Review of “Liquid water absorption and scattering effects in DOAS retrievals over oceans” by Peters et al.

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 NO_2 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.

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 H_2O_{res} 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.

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.

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 NO_2 (Fig. 7).

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.

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).

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.

P.2030, L.7. Pure water absorption is also important in UV attenuation because it significantly increases with wavelength decreasing (see the reference above).

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).

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.

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.

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 in no longer valid because phytoplankton concentration depends on depth.

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

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.

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.

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.

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?

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.

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?

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

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

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

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

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

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.

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

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.

Some technical corrections

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

P.5029, L.12. Should be “rotational Raman scattering”

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.