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Quantitative observation of cyanobacteria and diatoms from space using PhytoDOAS on SCIAMACHY data

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Received: 7 October 2008 – Accepted: 14 October 2008 – Published: 28 November 2008

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

In this study the technique Differential Optical Absorption Spectroscopy (DOAS) has been adapted for the retrieval of the absorption and biomass of two major phytoplankton groups (PhytoDOAS) from data of 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). In order to identify phytoplankton absorption characteristics in SCIAMACHY data in the range of 430 to 500 nm, phytoplankton absorption spectra measured in-situ during two different RV “Polarstern” expeditions were used. The two spectra have been measured in different ocean regions where different phytoplankton groups (cyanobacteria and diatoms) dominated the phytoplankton composition. Results show clearly different absorption characteristics of the phytoplankton groups in the SCIAMACHY spectra. Globally distributed pigment concentrations for these characteristic phytoplankton groups for two monthly periods (February–March 2004 and October–November 2005) were derived from these differential absorptions by including the information of the sensor’s optical paths within the water column (i.e. light penetration depth) according to Vountas et al. (2007) derived from DOAS fits of inelastic scattering. The satellite retrieved information on cyanobacteria and diatoms distribution matches well the concentrations measured at collocated water samples with HPLC technique and concentrations derived from the global model analysis with the NOBM model (Gregg et al., 2003; Gregg and Casey, 2007). Identifying quantitative distribution of key phytoplankton groups from space allow to distinguish various biogeochemical provinces and will be of great importance for the global modelling of marine ecosystem and biogeochemical cycles addressing climate changes in the oceanic biosphere.

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1 Introduction

As well known, phytoplankton plays an important role in the global carbon cycle via the fixation of inorganic carbon during photosynthesis and its export to the deep sea by subsequent sinking of organic particles. However, the efficiency of this biological pump of carbon strongly depends on the kind of phytoplankton, e.g. diatoms usually represent an export system (Buesseler, 1998), compared to cyanobacteria which are indicative for an ecosystem of regenerating nutrients and less export (Waterbury et al., 1986). Monitoring spatial and temporal variations of the distribution of dominant phytoplankton groups at the global scale is thus of critical importance.

So far observations of the back scattered solar radiation above the oceans by instrumentation on satellite platforms, so-called ocean color data, provide the opportunity to assess globally marine phytoplankton biomass (e.g. O'Reilly et al., 1998) which is used to model global distributions of phytoplankton primary production (Behrenfeld and Falkowski, 1997). Knowledge of the chlorophyll-*a* concentration, chl-*a*, is not sufficient to assess adequately 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. The intensity of both carbon fixation and export is however strongly dependent on the size and composition of cells. Quite a few current global numerical models which estimate the efficiency of the marine biological pump represent independently the main phytoplankton groups (e.g. Gregg et al., 2003; Le Quere et al., 2005; Moore et al., 2004). 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; as well 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

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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. It partly explains why empirical approaches applied to case-1 waters from ocean color data cannot retrieve chl-*a* with a higher accuracy than typically around 35% (e.g. O'Reilly et al., 2000; Melin et al., 2003; Murakami et al., 2006). 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 retrieved and in-situ measured chl-*a* estimates and 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 reconcile with global satellite data processing. In addition, they do not provide any biological or physical interpretation of the observed variability in water optical properties.

Bio-optical models were developed to account for the specific optical properties of species like coccolithophorids (e.g. Brown and Yoder, 1994), diatoms (Cota et al., 2003; Sathyendranath et al., 2004), the cyanobacteria *Synechococcus* (Morel, 1997) and N₂-fixing cyanobacteria *Trichodesmium* (Subramaniam et al., 2002). Several recent studies have attempted to retrieve information on multiple types of phytoplankton. Several studies were able to demonstrate the retrieval of three major size classes: Up to three size classes of phytoplankton in open ocean waters have been derived by algorithms, which were based on the biooptical relationships determined from a large biooptical and pigment in-situ data set; some were developed for certain oceanic re-

gions (Aiken et al., 2007; Raitsos et al., 2008), but also models have been developed to retrieve global distributions from ocean color data (Devred et al., 2006; Uitz et al., 2006; Hirata et al., 2008). In addition, two methods have been developed to retrieve up to five dominant phytoplankton groups: Alvain et al. (2005); (optimized in Alvain et al., 2008) developed an algorithm which can be globally applied to SeaWiFS data and yields five major dominant phytoplankton groups from an empirical approach based on their spectral effects on ocean color. Aiken et al. (2007) is applied to MERIS data and the southern Benguela ecosystem only. This method uses biooptical traits retrieved from a complex in-situ data set measured during one cruise to classify phytoplankton into three size classes, and then backscattering characteristics to subdivide the size classes into functional types. All above mentioned approaches, except for the method by Uitz et al. (2006), only identify the dominant phytoplankton functional group or size class. Uitz et al. (2006) enables through a thorough parameterization of a large global and depth resolved HPLC data base to derive from SeaWiFS chl-*a* directly the vertically resolved chl-*a* conc. of the three size classes. Besides that, it was not possible previously to derive the composition of different phytoplankton communities in respect to their contribution to different phytoplankton groups (functional types) from satellite observations. To do this is the objective of this study where high spectrally resolved satellite data were analysed and used to separate different phytoplankton groups.

The satellite sensor SCIAMACHY onboard the European satellite ENVISAT measures since 2002 successfully UV-VIS-NIR backscattering and solar spectra with high spectral resolution. SCIAMACHY was designed and is mainly used to derive geophysical information on the Earth's atmosphere. However, in a study by Vountas et al. (2007) it was shown that it is possible to identify phytoplankton absorption in SCIAMACHY visible earth spectra by using the Differential Optical Absorption (DOAS) method. The differential signal of the molecular absorbers along the optical path is used to retrieve slant columns of the absorbers from the satellite observations of solar backscattered electromagnetic radiation and the extra terrestrial solar measurements. In this study the phytoplankton absorption of a community with a well mixed species composition

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was identified within the satellite spectra. In addition, these data were analysed to derive the amount of phytoplankton along the effective under-water light path, by also exploiting the signal from vibrational Raman scattering by water molecules within the UV-A range of the SCIAMACHY spectrum. By that global phytoplankton biomass concentrations (chl-*a*) were derived which overall compared well with case I chl-*a* products of MERIS and MODIS ocean color data.

As part of the study presented here, the DOAS method was used for identifying the specific absorption signal of the different phytoplankton groups of cyanobacteria and diatoms. Globally distributed pigment concentrations for these characteristic phytoplankton groups for two monthly periods within 2004 and 2005 were derived. These satellite data on phytoplankton groups distribution have been compared to in-situ measurements and model calculations.

2 Instrumentation and methods

2.1 Satellite sensor SCIAMACHY and principles of retrieval technique DOAS

SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric CHartography; described in more detail in Burrows et al., 1995; Bovensmann et al., 1999) was launched on board ESA's ENVironmental SATellite, ENVISAT, in 2002. The instrument is designed to measure a broad band of solar radiation, spanning from the UV to the near infrared. One unique feature of SCIAMACHY is its ability to detect sunlight that has been transmitted, scattered and reflected in the Earth's atmosphere in different viewing geometries. In particular, the spectrometer continuously alternates between limb and nadir modes, this allows the observation of the same volume of air under different viewing angles, facilitating the separation of stratospheric and tropospheric components of molecular absorbers. The drawback of this potential is that no consecutive nadir measurements are provided. This study presented here exclusively uses spectra measured in nadir viewing and because of limb-nadir geometries alternating

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in SCIAMACHY the nadir scan along-track is therefore intermittent. The swath width for both measurement types is 960 km, implying global coverage in six days at the equator. The instrument takes backscatter measurements at high spectral resolution (in the UV-Vis.: 0.26–0.44 nm). The main objective of SCIAMACHY, as well as the new Ozone Monitoring Instrument (OMI) on AURA and GOME-2 (Global Ozone Monitoring Experiment-2) on METEOSAT, is to determine the abundances of atmospheric trace gases. Although SCIAMACHY is primarily an atmospheric mission, part of the detected solar radiation penetrates the ocean surface and picks up absorption and backscattering signals from sea water.

2.2 The retrieval technique: Differential Optical Absorption Spectroscopy (DOAS)

For our study the SCIAMACHY 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 by atmospheric constituents (e.g. Richter et al., 2005) or spectral re-distribution features as induced by the Ring effect (Vountas et al., 1998) or vibrational Raman Scattering (VRS) in ocean waters (Vassilkov et al., 2002; Vountas et al., 2003), or even from terrestrial plants (Wagner et al., 2007) and marine phytoplankton (Vountas et al., 2007). The high-frequency spectral structures are separated from the slowly varying attenuation due to molecular (Rayleigh) and aerosol (Mie) scattering by subtracting 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 30 km×60 km can be derived with this method from SCIAMACHY data (e.g. Richter et al., 2005).

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2.2.1 Retrieval of differential absorption by certain phytoplankton groups

The DOAS technique has been proven to be a powerful tool in atmospheric remote sensing. In this study its application to determine the different phytoplankton groups by the means of spectral absorption features is presented. The method is based on the DOAS method used to retrieve absorption of phytoplankton described in Vountas et al. (2007), but was refined in the following way:

- As described in Vountas et al. (2007) we accounted for unclear instrumental effects in SCIAMACHY spectra prior to the DOAS fit of phytoplankton absorption applied to a global monthly data set. SCIAMACHY data within the wavelength range of 425 to 499 nm were analysed by DOAS over a region with hardly any absorption by phytoplankton including the fitting of all pseudo-absorbers and absorbers as specified below except for phytoplankton. Then an Eigenvector analysis by Principal Component Analysis (PCA) was performed with the residuals from this regional DOAS-fit. In this study a different region for analysing the residuals was selected based on the criteria that both, cyanobacteria and diatoms, have very small absorption and the total phytoplankton biomass is below $0.05 \mu\text{g/l}$: the region chosen was 18°S to 28°S and 115°W to 125°W (as described in Morel et al., 2007).
- In a second step, the DOAS fit was applied to the global monthly data set within 429.0 to 495.0 nm accounting for all below specified absorbers, pseudo-absorbers, phytoplankton group absorption and the first Eigenvector from the PCA analysis.
- For fitting phytoplankton absorption, reference spectra specific for cyanobacteria and diatoms absorption obtained from absorption measurements at water samples from different regions in the Atlantic Ocean and characterised by pigment analysis (described in detail Sect. 2.3) were used.

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- To account for additional atmospheric constituents as molecular absorbers besides ozone and NO_2 , also the differential absorptions of the trace gases CHO-CHO and O_4 were fitted. Absorption cross sections were taken from Bogumil et al. (2003) for ozone, Burrows et al. (1999) for NO_2 , Greenblatt et al. (1990) for O_4 and Volkamer et al. (2005) for CHOCHO.
- For so-called pseudo-absorber spectra a ring spectrum calculated for SCIAMACHY application according to Vountas et al. (1998) was used.

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 σ , polynomial p , pseudo-absorber spectra such as a Ring spectrum r and phytoplankton absorption, to the measured optical depth $\tau(\lambda, \theta) = \ln(I/I_0)$, with I being the backscattered radiance, I_0 the extra-terrestrial irradiance. SCIAMACHY provides both measurements, from the Earth surface and atmosphere backscattered Sun light I and direct measurements of Sun light I_0 . τ is a function of the wavelength λ and the solar zenith angle θ (dependence omitted in the following).

The optical depth contains all radiative contributions from atmosphere and water including multiple scattering and surface reflectance effects. The fitting is formalized as a least square minimization where the target quantities called *slant column*, *scaling* or *fit factor* and the cross-sections for each trace gas, the phytoplankton absorption and the Ring-Effect are 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.

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2.2.2 Retrieval of cyanobacteria and diatoms chl-*a* concentrations from SCIAMACHY

In order to convert the extracted SCIAMACHY fit factor or slant columns of phytoplankton absorption specific for diatoms or cyanobacteria into concentration expressed as mg chl-*a*/m³ the method developed in Vountas et al. (2007) was applied where the combined SCIAMACHY information from the fits to VRS and specific phytoplankton absorption was used. VRS is a transspectral scattering process of clear water which leads to a filling-in of Fraunhofer lines in earthshine radiation spectra. This effect we can quantify by considering a pseudo-absorber VRS spectrum (from Vountas et al., 2007) in the DOAS-fit. The fit factor is assumed to have linear relation to the number of VRS scattering events in the fate of the lights path through the water and serves therefore as a proxy for the penetration depth. The extraction of the fit factor of VRS, S_v , from SCIAMACHY is described in detail in Vountas et al. (2007). Within the study presented here VRS was retrieved via a DOAS fit within the UV-A range for the same SCIAMACHY data set as for the cyanobacteria and diatom absorption fit. As described in Vountas et al. (2003; 2007) a bio-optical model from Morel (1988) has been used to describe the dependence of the elastic backscattering coefficient b_b . The backscattering coefficient scaled with the same factor as the VRS spectrum S_v is assumed to represent the true b_b for the phytoplankton absorption region. S_v has also to be converted from the wavelength window of the VRS DOAS-Fit (349.5 to 382 nm) to the window of the phytoplankton DOAS-fit (429 to 495 nm) which was done according to Bartlett et al. (2001). As b_b is the modelled penetration depth, $S_v * b_b^{-1}$ can be associated with the measured one. The fit factor S_{chl} for phytoplankton (or to be precise for the specific absorption spectrum) is given in [mg chl-*a*/m²] which is a mass column. If the penetration depth δ of light for the wavelength window considered is known this column can be converted into a concentration by the ratio: $C = S_{chl} / \delta$

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2.3 In-situ measurements of phytoplankton absorption and composition

For this study the absorption spectra measured on two surface water samples from two different cruises with research vessel RV “Polarstern” were used which were also analysed for the pigment composition using HPLC technique. The phytoplankton absorption was determined according to the method by Tassan and Ferrari (1995). In addition, for the ANTXXIII-1 cruise, the estimates of phytoplankton absorption were obtained from high spectral resolution measurements on the discrete water samples with a point-source integrating cavity absorption meter, PSICAM (Röttgers et al., 2005).

For the analysis of pigment composition of water samples from both cruises, the samples were immediately filtered on GF/F (Whatman) and stored at -80°C until analysis. The volume filtered was between one and 1–3 litres depending on the concentration of phytoplankton material in the water. The HPLC samples were measured as described by Hoffmann et al. (2006). The phytoplankton composition of the plankton community was classified into taxonomical groups applying the CHEMTAX program (Mackey et al., 1996). The input matrix was taken from Wright et al. (1996). Taxonomical phytoplankton groups are expressed in chlorophyll concentrations.

The specific spectra were chosen because they show high concentration of one of the two specific phytoplankton groups. The first absorption spectrum only composed of cyanobacteria was measured at a water sample taken from the ship’s moonpool via a pump during the cruise ANTXXIII/1 on 30 October 2005 at 22.3°N and 20.3°W at 12:50 GMT (further description of this cruise and the optical measurements are found in Stramski et al., 2008). The direct measurements using the PSICAM and the indirect measurements via the filtration method were in good agreement, but only the PSICAM method detected the absorption by phycoerythrine within the range of 530 to 570 nm (Fig. 1). Probably these pigments get already lost within the filtration process. The second absorption spectrum composed of around 80% diatoms was measured at a water sample taken by a CTD rosette sampler during the cruise the EIFEX cruise (ANTXXI/3) on 14 March 2004 at 49.4°S and 2.1°E at 05:50 GMT (further description

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of this cruise in Hoffmann et al., 2006).

3 Results

3.1 Phytoplankton absorption of cyanobacteria and diatoms from SCIAMACHY

Figure 1 shows the two chosen absorption spectra of the two in-situ measured phytoplankton groups (described in chapter 2.3) and a mixed phytoplankton community (from Bracher and Tilzer (2001), used in the study by Vountas et al. 2007) from samples taken in the Atlantic Ocean. After subtracting a low order polynomial the specific differential spectra are obtained (Fig. 2) which are used successively for fitting with PhytoDOAS within the wavelength range of 430 nm to 495 nm. These differential spectra show significant different structures, but correlate with pure water absorption (obtained from Pope and Fry, 1997). Therefore, no separate liquid water fit was performed and liquid water absorption was included with fitting the month specific Eigenvektor.

In Fig. 3 examples of the differential optical depths of the SCIAMACHY separate fits of different phytoplankton groups and of the results of the in-situ measured differential phytoplankton spectrum scaled with the fit-factor are shown. For both major phytoplankton groups, the cyanobacteria and the diatoms, there is a good agreement between the differential spectrum obtained from the PhytoDOAS-fit with SCIAMACHY satellite data and the in-situ measurement. The residuals of the same fit have very low values and are hardly differential (Fig. 4). These results support the conclusion of the good fit quality of phytoplankton group specific absorptions.

Figure 5 (upper panel) shows the monthly average of the global distribution of the fit factor (absorption strength) of cyanobacteria during the northern hemispheric fall and southern hemispheric spring (October/November 2005) retrieved from SCIAMACHY data with PhytoDOAS using the phytoplankton absorption spectrum typical for cyanobacteria. Their absorption appears mainly in the warmer seas of the subtropics and tropics, e. g. in larger parts of the Pacific, the Arabian Sea and off the West-African

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coast. Gaps in this global map are either due to that there have been neither cloud-free SCIAMACHY pixels for this region within this month nor there was no correlation of the SCIAMACHY data to the cyanobacteria absorption spectrum which means that this group was not present. Figure 5 (lower panel) shows for the same time period as Fig. 5 (upper panel) the global distribution of the absorption strength of diatoms retrieved with PhytoDOAS from SCIAMACHY. SCIAMACHY data show for this time of the year that diatoms show high absorption within the from the sensor detected water column at the coastal areas around up-welling regions at the West-American and West-African coasts and in the Southern Ocean.

3.2 Biomass of cyanobacteria and diatoms from SCIAMACHY

Figure 6 (upper panel) shows the monthly average of the global distribution of cyanobacteria biomass (expressed as chl-*a* conc.) for the same time period (Oct/Nov 2005) shown in Fig. 5 retrieved from SCIAMACHY data with PhytoDOAS. Cyanobacteria appear mainly in the warmer seas of the subtropics and tropics, e. g. in larger parts of the Pacific, the Arabian Sea and off the West-African coast. The distribution of cyanobacteria retrieved from SCIAMACHY data agrees well with the calculations made by the NASA Ocean Biochemical Model (NOBM, see Fig. 6 lower panel) developed by Gregg and Casey (2007). Also a first comparison with 5 match-ups of in-situ measurements from the Oct–Nov 2005 ANTXXIII-1 cruise (there were no match-ups for cyanobacteria for the EIFEX (ANTXXI-3) cruise) show a reasonable agreement with an moderate underestimation of cyanobacteria conc. by the SCIAMACHY PhytoDOAS in comparison to in situ data (details of this comparison in Table 1): the relative deviations range from around –4% to –70% and the absolute deviation from 0.003 to 0.098 mg m⁻³ chl-*a* between SCIAMACHY and the in-situ data.

Figure 7 shows for the same time period as Fig. 6 the global distribution of diatoms biomass retrieved with PhytoDOAS from SCIAMACHY (upper panel) and from calculations made for diatoms with the NOBM Model (lower panel). As expected from punctual measurements on water samples during various ship cruises and as cal-

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culated by the NOBM model also the analysis of the SCIAMACHY data shows that during hemispheric fall and southern hemispheric spring diatoms are quite abundant and the dominant group in the Southern Ocean (below 32° S) and at the coastal areas around up-welling regions at the West-American and West-African coasts. A first comparison with 5 match-ups of in-situ measurements from the February–March 2004 EIFEX cruise (there were no match-ups for diatoms for the October–November 2005 ANTXXIII-1 cruise) show a reasonable agreement of diatoms chl-*a* conc. from SCIAMACHY PhytoDOAS in comparison to in situ data (details of comparison in Table 2): the relative deviations range from around +40% to –23% and the absolute deviation from 0.025 to 0.255 mg m⁻³ chl-*a* between SCIAMACHY and the in-situ data.

4 Discussion and conclusions

Within this study for the first time high spectrally resolved satellite data were used to derive information on two major phytoplankton functional types, cyanobacteria and diatoms. Our SCIAMACHY satellite maps on the distribution of cyanobacteria and diatoms show overall a very good agreement with in-situ measurements on phytoplankton absorption and concentrations of these particular groups which are spatially and temporally collocated. Furthermore, their global distribution is in qualitative agreement with the calculations based on the NOBM model. These model simulations combine global ocean colour biomass data with global data sets on nutrient distributions, sea surface temperature and current conditions (Gregg et al., 2003). SCIAMACHY fit results for absorption by phytoplankton representing cyanobacteria and representing diatoms are of high quality with very little residuals and the first comparisons to in-situ data and model results give already a high confidence in the method.

In accordance to punctual measurements on water samples during various ship cruises and as calculated by the NOBM model, also the analysis of the SCIAMACHY data shows that during hemispheric fall and southern hemispheric spring diatoms are quite abundant and the dominant group in the Southern Ocean and at the coastal

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5 areas around up-welling regions at the West-American and West-African coasts. Diatoms are the phytoplankton group which contributes most to global carbon fixation and account for about 40% of the total marine primary production. Compared to most other plankton species, they need silicic acid (=silicate) to built their cell walls and therefore
10 diatoms blooms predominantly occur, where there are sufficient nutrients (Treguer et al., 1995). Usually these areas are where cool and nutrient-rich waters come to the surface (mainly cool waters in the higher latitudes during spring-summer) and coastal areas. Diatoms are known to aggregate and sink out, which is an important aspect in their life cycle, which serves as an important transport vehicle of organic material below the wind mixed layer (Nelson et al., 1995). Diatoms are further grazed by zooplankton, which produces big, fast-sinking faecal pellets with high sinking velocity. Therefore diatoms are representative for ocean export ecosystems in which nutrients and carbon are fast removed from the productive surface waters before they can be remineralised. Therefore diatoms are very important for biogeochemical cycles of carbon (C), nitrogen (N), phosphorus (P), silicon (Si) and iron (Fe) and referred to be the main drivers of export production (Smetacek, 1985).

15 The SCIAMACHY PhytoDOAS and the NOBM model show that cyanobacteria appear mainly in the warmer seas of the subtropics and tropics, e.g. in larger parts of the Pacific, the Arabian Sea and off the West-African coast, typical regions of low nutrients. Within cyanobacteria there are two different strategies to circumvent the nutrient depletions. The unicellular and colony forming cyanobacteria are capable to use atmospheric dinitrogen gas (N₂) and catalyse it to ammonia and introduce this way new formed nitrogen into the system (Zehr et al., 2001; La Roche et al., 2005). The other important cyanobacteria are the two small unicellar cyanobacteria *Synechococcus* and
20 *Prochlorococcus*. These are the main source of primary production in oligotrophic regions and are specialized in the nutrient limited conditions by their ability to use organic nitrogen (Zubkow et al., 2003). They can be considered as typical life form responsible for trapping nutrients in the surface ocean and being of minor role for global carbon export (Moran et al., 2004).

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By using PhytoDOAS on SCIAMACHY data it is possible for the first time to produce a near-real time picture in the open ocean of distributions in chl-*a* conc. of two phytoplankton groups on a global scale which each of them plays an important role within the global silicate or nitrogen budget, respectively, and has a different function within the marine ecosystem. As pointed out before, other methods to identify phytoplankton functional types PFTs- (Alvain et al., 2006; Devred et al., 2006; Aiken et al., 2007; Raitzos et al., 2008; Hirata et al., 2008) have only the potential to identify the dominating groups within the total chl-*a* biomass derived from remote sensing ocean color data. All these methods as well as the one developed by Uitz et al. (2006) to detect PFTs are empirical algorithms which are based on training of a neural network (Raitzos et al., 2008), parameterisation (all the other methods) of a large global or regional in-situ data set in order to get from satellite chl-*a* or normalised leaving radiances the PFTs. Unexpected changes in these relationships between these parameters due to a regional or temporal sampling bias lead to a bias in the detection of PFTs. In contrast, the PhytoDOAS method exploits the information of the whole spectrum and enables by the DOAS technique a reliable atmospheric correction which in common ocean colour retrievals a large source of errors introduced in the chl-*a* algorithm. In addition, this analytical method enables to directly retrieve the chl-*a* conc. of diatoms and cyanobacteria without assuming an empirical relationship. By that it is possible to detect changes in the global distribution of these PFTs biomass which are not foreseen. With this method it is also possible to get the depth until which the satellite picks up optical signals from the ocean; by that the PFT biomass derived is given as a depth-integrated mean over this depth while the other PFT methods, besides Uitz et al. (2006), give estimates for the surface only without a knowledge how much the chl-*a* conc. from deeper layers influence the estimate. The limitations to our method are the rather coarse resolution of SCIAMACHY pixels with at best 30 km to 30 km and a global coverage which is only about half as good as pixels from common ocean color sensors such as SeaWiFS, MERIS or MODIS. But, as stated by Aiken et al. (2007) phytoplankton distributions may be geographically distributed over 50 to 100 km and these structures persist over

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a few days.

Future objectives are to work on the extraction of additional biooptical information by synergistically using high spectrally (besides SCIAMACHY extend the analysis to the newer sensors GOME-2 and OMI) and high spatially resolved satellite data (MERIS, MODIS) in order to develop global data sets covering a time period of 10+X years. In detail, it is planned to intensively validate the satellite biooptical data with ship-based measurements on phytoplankton samples and the above-surface and underwater light. This additional biooptical satellite information shall be used for developing near-real time picture of the distribution of other than cyanobacteria and diatoms major phytoplankton groups (e.g. coccolithophorids, dinoflagellates) and an improved MERIS phytoplankton biomass retrieval. This new information shall be used as an input basis for primary production modelling and for developing improved atmospheric trace gas retrievals by accounting for the oceanic optical signal. The maps on the distribution of major phytoplankton groups and marine primary production are planned to be used within several climate change studies (e.g. identifying biogenic sources of greenhouse gas and short lived halogenated species, carbon cycle estimations).

Acknowledgements. The authors thank the crew, principal investigators and other scientists onboard the RV Polarstern cruises ANT XIII-2, ANT XXI-3 and ANT XXIII-1 for their support. We thank DLR and ESA for SCIAMACHY level-1 data. The images and data used to calculate the phytoplankton group distributions of cyanobacteria and diatoms with the NOBM model were acquired using the GES-DISC Interactive Online Visualization ANd aNalysis Infrastructure (Giovanni) as part of the NASA's Goddard Earth Sciences (GES) Data and Information Services Center (DISC). Funding has been supplied by the Deutsche Forschungsgemeinschaft (DFG) via the project PASAT, the Helmholtz Impuls and Network Fond, the Alfred-Wegener-Institute.

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Table 1. Comparison of chl-*a* conc. of cyanobacteria from SCIAMACHY PhytoDOAS and from in-situ measurements at collocated collocations (within 12 h and 180 km) in October–November 2005 (no collocations in February–March 2004). The mean of the absolute (SCIA – in-situ) and relative deviation ((SCIA – in-situ)/in-situ) is given.

Date	SCIAMACHY chl- <i>a</i> (mg/m ⁻³) and location	In-situ chl- <i>a</i> (mg/m ⁻³) and location	Mean absolute deviation and relative deviation
20051028	0.084 0.80 0.085 0.052 0.110 Mean: 0.408 at 10:00–11:00 29°–30° N/16°–17° W	0.085 0.086 Mean: 0.383 at 13:00–14:00 29.4°–30.2° N/16.2°–16.3° E	Absolute: 0.003 mg/m ⁻³ Relative: –3.86%
20051029	0.017 0.020 0.035 0.044 0.051 Mean: 0.029 at 11:00–12:00 25° N/17°–18° W	 at 13:25 25.3° N/17.5° W	Absolute: –0.022 mg/m ⁻³ Relative: –43.17%
20051101	0.087 0.128 0.093 0.173 0.157 0.197 Mean: 0.139 at 11:00–12:00 10–13° N/21° W	0.160 0.168 Mean: 0.164 at 13:00–21:00 12.3°–13.5° N/20.1°–20.5° W	Absolute: –0.025 mg/m ⁻³ Relative: –15.24%
20051102	0.088 at 10:00–11:00 10° N/19° W	0.128 at 21:00 9.2° S/19.2° W	Absolute: –0.040 mg/m ⁻³ Relative: –14.29%
20051106	0.244 0.236 0.232 0.227 0.232 0.252 0.268 Mean: 0.241 at 10:00–11:00 0°–2° S/10°–11° W	0.143 0.150 0.134 Mean: 0.142 at 01:30–13:30 1.5°–2.1° S/10.1°–11.2° W	Absolute: 0.098 mg/m ⁻³ Relative: –69.4%

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Table 2. Comparison of chl-*a* conc. of diatoms from SCIAMACHY PhytoDOAS and from in-situ measurements at collocated collocations (within 12 h and 180 km; except for 14 March 2004 which is 250 km) in February–March 2004 (no collocations in October–November 2005). The mean of the absolute (SCIA – in-situ) and relative deviation ((SCIA – in-situ)/in-situ) is given.

Date	SCIAMACHY chl- <i>a</i> (mg/m ⁻³) and location	In-situ chl- <i>a</i> (mg/m ⁻³) and location	Mean absolute deviation and relative deviation
20040209	0.446 0.242 0.481 0.463 Mean: 0.408 at 08:00–09:00 50° S–51° S/0° E–1° E	0.228 0.429 0.328 0.428 0.443 0.330 0.492 Mean: 0.383 at 03:00–21:00 48.8°–50.8° S/1.8°–2.1° E	Absolute: 0.025 mg/m ⁻³ Relative: +6.55%
20040210	0.568 0.502 Mean: 0.534 at 08:00–09:00 49.2°–49.5° S/6.0° E	0.273 0.360 0.491 0.405 Mean: 0.382 at 07:00–18:00 49.4°–50° S/2.5°–3.5° E	Absolute: 0.152 mg/m ⁻³ Relative: +39.76%
20040216	0.379 0.287 0.335 0.406 Mean: 0.352 at 08:00–09:00 51.2°–51.6° S/3.5°–4.2° E	0.320 0.217 0.207 0.182 Mean: 0.232 at 09:00–16:00 49.8°–50.4° S/1.9° E–2.3° E	Absolute: 0.070 mg/m ⁻³ Relative: +30.17%
20040309	0.373 at 08:00–09:00 47.6° S/2.9° E	0.510 0.381 0.402 0.231 Mean: 0.381 at 01:00–13:00 49°–49.4° S/1.7° E–2.5° E	Absolute: –0.008 mg/m ⁻³ Relative: –2.10%
20040314	0.857 at 08:00–09:00 46.0° S/8.7° E	1.070 0.581 1.685 Mean: 1.112 at 06:00–21:00 49.4°–49.6° S/1.7° E–2.1° E	Absolute: –0.255 mg/m ⁻³ Relative: –22.93%

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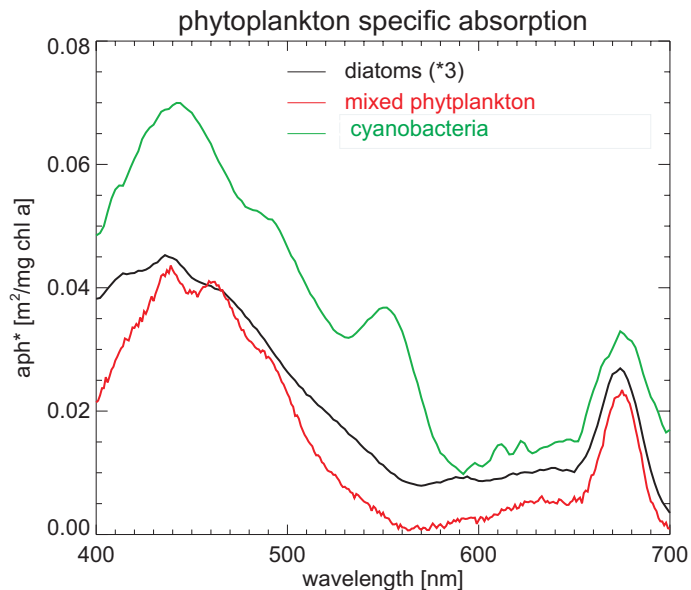


Fig. 1. Spectra of pigment-specific phytoplankton absorption determined in water samples of three different ship cruises with RV Polarstern within the Atlantic Southern Ocean: A phytoplankton absorption spectrum of a phytoplankton community dominated by over 80% diatoms measured during EIFEX cruise (ANTXXI-3) on 14 March 2004 at 46° S and 9° W (Diatoms=black) scaled by the factor of 3, a spectrum from a phytoplankton community with only cyanobacteria (green) measured during ANTXXIII-1 cruise on 29 October 2005 at 23° N and 22° W and scaled by factor 0.1, and a spectrum from a mixed phytoplankton spectrum (red; adapted from Bracher and Tilzer, 2001) measured during ANTXXII-2 on 17 January 1996 at 57° S and 6° E.

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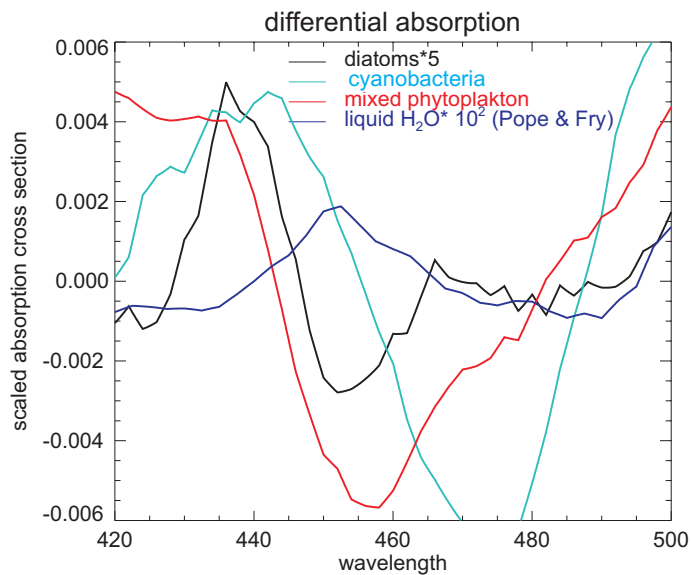


Fig. 2. Differential absorption of three in-situ measured phytoplankton absorption spectra shown in Fig. 1 and of pure sea water according to Pope and Fry (1997).

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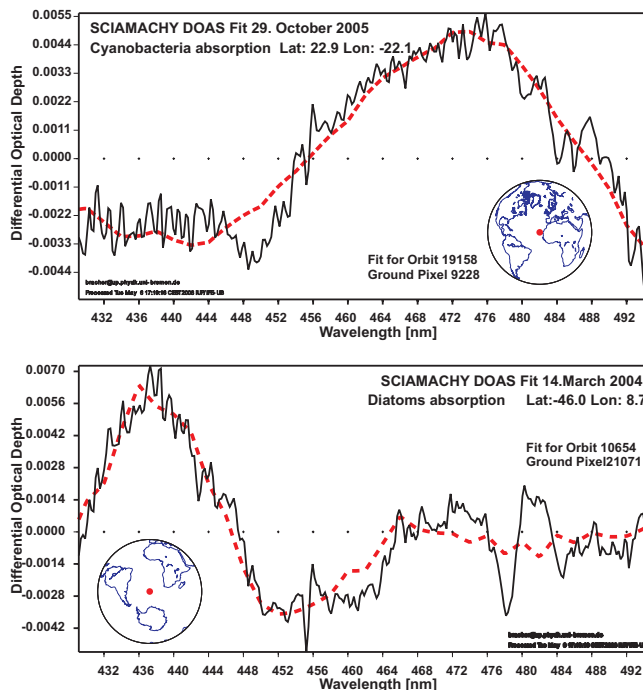


Fig. 3. Differential Optical Depth of a spectral PhytoDOAS fit with SCIAMACHY data (black) for a specific phytoplankton group (upper panel: for cyanobacteria and lower panel: for diatoms) using the phytoplankton group specific differential absorption cross sections from Fig. 2 and showing the scaled in-situ phytoplankton differential absorption (red) of the specific group. For the example in the upper panel the in-situ measurement for cyanobacteria (details described in Fig. 1) was taken and the SCIAMACHY measurement was within 20 h and 50 km of this in-situ measurement. For the example in the lower panel the in-situ measurement for a community dominated by diatoms (see details given in Fig. 1) was taken and the SCIAMACHY measurement was within 2 h and 200 km of the in-situ measurement.

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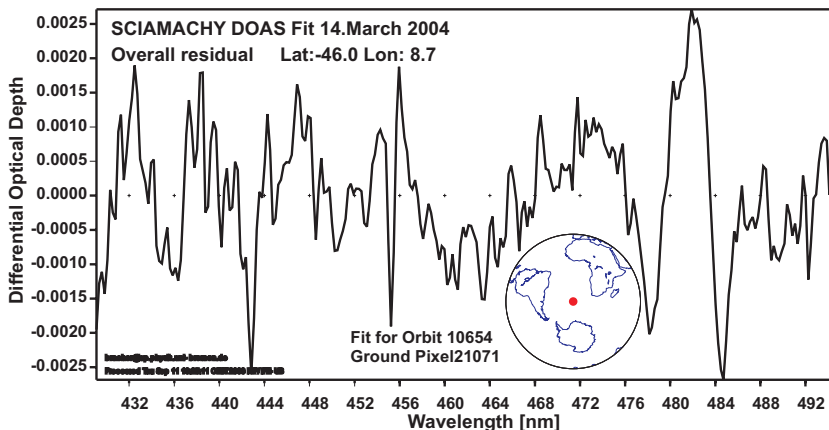
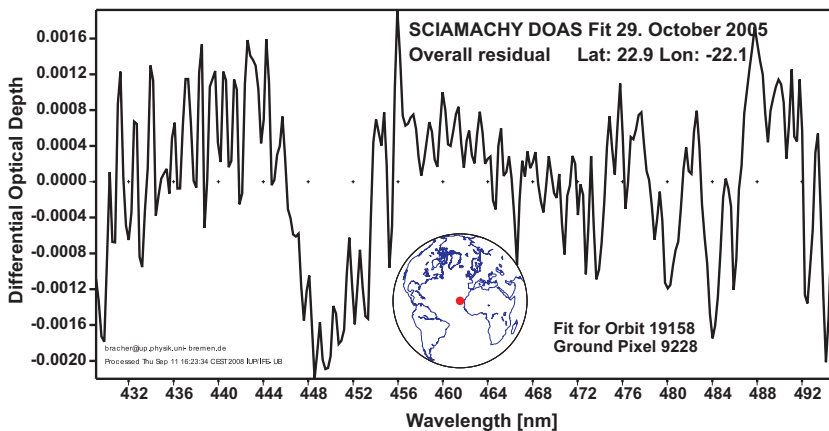


Fig. 4. Residuals of spectral DOAS fit with SCIAMACHY data (black) for a specific phytoplankton group (upper panel: for cyanobacteria and lower panel: for diatoms) for the same examples shown in Fig. 3.

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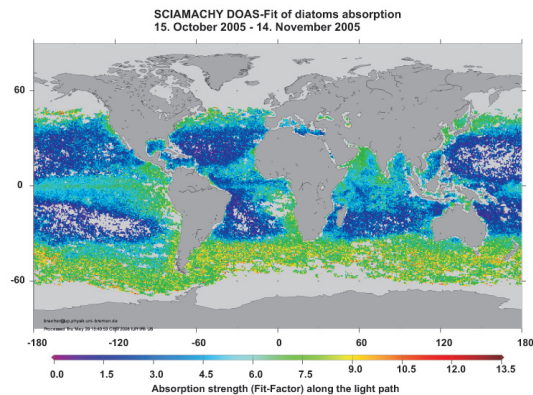
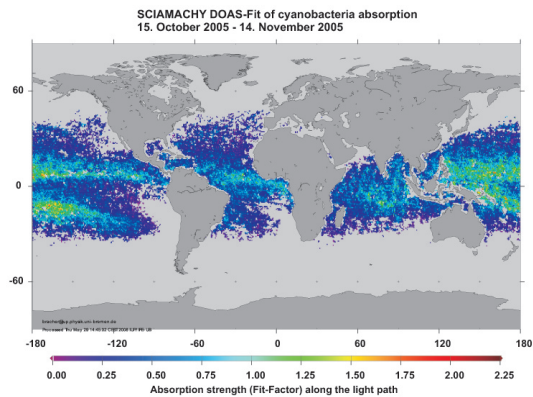


Fig. 5. Monthly average (from 15 October to 15 November 2005) of global distribution of cyanobacteria (upper panel) and diatoms (lower panel) obtained as “Strength of Absorption” (=Fit-Factor) by using PhytoDOAS with SCIAMACHY.

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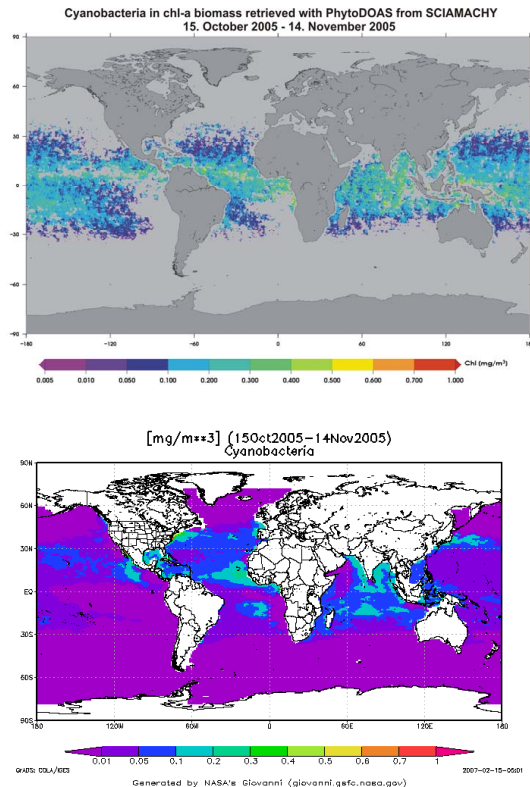


Fig. 6. Monthly average (from 15 October to 15 November 2005) of global distribution in chl-a conc. of cyanobacteria determined by using PhytoDOAS with SCIAMACHY data (upper panel) and from calculations with the NOBM model by Gregg and Casey (2007) (lower panel, figure from <http://reason.gsfc.nasa.gov/OPS/Giovanni/ocean.modelDay.2.shtml>).

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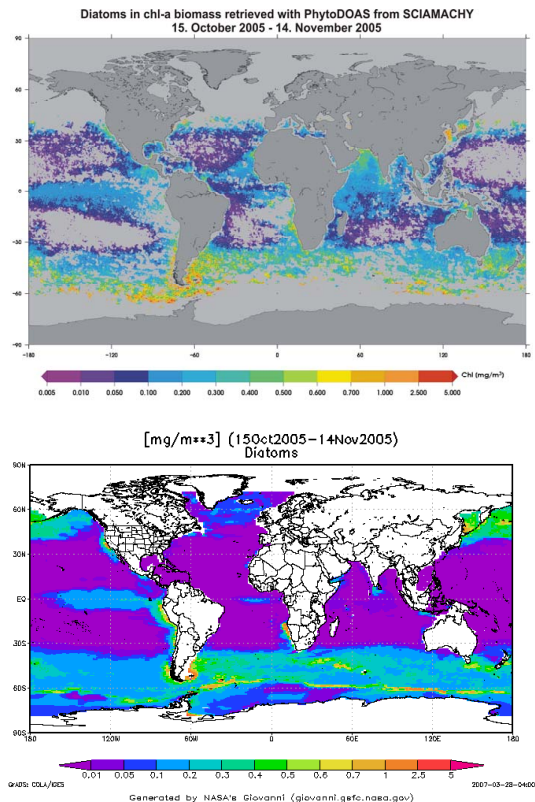


Fig. 7. Monthly average (from 15 October to 15 November 2005) global distribution in chl-a conc. of diatoms determined by using the PhytoDOAS with SCIAMACHY data (upper panel) and from calculations with the NOBM model by Gregg and Casey (2007) (lower panel, figure from <http://reason.gsfc.nasa.gov/OPS/Giovanni/ocean.modelDay.2.shtml>).

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