PHYTOPLANKTON DISTRIBUTION AND LIGHT ABSORPTION FROM SPACE USING DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY

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ABSTRACT/RESUME

Information on phytoplankton light absorption is necessary to derive accurate estimates of marine chl a concentration and primary production. Global satellite data on photosynthetically active radiation and chl a concentration are available from a suite of satellite imagers like CZCS, SeaWiFS, MODIS, MERIS and others, but spectral information of absorption by phytoplankton and other water constituents is still lacking. Therefore, we used Differential Optical Absorption Spectroscopy (DOAS) to study the retrieval of phytoplankton distribution and absorption with the satellite sensor Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY). SCIAMACHY measures back scattered solar radiation in the UV-Vis-NIR spectral region with a high spectral resolution (0.2 to 1.5 nm). First results showing global phytoplankton distribution and the distinction of phytoplankton absorption signatures from different phytoplankton communities are presented.

1 INTRODUCTION

Knowledge of chl a is not sufficient to properly assess the photosynthetic contribution to the oceanic carbon cycle. Indeed, all phytoplankton species contain chl a (or its substitute divinyl chl a), but they have different requirements and produce different organic substances. Many field measurements have confirmed that the spectra of phytoplankton absorption differ in magnitude and they are independent of chl a (e.g. Sathyendranath et al. 1987, Hoepffner und Sathyendranath 1991, Bracher und Tilzer 2001, Ciotti et al. 2002; see Fig. 1). Phytoplankton groups are generally characterized by some specific pigments – the biomarkers – and may thus be identified from pigment inventories derived from in-situ samples. Hoepffner and Sathyendranath (1993) determined the composition of pigments and that of the phytoplankton community from highly resolved phytoplankton absorption spectra with the Gaussian-band-method. However, it is often difficult to extract the individual contribution of each pigment to the measured absorption spectrum (Bricaud et al. 1995). Because the pigment molecules are not uniformly distributed but contained within discrete packages - chloroplasts, cells, cell colonies- (described by Kirk (1994) as package effect), the absorption spectrum can be modified and thus can lead to a wrong interpretation in terms of phytoplankton species. This varying phytoplankton absorption independent of pigment concentration significantly influences the chl a retrieval by empirical ocean color algorithms. This explains why empirical approaches applied to case-1 waters from ocean color data cannot retrieve chl a with a higher accuracy than 30%. Other factors causing such dispersion in water optical properties for a given chl a are usually attributed to the optical impact from yellow substances. Several regional studies have emphasized significant biases between satellite and in-situ chl a estimates. These studies led to various adaptations of ocean color algorithms, such as those developed for the oligotrophic Mediterranean waters (Bricaud et al. 2002, D’Ortenzio et al. 2002) and for the productive Antarctic waters (Arrigo et al. 1998, Bracher 1999, Dierssen and Smith 2000). Such regional approaches are, however, difficult to conciliate with global satellite data processing. Besides, they do not provide any biological or physical interpretation of the observed variability in water optical properties. More recently, bio-optical models were developed to account for the specific optical properties of species like coccolithophorids (Brown and Yoder 1994), diatoms (Cota et al. 2003, Sathyendranath et al. 2004), N₂-fixing cyanobacteria Synechococcus (Morel 1997) and Trichodesmium (Subramaniam et al. 2002). It is difficult to use species-dependent biooptical models in processing of global satellite data (see Moore et al. 2001), as they require some prior information on the dominant phytoplankton group.
spectral wavelength bands with 10 nm band width. The presented study focuses on identifying phytoplankton absorption in SCIAMACHY visible earth spectra by using the DOAS-method (see explanation below) and analysing these data to derive the amount of phytoplankton along the effective under-water light path. We show results of global comparisons of SCIAMACHY phytoplankton slant columns and chl a results with chl a conc. from the algal_1 product of MERIS and MODIS. In addition, we show first (preliminary) results of identifying different phytoplankton absorption spectra in SCIAMACHY backscattered measurements.

2 SCIAMACHY DATA SET AND DOAS METHOD

Apart from its broad spectral coverage, a unique feature of SCIAMACHY is the ability to detect sunlight that has been transmitted, scattered and reflected in the Earth’s atmosphere in different observation geometries, for more details see Bovensmann et al. (1999). For our study only the data acquired in nadir viewing geometry are analysed using the Differential Optical Absorption Spectroscopy (DOAS) technique (Perner and Platt 1979). This method exploits the sharp spectral features in Earthshine radiance spectra that are caused either by molecular absorption due to atmospheric constituents or spectral re-distribution features as induced by the Ring effect (Grainger and Ring 1962, Vountas et al. 1998) or vibrational Raman Scattering (VRS) in ocean waters (Vassilkov et al. 2002, Vountas et al. 2003). The high-frequency spectral structures are separated from the slowly varying attenuation due to molecular (Rayleigh) and aerosol (Mie) scattering by estimating a low-order polynomial in a spectral fit procedure. However, depending on the size of the fitting window the algorithm is also able to retrieve rather broad spectral structures (Eisinger et al. 1996). Global maps of trace gas concentrations with a typical ground-scene resolution of 30x60 km can be derived with this method from SCIAMACHY data (Richter et al. 2005). The DOAS technique has been proven to be a powerful tool in atmospheric remote sensing. In this study we present its application to the determination of marine phytoplankton absorption and concentration, which has been described firstly by us in (Vountas et al. 2007). On its round trip through the atmosphere, the radiation picks up spectral signatures from absorbing molecular species, like ozone, nitrogen dioxide and water vapour. As direct and scattered light penetrates the ocean surface and therefore interacts with phytoplankton, the phytoplankton absorption spectra are imprinted on the backscattered radiance spectrum in the visible. For the DOAS technique to quantify phytoplankton from the

Fig. 1: Spectra of pigment-specific phytoplankton absorption determined in water samples of three different biogeochemical provinces within the Atlantic Southern Ocean during spring/summer 1995/96: The Antarctic Circumpolar Current (ACC), the Polar Front, and the Marginal Ice Zone (from Bracher and Tilzer 2001).
detected radiation, it is essential that the atmospheric absorption signals can be separated from the under-water phytoplankton absorption signal.

The first step in a DOAS retrieval involves the fitting and scaling of a set of reference spectra, composed of:

- trace gas absorption cross-sections \( \sigma \)
- polynomial \( p \) and
- pseudo-absorber spectra such as a Ring spectrum \( r \) and a reference spectrum for VRS in liquid water \( \nu \),

to the measured optical depth \( \tau(\lambda, \theta) = \ln(I/I_0) \), with \( I \) being the backscattered radiance, \( I_0 \) the extra-terrestrial irradiance. \( \tau \) is a function of the wavelength \( \lambda \) and the solar zenith angle \( \theta \) (dependence omitted in the following). The fitting is formalized as follows:

\[
\left\| f(\lambda) - \sum_{i=1}^{N} S_i \sigma_i(\lambda) - S_r(\lambda) - S_\nu(\lambda) - p(\lambda) \right\|^2 \rightarrow \min (1)
\]

Where \( S_i, S_r, \) and \( S_\nu \) are the target quantities called slant column, scaling or fit factor and \( \sigma_i(\lambda) \) are the cross-sections for each trace gas \( k \) and pseudo-absorber fitted. As a scalar indicator of fit quality \( X^2 \) values are often used. The \( X^2 \) values are defined as the square of the wavelength-integrated fit residual weighted with the square of the measurement error. Therefore high \( X^2 \)-values indicate poor fit quality. It should be noted that the DOAS method will lead to erroneous results if the reference spectra used in the fit have spectral correlation, i.e. the fit algorithm will not be able to distinguish between similar spectral features.

3 DOAS-FITTING OF OCEANIC SIGNATURES USING SCIAMACHY DATA

The key innovation in the DOAS analysis for phytoplankton retrieval is the introduction of the in-situ measured specific spectrum of phytoplankton absorption measured in the ACC region plotted in Fig. 1. In a non-linear least squares fit, they are scaled by the slant column \( S_{\text{phyco}} \), which is estimated simultaneously with the slant columns of the atmospheric trace gases included in the analysis (in our case \( \text{O}_3, \text{NO}_2, \text{O}_4, \text{H}_2\text{O} \), plus a pseudo-absorber for the Ring effect [8]). In addition, we included liquid water absorption cross sections in the analysis, which was performed in the wavelength window 428-496 nm. A typical result for the specific phytoplankton absorption fit is depicted in Fig. 2. The solid line represents the phytoplankton reference spectrum, scaled by the result for \( S_{\text{phyco}} \), and reduced by the low-order polynomial in wavelength. Adding the fit residual yields the broken line. The agreement between the two curves is a measure of how well the observations fit the reference spectrum used in the analysis. As we see from the plots, the space-borne observations match the in-situ measured reference spectra remarkably well (Fig. 2 left), on Fig. 2 right the (low) fit to a pixel with low chl \( a \) (as seen in coincident MODIS measurement, data not shown). The analysis of the fit quality suggests that the under-water absorption signal from photosynthetic pigments in phytoplankton is sufficiently strong to be detected by SCIAMACHY. They can be well distinguished from contributions of atmospheric constituents, which allows for a quantitative retrieval of the phytoplankton amount along the under-water light path.

![Fig. 2: Spectral DOAS fit for phytoplankton with the PCA applied using the phytoplankton absorption cross sections from the ACC plotted in Fig. 1 for a SCIAMACHY pixel with high chl a conc. (>5 \( \mu \)g/l at 25°N and 16°W, left) and with low chl a conc. (<0.01 \( \mu \)g/l at 25°N and 50°W/15.8°E, right). Figures from Vountas et al. 2007.](image)

In addition, also inelastic scattering of seawater in ocean waters (vibrational Raman scattering, VRS) and its impact on trace gas retrievals from satellite data was studied and detected in GOME (Vountas et al. 2003) and SCIAMACHY data (Dinter 2005, Vountas et al. 2007).
VRS slant columns/fit factors from SCIAMACHY data are obtained by using the DOAS method described for phytoplankton absorption fits in the range of 349.5 nm and 382 nm and fitting to a modelled VRS spectra (details described in Vountas et al. 2007). It has been found, that over clear ocean waters, photons scattered within the water body contribute significantly to the upwelling flux. In addition to elastic scattering, inelastic Vibrational Raman Scattering (VRS) by liquid water is also playing a role and can have a strong impact on the spectral distribution of the outgoing radiance.

The above described retrieval technique has been applied for fitting both, spec. phytoplankton absorption and VRS, to several SCIAMACHY groundpixels of one month (July 2005) and global maps of these fits are shown in Fig 3. Both approaches, fitting VRS or phytoplankton absorption spectra, exhibit expected clear correlations to global chl a from other satellite measurements (see Fig 6). Obviously both methods could be used to retrieve this quantity. An optimized retrieval technique would take advantage of a hybrid approach: VRS fits strongly in regions where low chl a prevail whereas direct fitting of phytoplankton behaves vice versa.

4 COMPARISONS TO MODIS/MERIS AND SCIAMACHY CHL RETRIEVAL

Fig. 3: Monthly global averages for July 2005 of phytoplankton (top) and vibrational Raman Scattering (VRS, bottom) fit factors from DOAS-fits of SCIAMACHY data, figure from Vountas et al. 2007

Fig. 4: Scatter plots of coincident July 2005 of MODIS chl a level-2 data (from http://oceancolor.gsfc.nasa.gov) vs. phytoplankton (top) and vibrational Raman Scattering (VRS, bottom) fit factors derived from SCIAMACHY data using DOAS; figure from Vountas et al. 2007.

We performed a large quantitative comparison between MODIS OC4V4-Aqua chl a data (~ 1 km²) with results derived from SCIAMACHY data using DOAS-fitting of phytoplankton absorption and of VRS. Collocations were chosen with comparing the mean of all MODIS data measured within a SCIAMACHY pixel at the same day. In order to avoid artefacts, only comparisons were made when at least 10 MODIS pixel were collocated to a SCIAMACHY observation. Fig. 4 (top: compared to SCIAMACHY phytoplankton absorption and bottom: to
VRS fit) shows a scatter plot for all collocations in July 2005. Results show a "gamma"-shaped ($I'$) and mirrored $I'$ relation between the DOAS fit factor (slant column) of specific phytoplankton absorption and VRS, respectively, and the MODIS chl $a$. The absolute value of the phytoplankton absorption fit factor increases, while of the VRS fit factor it decreases with increasing MODIS chl $a$, which is expected behavior. A simple exponential curve could be fitted according to the equation $I (\Phi) = a_0 - a_1 \exp(-a_2 \Phi)$, with $\Phi$ being the chl $a$ as obtained from MODIS. The scatter around the fitted curve might partially be attributed to spatial and temporal variations of chl $a$. The curve shows a "saturation" of the SCIAMACHY fit factors for MODIS chl $a$ higher than 0.5 mg/m$^3$. Obviously, the input radiance spectra from SCIAMACHY are not changing significantly with higher chl $a$ which is likely to be related to the selected wavelength interval where the penetration depth of light is not sufficient and should be adapted in further studies.

![Image](image_url)

Fig. 5: Monthly global averages for July 2005 of chlorophyll conc. derived from SCIAMACHY (upper panel) data fitting to phytoplankton absorption (to derive slant column of specific phytoplankton absorption along the under-water light path) and to VRS (to derive penetration depth); figure from Vountas et al. 2007

In order to retrieve chlorophyll conc. from SCIAMACHY measurements we used the combined information from the fits to VRS and specific phytoplankton absorption. The fit factor $S_{sl}$ for phytoplankton (or to be precise for the specific absorption spectrum) is given in [mg/m$^2$2] which is a mass column. If the penetration depth $\delta$ of light for the wavelength window considered is known this column can be converted into a concentration by the ratio:

$$C = S_{sl} / \delta$$  \hspace{1cm} (2)

VRS is strongly related to $\delta$ and serves therefore as a proxy: A single vibrational Raman scattering event is always accompanied by an elastic scattering process. Therefore the fit factor of VRS, $S_{\epsilon}$ is directly related to the same quantity for elastic scattering only. As described above (and in more detail in Vountas et al. 2003) a bio-optical model from Morel (1988) has been used to describe the dependence of the elastic backscattering coefficient $b_{\epsilon}$. The backscattering coefficient scaled with the same factor as the VRS spectrum $S_{\epsilon}$ can be understood as the true $b_{\epsilon}$ for the real situation considered. As $b_{\epsilon}$ is the modelled penetration depth, $S_{\epsilon} * b_{\epsilon}^{-1}$ can be associated with the measured one. For the whole retrievals of $S_{sl}$ for July 2005 (as described above) all corresponding values of $S_{\epsilon}$ have been used within Eq. (2) to model a global map of chl $a$ ($C$), which is displayed in Fig. 5.

![Image](image_url)

Fig. 6: Monthly global averages for July 2005 of chlorophyll conc. derived from level-3 products of MODIS (http://oceancolor.gsfc.nasa.gov/cgi/level3.pl, top) and MERIS algal_1 (http://www.enviport.org/meris, bottom)

First visual comparisons with MODIS and MERIS global chl $a$ of the same time period (Fig. 6) show good agreement. Further studies will optimize this approach and will also include a thorough quantitative comparison.
An important point of investigation must be the impact of the “saturation effects” (discussed in the paragraph above) on the chl $a$ conversions. The patchy appearance of the mapped chl $a$ is related to the fact that due to fitting failures, either in case of VRS or phytoplankton fitting, not both corresponding quantities could be related.

5 FIRST (PRELIMINARY) DISTINCTION OF SPEC. PHYTOPLANKTON ABSORPTION

![Graph 1](image1)

**Fig. 7:** Example of two phytoplankton absorption DOAS fits performed at SCIAMACHY nadir measurements from 1 Nov 2005 using in-situ measurements from phytoplankton communities dominated by diatoms (left panel) and by dinoflagellates (right panel). Preliminary results!

Since the DOAS method is highly sensitive to spectral structures, further DOAS analyses were performed using absorption spectra measured during to Polarstern cruises, one “ANTXIII-1” in 1995/1996 (data published in Bracher and Tilzer et al. 2001) and one “ANTXXIII-1” a North-South transect in the Atlantic in Oct/Nov 2005 (measurements by R. Röttgers, see Poster #104 by Röttgers et al.) whether to check if the discrimination between different phytoplankton groups dominating the chl $a$ is possible. First tests fitting different phytoplankton absorption spectra from Bracher and Tilzer (2001), in different areas of the globe (close to New Zealand, Fig. 7 left, and close to Nova Scotia, Canada, Fig. 7 right) showed that the overall residuals were far better when using the two presented ones in the specific areas. These results give us the motivation to proceed further with our work.

6 CONCLUSIONS AND OUTLOOK

For the first time the Differential Optical Absorption Spectroscopy (DOAS) retrieval method has been used fitting specific phytoplankton absorption and VRS to optical depths measured from SCIAMACHY. Either fitting VRS or phytoplankton absorption lead to consistent results. VRS fit factors clearly correlate with chl $a$. Low factors correspond to high chl $a$ and vice versa. As expected opposite behavior is observed when fitting phytoplankton spectra: here, low factors correspond to low chlorophyll concentration and vice versa. Both approaches are promising tools for retrievals of chl $a$. First results of a hybrid approach show good agreement with chl $a$ derived from MODIS and MERIS; validation results will be shown in a consecutive study.

Despite that the spatial resolution of SCIAMACHY (and OMI or GOME-2) is far lower than for the new ocean color imagers such as MODIS, SeaWIFS, MERIS, MOS, etc. further developments of our method to identify phytoplankton absorption in satellite spectra are of great relevance for improving chl $a$ determinations for ocean color imagers. So far, it has become clear that remote sensing algorithms derived for ocean color imagers are designed for use at global scales but less accurate at regional and local scales (Sathyendranath et al. 2004). As pointed out in the introduction, the varying of specific phytoplankton absorption which can vary independently of changes in chl $a$, at least in the open ocean waters generally referred to as case-1 waters, can lead to errors in the common ocean color retrievals because a constant specific phytoplankton absorption is assumed. There, we sought in our study to use the high-resolution spectra of the satellite instrument SCIAMACHY in order to look for phytoplankton absorption in open ocean areas. Future plans after successfully retrieving different specific absorptions from SCIAMACHY, are to use this variable information to improve chl $a$ retrievals from common ocean color sensors by using the right regional phytoplankton spectrum, but also will improve modelling primary production and food web dynamics in the global open oceans. In addition, also retrievals of atmospheric
constituents from backscatter UV satellite measurements will improve when the ocean optical signals, such as phytoplankton absorption are also considered in radiative transfer models used in these retrievals.

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8 REFERENCES


