Empirical correction spectra for the liquid water absorption and VRS effect in DOAS retrievals

E. Peters[1], F. Wittrock[1], A. Richter[1], J. P. Burrows[1]

[1] Institute of Environmental Physics / Remote Sensing, University of Bremen, Otto-Hahn-Allee1, D-28359 Bremen, Germany

Email: Enno.Peters@iup.physik.uni-bremen.de

Introduction & TransBrom field campaign

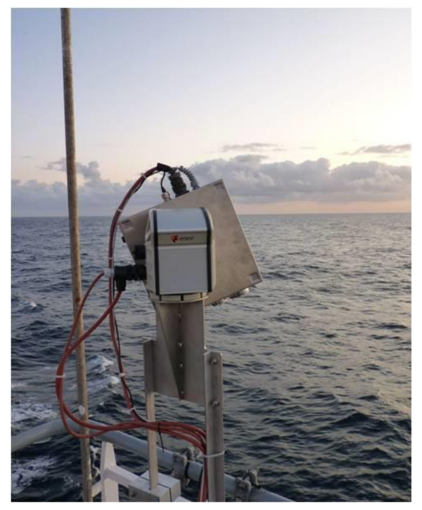
"TransBrom" campaign facts:

- Ship-based campaign onboard the research vessel „Sonne" [1]
- October 2009
- Across western Pacific from Tomakomai (Japan) to Townsville (Australia)
- Organized by GEOMAR Kiel (focusing on short-lived bromine compounds and flux ocean – stratosphere)

IUP-Bremen MAX-DOAS instrument:

- Two-channel instrument, a Y-shaped optical fibre bundle leads the light collected by the telescope unit into two spectrometers
- Any viewing direction possible, telescope unit was installed at monkey deck (Fig. 1)
- Visible spectrometer: 400-573 nm, 0.8 nm resolution (UV measurements not on focus here)

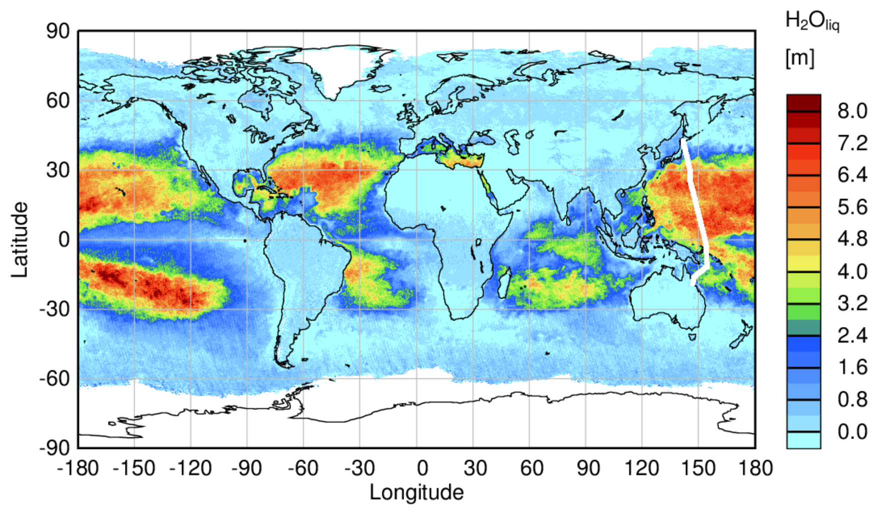
Fig. 1: MAX-DOAS telescope unit pointing towards the water surface



Presented here:

- MAX-DOAS measurements pointing towards the water surface (Fig. 1)
- The campaign was entirely carried out in a region of very clear water (Fig. 2) Underwater light paths of up to 50 m were achieved from MAX-DOAS → well suited for studies of liquid water spectral effects in the DOAS analysis

Fig 2: Liquid water absorption (from literature) fitted in OMI data (August 2007), cruise track indicated



Measurements

- Very short exposure times (100 ms) → Snapshots
- Observed scene is either clear water or sea spray (from ship's bow wave)
- Apply color index to distinguish between white sea spray measurements (used as reference spectra I_0) and undisturbed water measurements (I)
- Difference is liquid water spectral effects

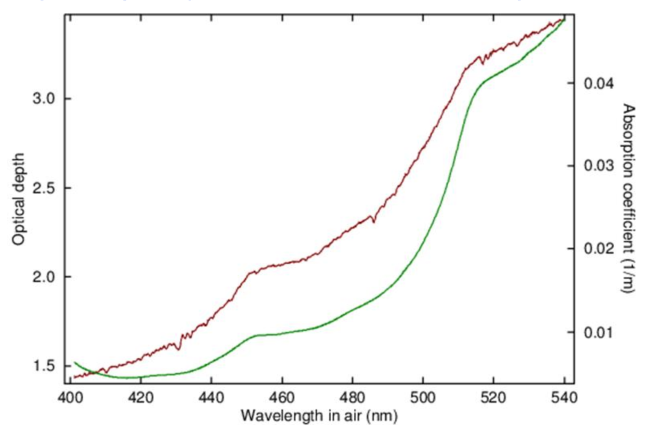
Optical depth of liquid water spectral effects

$$\tau_{liq} = \ln\left(\frac{I_0}{I}\right) = \sum_i \sigma_i(\lambda) \cdot \rho_i \cdot s_i \quad \text{(Lambert-Beer law)}$$

(brown line in Fig. 3).

- Note 1 (Fig. 3): Brown line is superposition of all liquid water effects, i.e. VRS and liquid water absorption (H_2O_{liq})
- Note 2 (Fig. 3): Brown line is obtained from scattered light, i.e. a polynomial has to be subtracted for elastic effects

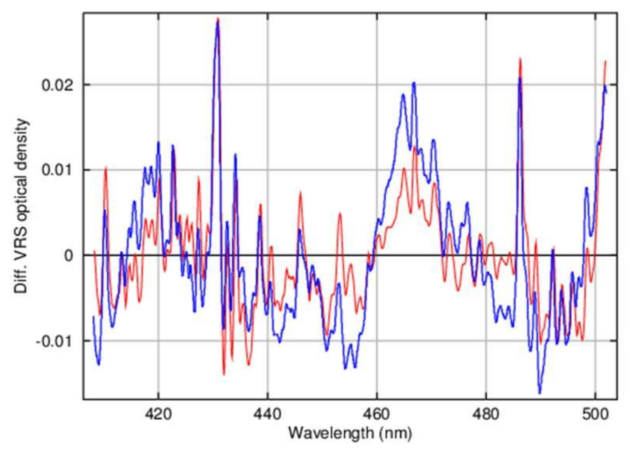
Fig 3: Green: Liquid water absorption from literature [2]. Brown: Optical depth of water from MAX-DOAS measurements (exemplarily from 14 October 2009).



Example: Retrieval of experimental VRS spectrum

- DOAS fit including literature H_2O_{liq} cross-section [2] and polynomial but excluding VRS
- Analysis of fit residuals (PCA, averaging) to retrieve an experimental VRS spectrum (Fig. 4)
- On OMI data, 5% decrease of chisquare is observed
- Even larger improvement observed when retrieving a correction spectrum for both, VRS and H_2O_{liq}

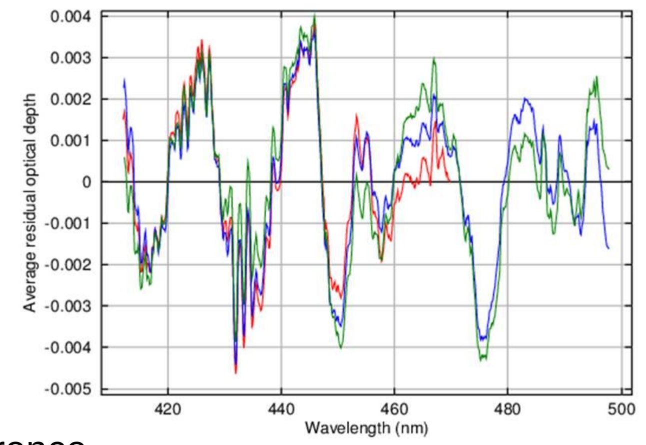
Fig 4: Blue: Differential VRS cross-section simulated using SCIATRAN [3]. Red: Diff. VRS cross-section retrieved from MAX-DOAS measurements.



Correction spectrum for VRS and liquid water

- Both, VRS and H_2O_{liq} depend very similarly on the light path under water → uncertainties of both can be compensated by one correction spectrum
- Performing multiple DOAS fits (different fit range and order of polynomial) including H_2O_{liq} [2] and VRS [3] → systematic (differential) residual structures (Fig. 5)

Fig. 5: Average residuals of different MAX-DOAS retrieval fits



Validation of the correction spectrum

- On OMI data (August 2007)
- Test fit settings: 410-495 nm, 4th order polynomial, sun reference, absorbers: O_3, NO_2, O_4, H_2O_{gas}, Ring (RRS), VRS, H_2O_{liq}, correction spectrum, straylight
- Correction spectrum found reliably over clear water surfaces (Fig.6a,b), reproducing the global pattern of liquid water absorption (compare to Fig. 2)
- Correction spectrum improves fit quality (chisquare) where it is found reliably (Fig. 6d), i.e. the improvement is again reproducing the pattern of liquid water absorption (compare to Fig. 2)
- Improvement is in the order of 10% (up to 30% in the region of the South Atlantic Anomaly)

Fig. 6a: Fitted slant columns of corr. spectrum

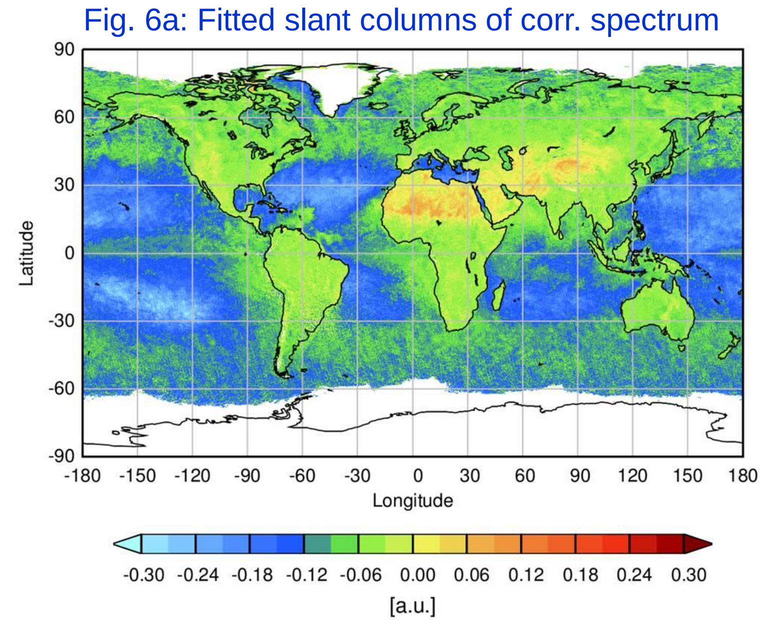


Fig. 6b: Fit error of Fig. 6a.

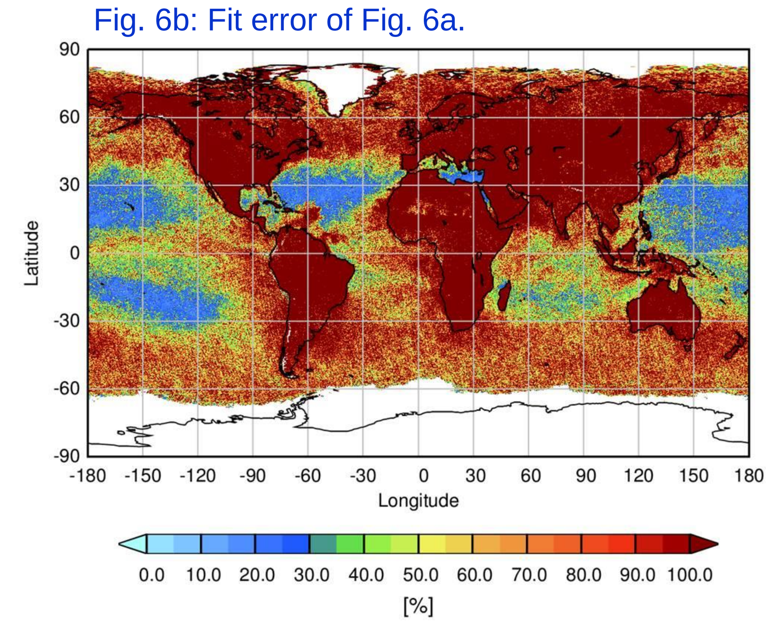


Fig. 6c: Chisquare of an OMI fit without the Retrieved correction spectrum

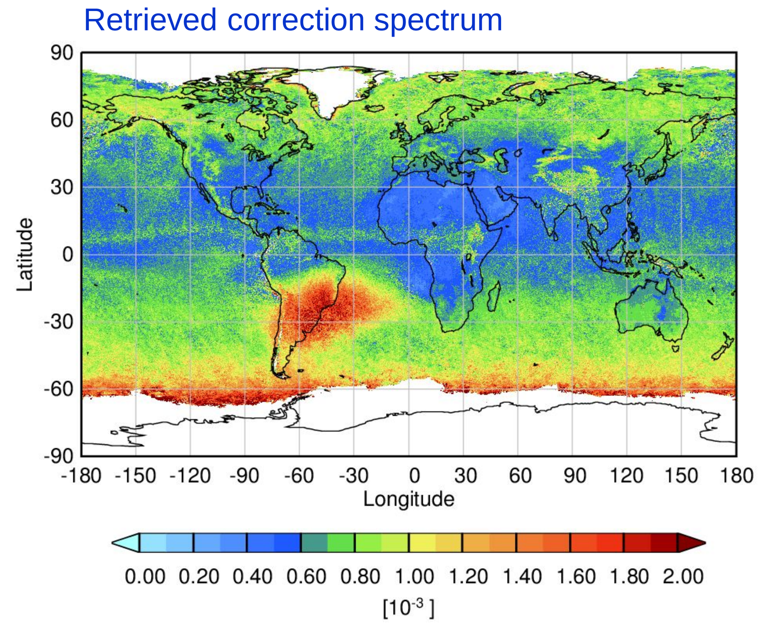


Fig. 6d: Chisquare difference between excluding (Fig. 6c) and including the correction spectrum

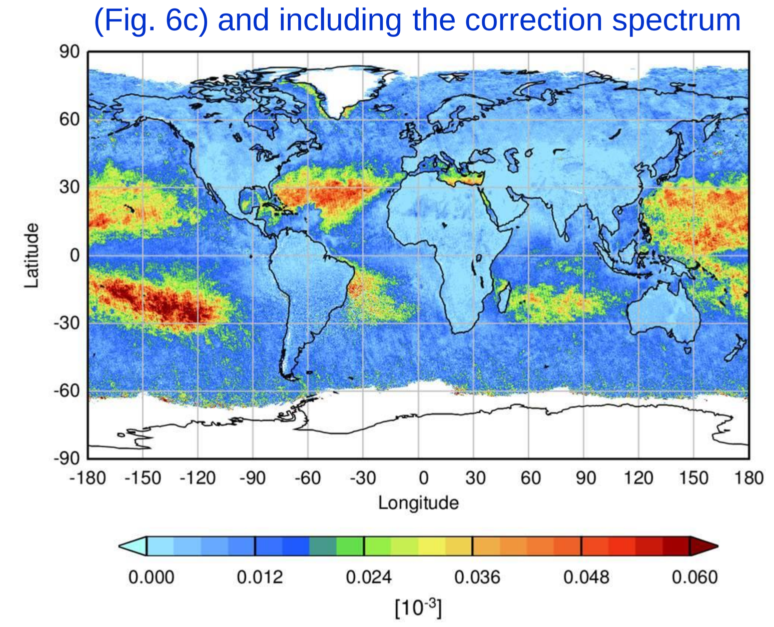


Fig. 6: OMI validation fit of the retrieved correction spectrum from Fig. 5

References

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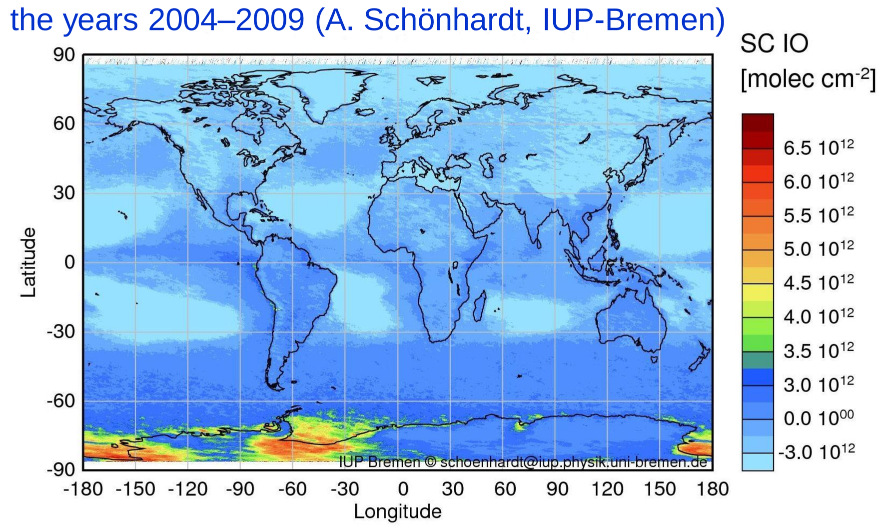
[2] Pope, R. M. and Fry, E. S.: Absorption spectrum (380-700 nm) of pure water. II. Integrating cavity measurements, Applied Optics, 36, 8710–8723, 1997.

[3] Rozanov, V. V. et al.: Radiative transfer through terrestrial atmosphere and ocean: software package SCIATRAN, J. Quant. Spectr. Radiat. Transfer (accepted), 2013.

[4] Schönhardt, A., et al.: Simultaneous satellite observations of IO and BrO over Antarctica, Atmospheric Chemistry and Physics, 12, 6565–6580, 2012.

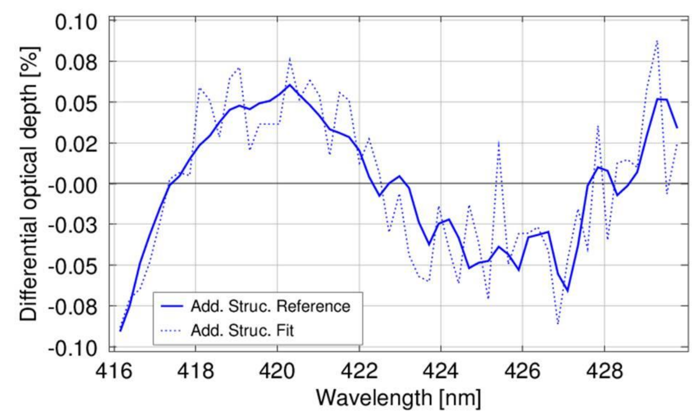
Example: Liquid water in the SCIAMACHY IO fit

Fig. 7: Iodine monoxide as measured from SCIAMACHY for the years 2004–2009 (A. Schönhardt, IUP-Bremen)



- In this fit, the broad liquid water structures are thought to be compensated by the DOAS polynomial
- **Problem**: IO slant columns are negative above regions of strong liquid water effects (Fig. 7)

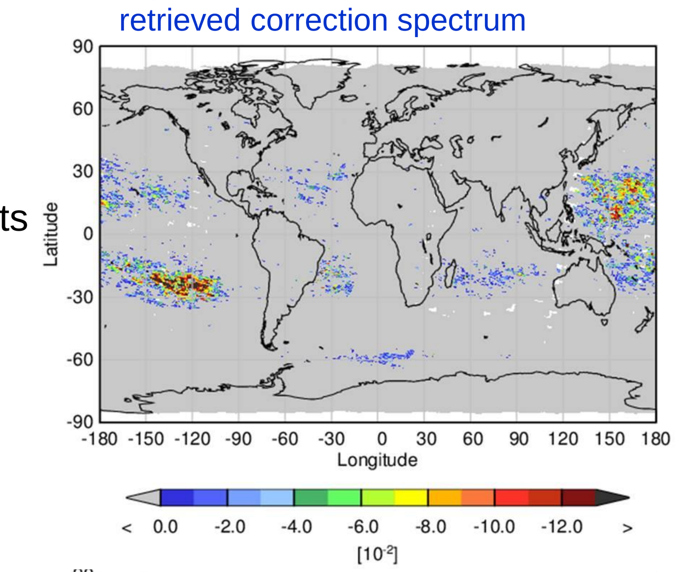
Fig. 8: Retrieved corr. spectrum used as an additional absorber in SCIAMACHY data (here: Over the southern Pacific, 120° E, 27° S).



Correction spectrum retrieved from MAX-DOAS measurements using the SCIAMACHY IO fit parameters [4] (Fig. 8)

Including this correction spectrum in the SCIAMACHY IO fit
→ Retrieved spectrum is found correctly only above very clear water surfaces (Fig. 8, 9a) due to its unstructured shape
→ Increases IO where it is found correctly, but decreases it elsewhere (Fig. 9b)

Fig. 9a: Fitted slant columns of the retrieved correction spectrum



Conclusion and Outlook:

- Interference between IO and H_2O_{liq} residual structures demonstrated. Correction spectrum not recommended for operational use since it is easily misfitted influencing also IO
- If the SCIAMACHY IO fit may improve in the future (larger fit window), the retrieval of a corr. spectrum could be repeated → hopefully a larger corr. spectrum is not as easily misfitted (i.e. influencing the IO selectively only above the ocean).

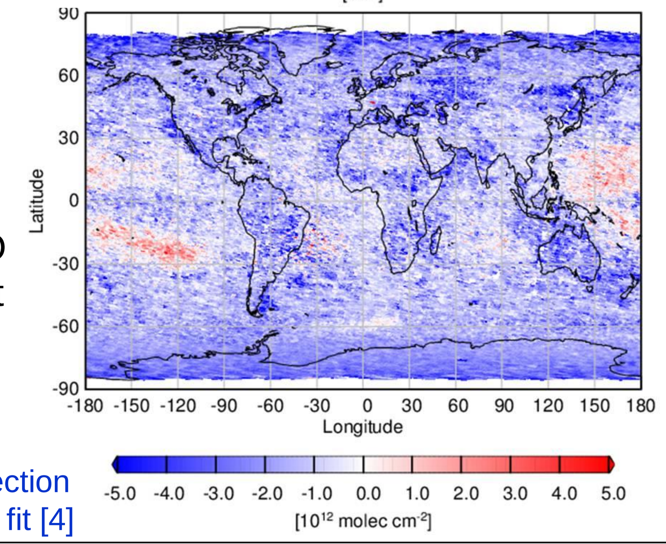


Fig. 9b: IO slant columns of fit including the correction spectrum minus IO SCs of standard SCIAMACHY fit [4]

Conclusions

- In the DOAS analysis of measurements over water surfaces spectral effects of liquid water in the visible range are insufficiently accounted for by currently available cross-sections.
- Ship-borne MAX-DOAS measurements pointing towards the sea surface were performed in a region of remarkable clear water (light paths under water up to 50 m).
- From these measurements, correction spectra for currently available liquid water absorption and VRS cross-sections have been retrieved.
- An improvement of the DOAS fit quality over water surfaces (chisquare decrease) of 10-30% is observed → strong need for a better resolution liquid water absorption spectrum.
- In particular, the interference between IO and H_2O_{liq} residual structures has been demonstrated.

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