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Interactive comment on "Liquid water absorption and scattering effects in DOAS retrievals over oceans" *by* E. Peters et al.

Anonymous Referee #1

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General Comments

The manuscript entitled "Liquid water absorption and scattering effects in DOAS re-trievals over oceans" by Peters et al. describes ship borne measurements of aqueous vibrational Raman scattering and liquid water absorption structure. It has been shown by the authors that the retrieved spectral signatures of liquid water significantly improve the DOAS retrieval, in particular for nadir-looking satellite (and probably also airborne) measurements, but also for ground-based observations if all or parts of the observed light has been scattered by liquid water. Therefore the topic of this paper is of general importance for the UV/Vis spectroscopic community and well suited for a publication in AMT.

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The methodological approaches appear to be valid. In particular, the retrieval of spectral structures of water by separating measurements with short integration time pointing on clear water and white caps is in my opinion an excellent idea since any structures from atmospheric trace gases or aerosols automatically cancel out. However, as detailed below there are several technical and language-related issues which should be resolved before final publication in AMT.

Large parts of this study rely on model calculations of the impact of liquid water on radiation using the SCIATRAN radiative transfer model. Although this has already been published elsewhere, I think it is very important for the reader to have some knowledge on how these simulations were actually performed. A short section describing the methods for the simulation of the spectral structures of liquid water should therefore be added.

In order to assess the improvement of the DOAS analysis using the retrieved spectral structures of water, relative changes in residual RMS for different fit scenarios are discussed. For the ship-borne measurements mean values of these changes are reported, whereas for OMI satellite measurements maximum values are listed. First of all, it is not possible to compare these two values. Secondly, a maximum value of a large dataset is not meaningful at all because it might represent an outlier. For these reasons I strongly recommend to report mean values of the relative change in residual RMS for the satellite observations as well.

Specific Comments

5028.6: I do not think that the term "hyperspectral" is appropriate here, since hyperspectral imaging refers to imaging techniques, for which each pixel contains spectral information. The measurements described here, however, deal with spectroscopic measurements along a single line of sight and therefore not hyperspectral.

5028.19 and 5028.24: Specify what you mean with "values of improvement" and "fit quality improvements" (i.e., decrease in residual RMS).

5030.7: I do not really understand why the absorption of radiation by particles in the water body should lead to a decrease in the filling-in of Fraunhofer lines by VRS. Actually, the strength of the filling-in is determined by the amount of Raman-scattered light relative to the total observed intensity, and both are equally affected by absorption. Therefore there should be no direct impact of absorption on the filling-in, except for subtle changes in the average light path.

5031.23: I suppose that not only salinity, but also impurities have an impact on the apparent water absorption spectrum.

5031.29: I cannot see why the retrieved H_2O_{res} spectrum should be "hyperspectral".

5032.5: Please specify what you mean with "The H_2O_{res} spectrum was tested...". What kind of tests did you perform?

Section 3.1: In its present form, equation 3 does not follow from equation 2. I therefore recommend to use the integral form of the Beer-Lambert Law (i.e., $\sum_i \int_0^L \sigma_i(\lambda)\rho_i(s)ds$ in the exponent of equation 2, and also to include terms for scattering by air molecules and aerosols. Then you could later (5035.25) explain that for liquid water ρ is nearly constant along the light path, and equation 3 would directly follow from equation 2. Furthermore, only the density of water is nearly constant along the light path, but other constituents (impurities, organic compounds, algae, etc.) are not necessarily homogeneously distributed but also affect the radiative transfer and therefore, strictly speaking, need to be considered in Equation 2.

5036.4: "This leads to the DOAS equation" – it is not clear what leads to this equation, as this statement certainly does not refer to the previous sentence. After modification of equation 2 as proposed above, you could simply state that the DOAS equation follows from equation 2, with the polynomial accounting for the broad-band component due to Rayleigh and Mie scattering.

5036.25: The chisquare (χ^2) normalised by the number of spectral points is not equal

to the RMS, but its square is: RMS $= \sqrt{\chi^2/N}$.

5037.7: You mention the dark current as a possible source for an intensity offset. Didn't you remove the dark current prior to the analysis? In this case, it should not cause an offset except if there are temporal variations of the dark current, e.g. due to an unstable detector temperature.

5038.6: Usually, the Ring effect refers to the impact of *rotational* Raman scattering on skylight. Here your state that *vibrational* Raman scattering is responsible for the Ring effect. Furthermore, it is not clear whether this sentence refers to scattering in the atmosphere or in the water body.

Section 3.6: It is not well explained how spectra representative for white caps and for undisturbed water were created. If I understand it right, you stored each 100 ms scan as an individual spectrum and afterwards averaged over spectra which you classified as "white caps" and "clean water". Furthermore, you should mention the important aspect that, by looking at the ratio between white caps and clean water measurements, any impact of the atmosphere cancels out.

5040.26: I do not understand why measurements with 100 ms integration time have no "temporal evolution". Perhaps you should better state that the scene did not change significantly during such a short measurement time.

5042.3: Please specify what you mean with "correction spectra" (it becomes clear much later).

Section 4.1 is very technical and also a bit difficult to understand. Why do you need to interpolate the literature spectrum exactly on a 0.1 nm grid, and not on the grid of your detector? Why should "sharp peaks" occur if you interpolate linearly (or do you mean a lack of smoothness)? A spline interpolation of spectral data is a very common procedure that does not need to be discussed in detail. Furthermore, you state later on (sect. 4.4) that the differences between linearly interpolated and spline interpolated

spectrum are negligible. Therefore I suggest to remove section 4.1 and replace it with a short statement that describes how the spectrum has been treated.

Section 4.2: It is stated that spectral structures of VRS and H_2O_{liq} are closely linked to each other, which means that both can be summarised to a single correction spectrum instead of fitting these structures independently. Empirical evidence from the PCA analysis of the residual data is presented (which I assume is valid), but I do not agree with the explanation of this feature: Why should the strength of VRS structures (proportional to the amount of Raman scattered light relative to the total intensity) be proportional to the length of the light path?

Section 4.3: You mention that your approach leads to a correction spectrum that represents only the broad-banded VRS structures. However, the correction spectra shown in Fig. 5a show significant narrow-banded structures which are similar to the VRS structures shown in fig. 4 (see also comment 5054.2 below). Can you comment on this?

5045.20: It would be useful to have some error discussion on the resulting H_2O_{res} spectrum, e.g. based on the standard deviation of the averaged residual spectra.

5046.3ff: Again, the differences between linearly interpolated and spline interpolated liquid water absorption spectrum represent a very technical aspect which does not deserve such a lengthy discussion, in particular since the differences between both turn out to be negligible. I also suggest to remove fig. 5b which does not give any support to the findings of this paper.

5046.26: I do not really understand why the use of the H_2O_{res} spectrum instead of the VRS spectrum helps the reliability of the DOAS fit. In a DOAS fit, two very similar (linearly dependent) spectra will be subject to a very high fit error (or a failed matrix inversion), but this should not affect the results of the other absorbers.

5047.3: What do you mean with "real NO_2 analysis"? Please specify.

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5047.13: It is not clear what "vertical scanning measurements" means. Do you mean MAX-DOAS measurements?

5049.20: The argument that NO_2 is found correctly if it is present in the measurements is circular. Apart from the results of the different fits, how do you know that it is really present in the atmosphere? And how do you judge which fit scenario yields correct results without consulting independent measurements? In my opinion, a reasonable argumentation would be to state that the negative NO_2 SCDs from Fit1 are physically not meaningful, whereas results from Fit2 (and to a certain extent also Fit3) are always above zero, and that Fit2 is equal to Fit1 whenever NO_2 SCDs from Fit1 are above zero. Thus results from Fit2 are more realistic and likely to be closer to the truth.

5049.23 and 5050.20: It is not clear what you mean with "positive NO_2 values" (I guess the NO_2 SCDs from Fit3).

5050.2: The statement that the amount of contamination with liquid water structures affects the NO_2 error should be supported by a figure showing the NO_2 fit error as a function of H_2O_{res}, or alternatively by figures similar to Fig. 7c and d, but with the H_2O_{res} fit coefficient as colour code.

5051.11: It is not clear for which time period the data for Table 3 has been averaged.

5052.6: Why did you analyse OMI data for a different period than the Transbrom campaign?

5052.13: The OMI data is not only shown for a different period, but more importantly also for different regions of the world.

5054.2: "Differential broad-band absorption" is somehow a contradiction, since the term "differential" usually refers to narrow-band structures which is the opposite of broad-band structures. I think here the difficulty is that the frequency distribution of the retrieved H_2O_{res} spectrum lies between the narrow-band structures from the VRS (which are approximately proportional to the inverse of the intensity and removed by

the intensity offset) and the broad-band absorption which has been removed by the DOAS polynomial.

5054.15: I do not understand why you state that the improvement of satellite retrievals using the new H_2O_{res} spectrum is not the topic of your study, as you did show in Section 6 that it leads to a significant improvement.

Technical corrections

It would be much more convenient for the reader if most figures would have legends instead of descriptions of the meaning of the different lines in the figure captions.

5028.7: "... not considered or compensated for ..."

5028.10: Replace "MAX-DOAS measurements were performed into very clear natural waters..." with something like "MAX-DOAS measurements of light penetrating very clear natural waters were performed...".

5028.18: The sentence "This was not achieved using a liquid water cross section..." is ambiguous since it could also imply that you did not make the attempt to use a liquid water cross section.

5029.2: Replace "Visible" with "visible wavelength range" (here and anywhere else).

5029.14: "...both absorption and in-filling of Fraunhofer lines by liquid water..."

5029.18: "For example" -> "As an example"

5031.13: "...requires *a* spectra resolution..."

5031.22: "...applies not to..." -> "...does not apply to..."

5031.26: "remarkable" -> "remarkably"

5033.28: "... the high density of water" -> "... its high density"

5035.7 and 5035.9: "Brillouin Scattering" -> "Brillouin scattering"

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5035.8: "the water" -> "water"

5035.13: "linewidth" -> "line width"

5036.19: "$k\epsilon[0, 2]$

5037.18, 5041.6, 5042.4, 5051.7 5052.3, 5052.22: You use "therefore" (= "for this reason"), but you mean instead "for this purpose"

5040.20: Replace "cleanliness" with, e.g., "purity".

5042.1: I suggest to replace "experimental spectra" with "empirical spectra" (here and anywhere else). "experimental" has the connotation of something incomplete. Why did you put the term "correction" into brackets?

5043.13: "old" -> "initial"

5045.20: I guess you mean "individual fit range" when you state "DOAS fit"

5047.4: "fit" -> "fit settings"

5047.24: "clear" -> "distinct"

5049.3: "(almost) no NO_2" -> "very low NO_2". Here a quantification of a mean value or an upper limit would be useful.

5049.15: "problem" -> "problems"

5049.16: "effect" -> "effects"

5049.19: "independently" -> "independent"

5054.6: "reasonable" -> "meaningful"

Are Fig. 1 and Fig. 8 showing monthly means? Please specify

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Interactive comment on Atmos. Meas. Tech. Discuss., 7, 5027, 2014.