZA and vice versa. However, there is a shift as the maximum of H_2O_{liq} occurs only around 13-14 LT while the SZA has its minimum earlier at approx. 12 LT. The explanation of this shift is most likely an azimuthal dependence. Fig. B9 shows the H_2O_{liq} slant column in comparison to the SAA calculated clockwise w.r.t. South (e.g. -90° is East). The instrument’s azimuthal direction was approx. -100° , i.e. looking almost directly towards the sunrise in the morning while in the evening the relative azimuth is approx. 180° . In this plot, maximum H_2O_{liq} slant columns occur at approx. 40° SAA.

In Fig. B10, the H_2O_{liq} slant columns are plotted in comparison to the intensity of the measurements. Obviously, the very high intensity in the morning when the sun is close to instrument’s line of sight corresponds to H_2O_{liq} slant columns around zero. We think this is reflection of sunlight on the ocean surface (sunglint), i.e. the majority of photons in these morning measurements were not under water but reflected at the surface.

An extensive investigation of the H_2O_{liq} slant column dependence on the viewing geometry is not the focus of this study (although in principle possible using SCIATRAN). As the importance of the sun’s position for our measurements is obvious, we provided these figures here but not in the revised manuscript.

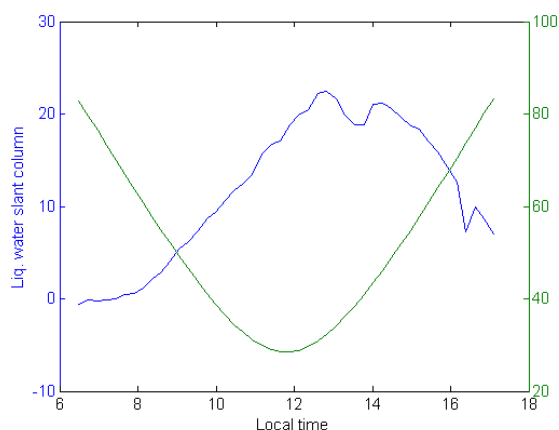


Fig. B8: Liq. water slant column vs. SZA

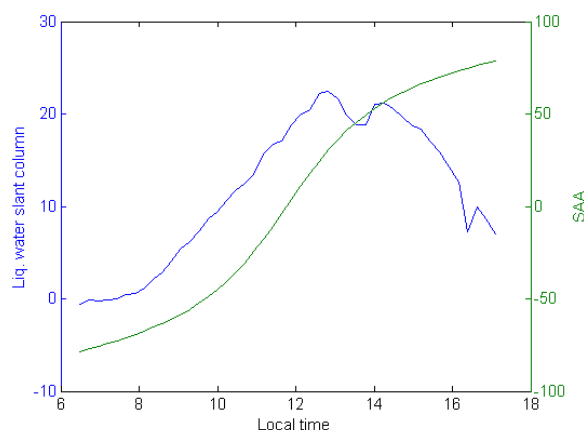


Fig. B9: Liq. water slant column vs. SAA

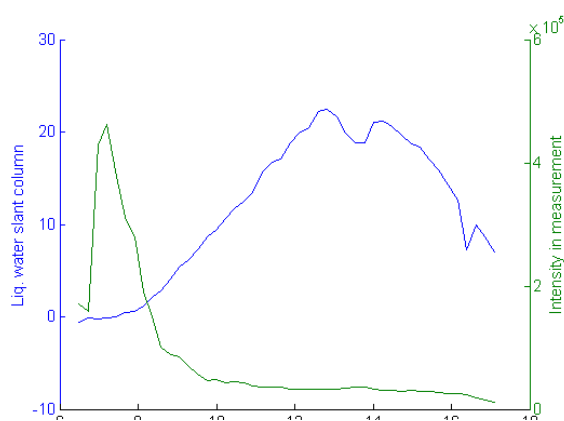


Fig. B10: Liq. water slant column vs intensity

P.5049, L.7. A description of colors in Fig. 7 would be better to move to the figure caption.

This is a question of personal preferences, e.g. Referee 1 asked for legends in the other figures as well. In the revised version, we provide legends for plots with more than 2 color-codings, i.e. Fig. 5, Fig. 6 and Fig. 7. In addition, we put the description always in the figure caption.

In this context, please note that we corrected the legend of Fig. 7 where the description of blue and green data points were mixed up (in the text it was correct).

P.5050, L.14&15. Photons coming from water can be scattered into the instrument line of sight even for elevation angles larger than “slightly above the horizon”.

This is true and the sentence was misleading. The reference measurement here is the zenith direction and thus the smaller the elevation angle the larger the difference between measurement and reference.

The point is that water-related effects (and problems for our fit) are present in small elevation angles of the tropospheric NO₂ fit and using the H₂O_{res} spectrum overcomes these problems which is an important result. We rephrased the text accordingly.

P.5051, Table 3. Do the values (4.1% and 3.2%) in the last line of Table 3 are statistically significant?

We performed a Wilcoxon paired sample test between the RMS values of each two DOAS fits compared in Table 3 (i.e. the null hypothesis is that the RMS values of both fits originate from the same probability distribution). The resulting p-value was always < 0.05 meaning that the null hypothesis is rejected (differences of mean RMS of different fits are statistically significant).

P.5052, L.11. "... the pattern of liquid water absorption ...". That's not correct. Fig. 8a resembles the spatial distribution of chlorophyll-a concentration derived from satellite observations.

We certainly agree on what these pictures show, please be referred to our answer to the referee's first point. To clarify, we rephrased the above sentence to "the pattern of clear natural water".

P.5052, L.16 and afterwards. The water residual spectrum found over desert regions may cause overall doubts about the proposed method of accounting for water absorption effects in DOAS. The finding should be explained in detail.

This is a very interesting feature (please see also our answer to the referee's first point and Fig. B3 above) and is most likely caused by interference between surface spectral reflectance and the retrieved correction spectrum. The influence of broad-band sand structures on the DOAS NO_2 fit is well-known and a spectral interference with the liquid water absorption spectrum has already been discussed in Richter et al., 2011. The results imply that our retrieved spectrum should probably not be included in satellite DOAS fits over land, which we state in the revised manuscript.

However, over the ocean (and most parts of continents) the $\text{H}_2\text{O}_{\text{res}}$ spectrum is not found at locations of enhanced chlorophyll, but only over regions of very low chlorophyll and thus larger liquid water absorption. This is strong evidence that our spectrum corrects insufficiencies of the applied liquid water correction.

P.5052, L.26. Maximum values of the changes are not representative. Please provide average values as well.

This point was also mentioned by Referee 1. We provide mean values in the revised manuscript.

P.5054, L.21. The statement "a complete compensation of all liquid water effects" is too ambitious. The phytoplankton pigment absorption is not accounted for in the proposed DOAS technique.

We agree and rephrased that.

Some technical corrections

P.5028, L.19. "Typical values of improvement ..." sounds confusing. Do you mean RMS of residuals?

We agree and changed that in the revised manuscript.

P.5029, L.12. Should be "rotational Raman scattering"

Yes, of course! Thank you very much!

P.5029, L.19. A reference to Fig. 1 in Introduction does not look appropriate because it is not sufficiently related to the previous text.

With the changes made in response to the referee's comments this should be appropriate now.