The influence of scattering and absorption processes in sea water on atmospheric radiation

Results from ship-borne DOAS measurements

Anja Schönhardt, F. Wittrock, A. Richter, H. Kirk, H. Schulte in den Bäumen, and J. P. Burrows
Institute of Environmental Physics, University of Bremen, Germany
*Email: anja.schoenhardt@iup.physik.uni-bremen.de

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Motivation & physical background

Measurements of atmospheric trace gases over water bodies with optical absorption methods are affected by interactions of light with sea water: absorption by sea water itself, and not well known absorption processes by substances in the water (organic & inorganic) or scattering processes (elastic & inelastic).
Unaccounted processes lead to residual structures which can interfere with trace gas retrievals as seen in certain satellite data.

Processes that are mostly well known or not critical:

- **Absorption** cross section of pure liquid water molecules
- **Elastic scattering** at atoms, molecules & particles (Rayleigh, Mie) This is a broad-band effect and is fitted by a polynomial.

Processes that are critical or not well known:

- **Absorption** cross sections of substances in sea water (e.g. various types of phytoplankton): only partly known, usually not accounted for in DOAS retrievals.
- **Inelastic scattering** at molecules, e.g. Raman scattering → "Ring effect" Scattered photons change energy → in-filling of strong absorption lines

The spectral effect of scattering in air (O_2, N_2) is calculated by a radiative transfer model and is generally taken into account in the fitting routine. Scattering at liquid water or molecules contained in sea water might not be fully accounted for. The effect is known, but calculations haven't solved all problems yet.

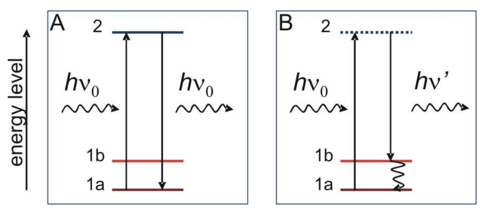


Figure (left): Principle of elastic (A) & inelastic (B) scattering

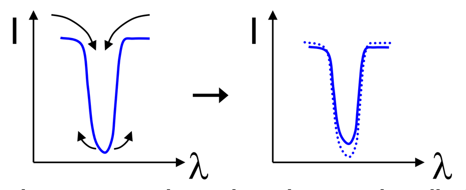


Figure (right): Effect of inelastic scattering on absorption lines in scattered sunlight. The scattering probability is proportional to intensity (left graph). The result is an in-filling of absorption lines (right).

Further processes (probably less influential): Polarisation effects, fluorescence of substances in water, etc.

Main objectives:

- Use spectroscopic measurements of upwelling radiation over sea water to retrieve effective scattering and absorption features.
- Application of this retrieved water effect as reference spectrum to improve observations over water.

Instruments and measurement geometry

Activities:

Performance of ship-borne **DOAS** measurements on RV POLARSTERN.
DOAS: **D**ifferential **O**ptical **A**bsorption **S**pectroscopy

→ Viewing upwards to the atmosphere and down towards the sea water
→ Measurements of trace gases
→ Measurements and analysis of upwelling radiation over sea water

Instrumentation: Two spectrometer units (UV/vis) served with light by same telescope

VIS instrument: range 400–715 nm
Trace Gases: O_3, NO_2, H_2O, CHOCHO, IO…

UV instrument: range 325–410 nm
Trace Gases: O_3, BrO, HCHO, NO_2 …

Usual viewing angles:

- 180 (zenith)
- 120 (into sky)
- 88 -104 (in 2 steps)
- 30 (into water)

Additional angles at station periods: Directions into water between 32 -40 and 76 -88

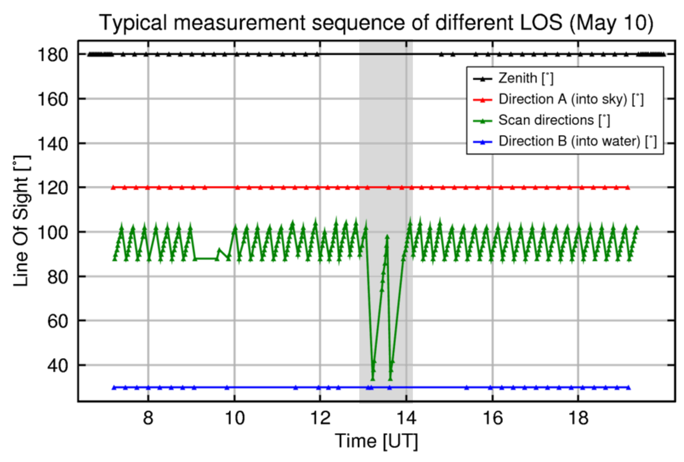
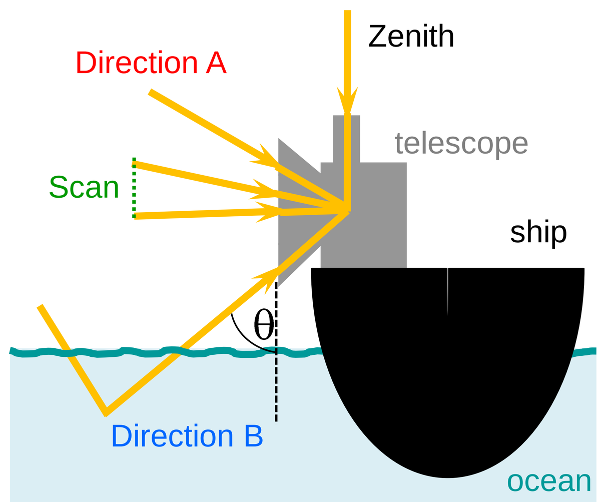
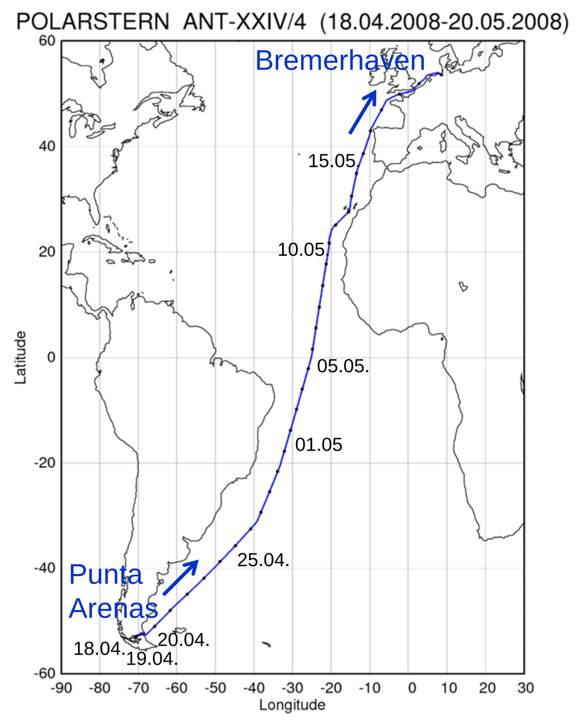


Figure (above): Typical sequence of different lines of sight (LOS) for measurements of one day.
shaded: ship quiet at station

Figure (below): Viewing geometry on the ship. θ (LOS): angle between nadir direction and viewing direction.





- *Typical speed: 11kn (20km/h)*
- *Daily station periods of 1-2 hrs*

Liquid water absorption structures

First test: Did the recorded light pass through sea water?
→ Look for the known water absorption bands in the visible wavelength region

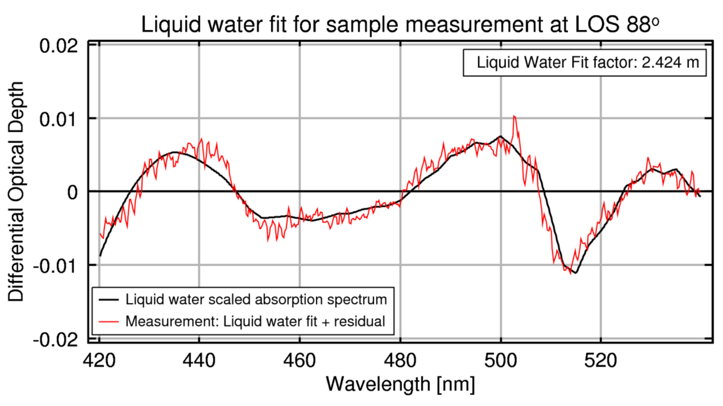
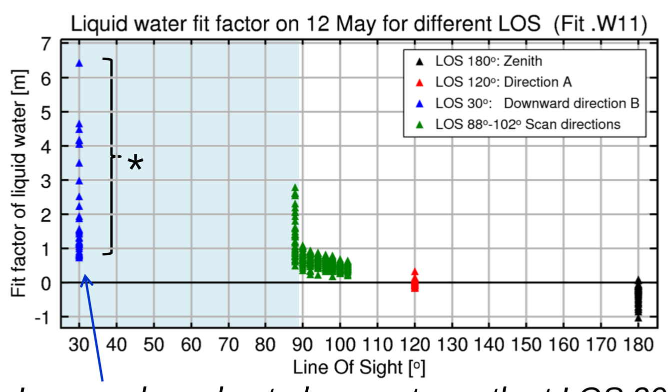
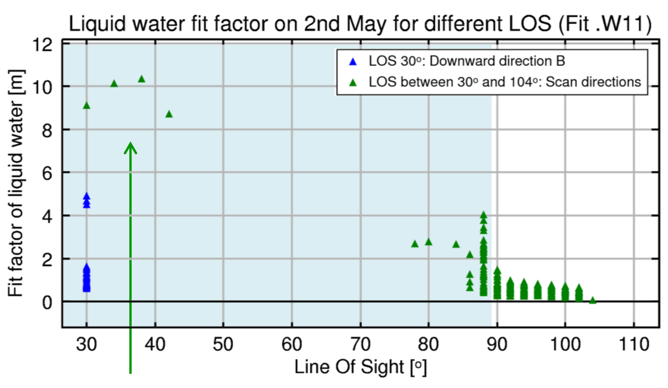


Figure (left): Typical fit result for water absorption. The differential optical depth vs. wavelength is shown. As reference, the absorption spectrum [Pope and Frey, 1997] (black) was fitted to the measured spectrum of scattered sunlight. The fit result including the residual structure is shown in red. The measurement was taken at 88 LOS (2 below horizon).

Figures (below): Example results for the water absorption fit factor (water path length). As background, direction A was used, leading to fit factors around zero at 120 . Largest values are observed for viewing angles into water (LOS 30 -88). Fit factors increase for low LOS as expected.



Large values due to long water path at LOS 30
* *Spread of values due to varying weather conditions & water surface properties*



Additional low angles into water (here at ship station - calm water), resulting in large fit factors indicating long water path

Shaded area: Directions viewing into water

Extracting the mixed water effect

- Choose suitable DOAS fit settings, e.g.:
- interesting spectral region (e.g. 411–455 nm), here only VIS instrument used
- background spectrum similar to actual measurement (to reduce structures from other effects)
- included absorbers: NO_2, O_3, O_4, H_2O(g), Ring effect, 5^{th} order polynomial, stray light effect
- Select only those residuals from measurements taken during station periods
- Average all suitable residuals → receive correction spectrum containing mixed water effects
- The correction spectrum exhibits fairly high frequent structures

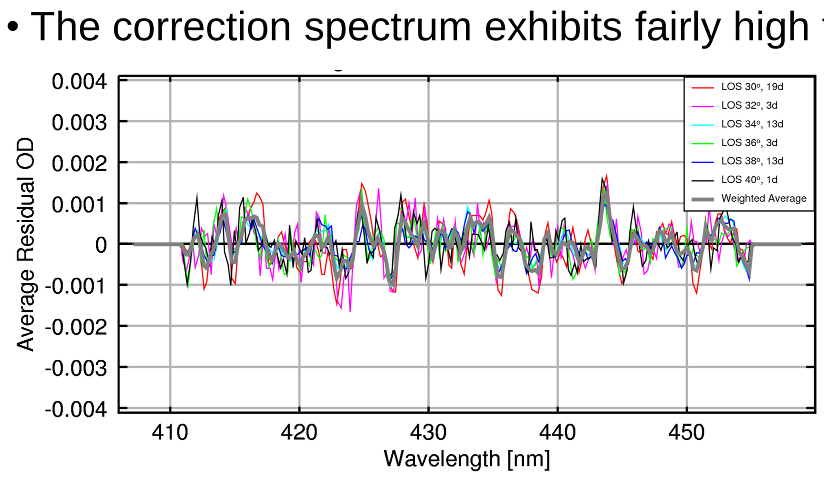


Figure: Averaged residuals for different low LOS (colours) from all measurements at ship station. The grey line represents the weighted average over all LOS.

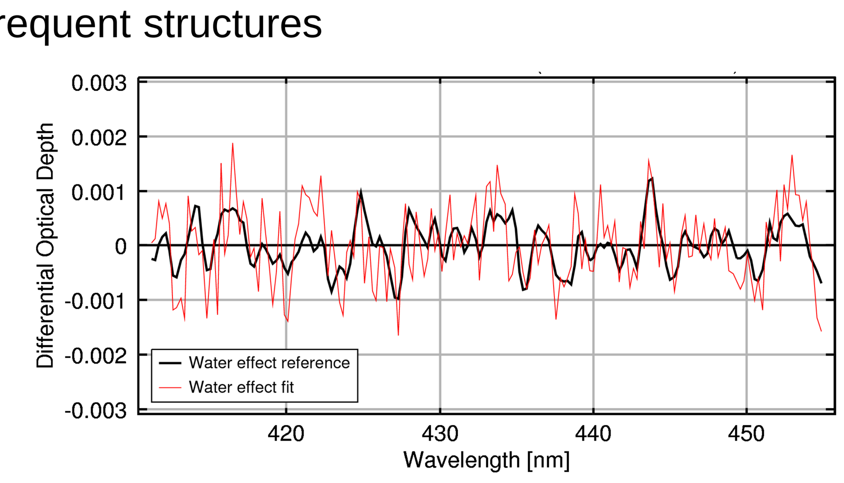


Figure: Example fit result from the fitting of the water effect correction spectrum for a LOS of 34 .

DOAS fit factors of the mixed water effect

The correction spectrum containing the mixed water effect is used in a DOAS retrieval on the Polarstern data.

- A negative fit factor means a detection of the water effect.
- The fit factor becomes more negative when more sea water was traversed (low LOS), see figure on the right.
- The relatively large spread of the values is due to varying properties of the water surface and to the remaining noise in the applied correction spectrum.
- No LOS from 40 -76 due to low intensity (blocked view)

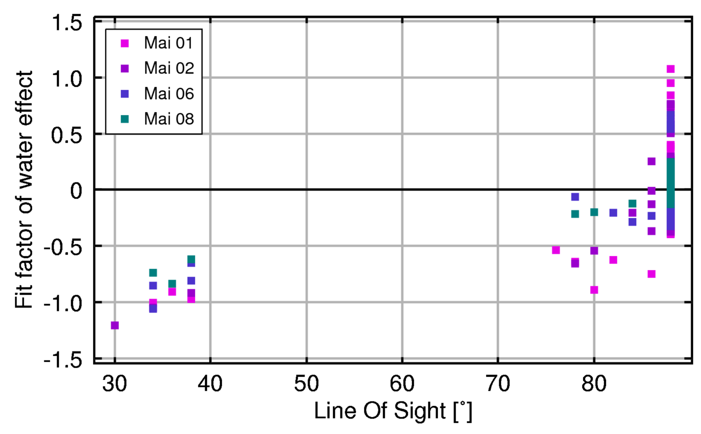


Figure: Fit factors of the water effect vs. LOS for different days of the ship cruise. Tendency: lower LOS, more negative factor.

Retrieval of the water effect in satellite data

The water effect is then included in established DOAS fits also for satellite data. The resulting fit factor is shown in the figures below. A negative fit factor (blue) indicates a detection of the water effect spectrum. The effect should be found over water, especially when the light path through water is long. The length of this path can be recognized in the retrieval of liquid water absorption. The global patterns agree quite well. So far, the resulting improvements for satellite data fits is not large, but this is still ongoing work.

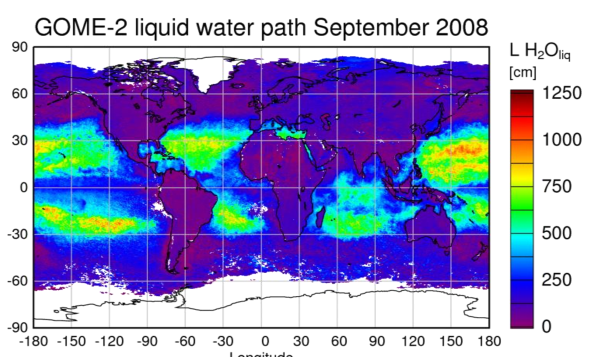
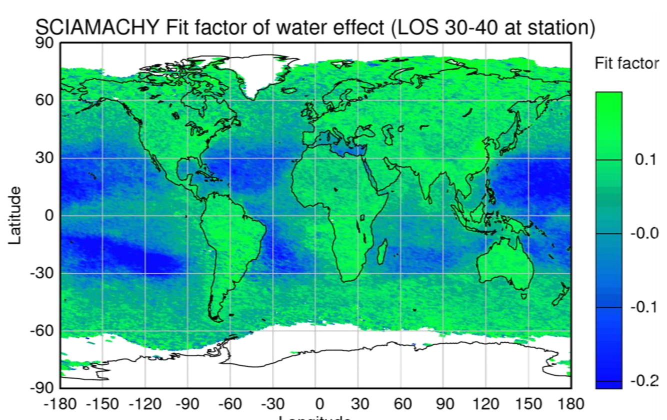
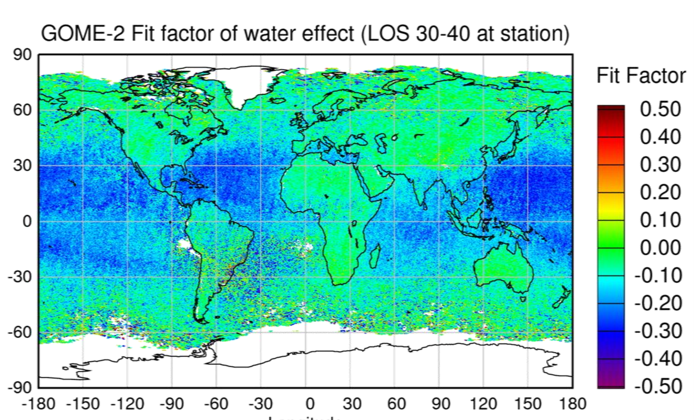


Figure (above): Fit factor of liquid water detection illustrating the global pattern of deep/clear water regions.

Figures (right): Fit factors of the water effect retrieved from satellite measurements (for the sensors SCIAMACHY & GOME-2). Negative fit factors indicate the detection of the supposed water effect. Deep water regions are distinguished from land masses. The absolute values are slightly different for the two retrievals shown.





Conclusions

- Ship borne DOAS measurements of water leaving radiances were used to extract persistent structures which are presently unaccounted for and might contain some spectral water effects.
- This water effect was used as reference spectrum in DOAS retrievals and the effect was indeed detected in observations at low lines of sight (when the instrument was viewing into the water).
- Retrievals of this water effect spectrum using satellite data positively reveal the structure of deep water regions and the contrast between water and land masses in different wavelength windows.
- The exact origin of the spectral structures is not fully solved yet.
- In future DOAS analyses of nadir data over water bodies the application of such water effect correction spectra may improve fit quality and consistency of trace gas results.

Selected References

- Pope, R.M. and Fry, E.S.: Absorption spectrum (380-700nm) of pure water. II. Integrating cavity measurements, Appl. Opt., 36, 1997.
- Vountas, M., et al: Inelastic scattering in ocean water and its impact on trace gas retrievals from satellite data, ACP, 3, 1365, 2003.

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see also: www.iup.uni-bremen.de/doas