Remote sensing and DMS

By Femkje Sierdsma

Remote Sensing and DMS

by Femkje Sierdsma

Date: November 2002

Supervisor: Wim Klaassen
Department: Marine Biology of the University of Groningen

On the frontpage: Satellite image of chlorophyll distributions in October 2002 from the
SeaWiFS homepage http://seawifs.gsfc.nasa.gov

Abstract

Oceanic dimethylsulphide (DMS) is one of the major sources of sulphur to the atmosphere. Sulphur, in the form of sulphate in the atmosphere, is known to have a climate effect, through the backscattering of solar radiation or through cloud condensation nuclei (CCN) which increase cloud albedo.

In the eighties the CLAW feedback hypothesis was formulated. It states that if an increase in ocean temperature (e.g. due to global warming) leads to an increase in the production of the DMS precursor dimethylsulphoniopropionate (DMSP), and thus to DMS, this would result in a cooling effect of the planet due to an increase in cloud albedo. Since the postulation of the climate feedback hypothesis many papers have been published discussing the biochemistry of DMS (and its precursors) and its link to climate.

It is important to quantify the concentrations of DMS in the ocean and the flux to the atmosphere. Classical measurements of DMS rely on shipboard observations and experiments, but the methodology is intrinsically limited to small space and time scales. Satellite remote sensing offers the potential for synoptic, global observation of the oceans and could resolve many of the current uncertainties, but can remote sensing be used to determine DMS concentrations in the ocean and the DMS flux to the atmosphere?

Satellite instruments measure ocean colour by detecting the upwelling radiance in a number of wavelengths which correspond to high, medium and low absorption by phytoplankton pigments (chlorophyll). Thus, sensors measure chlorophyll (Chl) concentrations instead of DMS. Once a Chl-DMS link is established, it would be very easy to predict DMS values in the water, but some fences have to be taken. Until now, no tight relations have been found, but the species composition seems to be an important factor influencing DMS concentrations and models have been developed. It should be possible to use remote sensing to determine DMS concentrations in the ocean and the flux to the atmosphere, when the DMS cycling processes are well understood.

Table of contents

Introduction

The oceans play a fundamental role in the global climate system on account of their capacity to store and transport heat and absorb and emit trace gases, which directly or indirectly affect the earth's radiation budget [Aiken et al., 1992].

Oceanic dimethylsulphide (DMS) is one of the major sources of sulphur to the atmosphere [Kwint, 1997 and Gondwe et al., *in press*]. Sulphur, in the form of sulphate in the atmosphere, is known to have a climate effect, through the backscattering of solar radiation or through cloud condensation nuclei (CCN) which increase cloud albedo. Low concentrations of DMS in the water and the atmosphere can be found in all marine areas. High concentrations often coincide with blooms of specific marine phytoplankton species [Stefels, 1997].

In the eighties (1987) the CLAW feedback hypothesis was formulated by, and named after, Charlson, Lovelock, Andreae and Warren. It states that if an increase in ocean temperature (e.g. due to global warming) leads to an increase in the production of the DMS precursor dimethylsulphoniopropionate (DMSP), and thus to DMS, this would result in a cooling effect of the planet due to an increase in cloud albedo. So, biological regulation of the climate could be possible through the effects of temperature and sunlight on phytoplankton population and DMS production. To counteract the warming due to doubling of atmospheric CO_2, an approximate doubling of CCN would be needed [Charlson et al., 1987].

It was originally thought that phytoplankton produce DMS directly, but this is not true. Phytoplankton form DMSP. Part of the DMSP is then converted to DMS. This occurs outside the algal cell. In the marine mixed layer DMS is subject to a number of removal mechanisms, including emission to the atmosphere but this is only a small fraction. The DMS that escapes to the air reacts to form sulphate and methane sulphonate (MSA) aerosols. These non-sea-salt (NSS) sulphate (SO_4^{2-}) aerosols are found everywhere in the marine atmospheric boundary layer. The aerosol particles act as cloud-condensation nuclei (CCN) in the marine atmosphere. They have a direct backscattering effect on solar radiation and an indirect effect through the formation CCN that increase the global cloud albedo [Charlson et al., 1987].

Since the postulation of the climate feedback hypothesis many papers have been published discussing the biochemistry of DMS (and its precursors) and its link to climate. The potential of DMS to affect the radiative balance and climate seems well established. However, tests of whether this constitutes a self-regulated plankton-climate interaction, as suggested by Charlson et al., have remained elusive, essentially because little is known about the feedback effects of climate on marine DMS production. The possible role of DMS was studied by scientists from roughly two disciplines, with emphasis either on the atmospheric (figure 1) or the aquatic environment (figure 2) [Kwint, 1997].
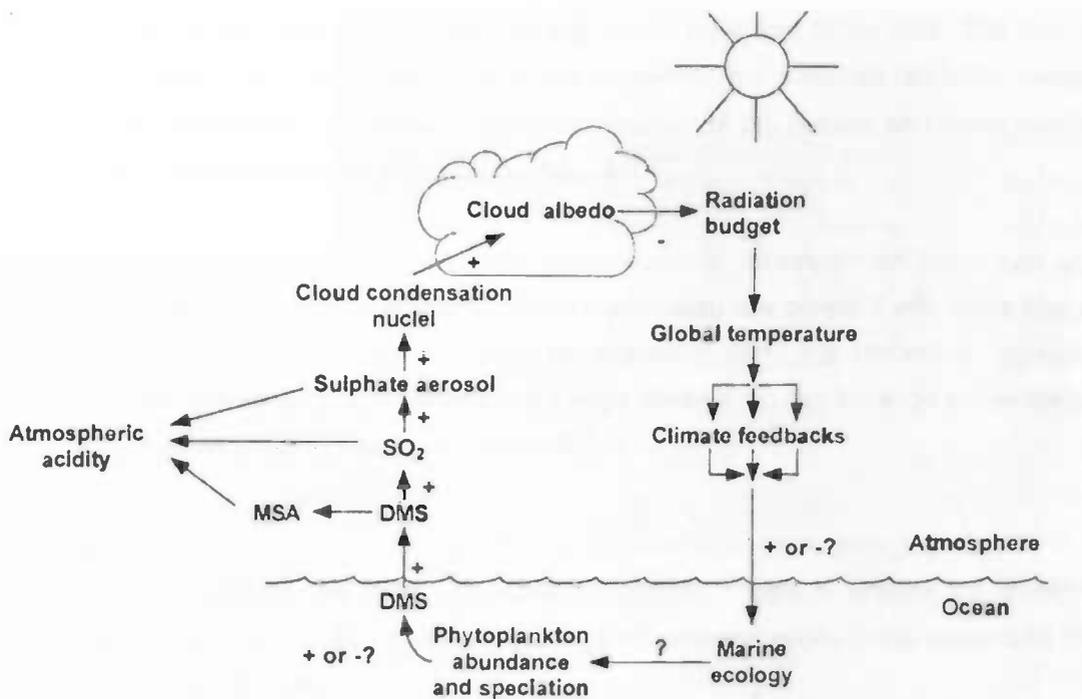
Figure 1. Schematical representation of the "atmospheric" point of view in DMS studies.
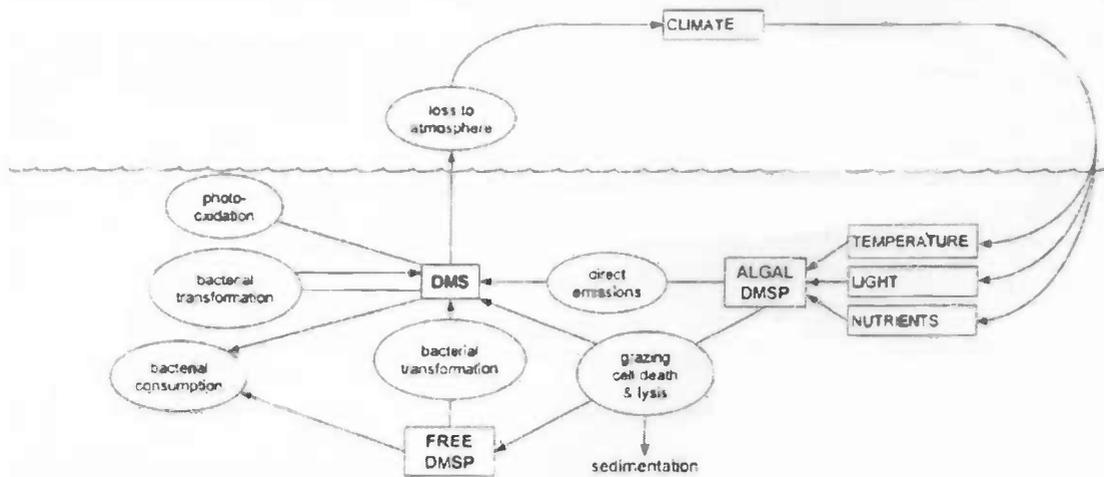

Figure 2. Schematical representation of the "aquatic" point of view in DMS studies.

Measurement of DMS

It is important to quantify the flux of DMS to investigate its impact on atmospheric chemistry and radiative transfer to clarify for example whether the change in albedo, caused by DMS, will cause a positive or negative feedback on the climate. DMS is produced by algae (indirectly via DMSP), but how efficient is this production? How much DMS is in the water and how much DMS is emitted to the atmosphere?

As DMS is a product of the biological activity, it is expected to show large seasonal variations, especially in the high latitudes [Aumont et al., 2002]. Classical measurements of DMS rely on shipboard observations and experiments, but the methodology is intrinsically limited to small

space and time scales, and many regions of the ocean have few or no data. The lack of observations means that short-lived events are frequently not sampled. Satellite remote sensing offers the potential for synoptic, global observation of the oceans and could resolve many of the current uncertainties [Joint and Groom, 2000].

The advantages of satellites over convential oceanographic measurement techniques are clear: satellites sample over much greater space scales than are possible with ships and at frequencies which are impossible to match by any other sampling procedure. Synoptic sampling at high frequency is now possible over large oceanic regions because ocean colour satellites are now operational [Joint and Groom, 2000].

Question

Based on the hypothesis that DMS influences the climate, I want to answer the question whether remote sensing can be used to determine DMS concentrations in the ocean and the DMS flux to the atmosphere.

Remote sensing

Definition of remote sensing

In 1960 the name remote sensing was first coined. It simply referred to the observation and measurement of an object without touching it. Nowadays, remote sensing can be described more specifically as the science of sensing and recording reflected or emitted energy to acquire information about the Earth's surface without actually being in contact with it [http://ccrs.nrcan.gc.ca]. It is being applied in several fields, like the geography, geology, botany, zoology, civil engineering, forestry, meteorology, agriculture and oceanography.

In the oceanography remote sensing is concerned with how much sunlight is backscattered out of the sea, from what depth, and whether the magnitude and colour of the reflected light conveys information about the optically active constituents of seawater [Robinson, 1990], but is also concerned with the measurement of wind, temperature and waves. Satellite marine remote sensing data now offer daily global maps of surface chlorophyll, temperature, surface wind speed, aerosol optical depth and other parameters. However, other data such as nutrients and ecological rate constants still need to be derived from field or laboratory experiments [Gabric et al., 2001].

Working of remote sensing

A remote sensing system using electromagnetic radiation, has four components: a source, interactions with the Earth's surface, interaction with the atmosphere and a sensor:

➤ Source: may be natural like the Sun's reflected light or the Earth's emitted heat, or man made.

➤ Earth's surface interaction: amount and characteristics of radiation emitted or reflected from the Earth's surface is dependent on the characteristics of the objects on Earth's surface.

➤ Atmospheric interaction: electromagnetic energy passing through the atmosphere is modified and scattered.

➤ Sensor: the electromagnetic radiation that has interacted with the surface of the Earth and atmosphere is recorded by a sensor, for example a radiometer or camera.

Electromagnetic radiation occurs in a continuum of wavelengths and frequencies from short wavelength, high frequency cosmic waves to long wavelength, low frequency radio waves. The wavelengths that are of greatest interest in remote sensing are visible and near-infrared radiation in the waveband 400-3000 nanometer (nm), infrared radiation in the waveband 3000-14000 nm and microwave radiation in the waveband 5-500 millimetre [Curran, 1985].

Ocean colour is an important indicator of phytoplankton, yellow substance and suspended sediments [http://envisat.estec.esa.int]. For the measurement of ocean colour, only wavelengths in the visible and near-infrared are used (see table 1).

Table 1. Overview of the visible and near-infrared part of the wavelength spectrum used for the measurement of ocean colour.

Wavelength	Colour
443 nm	Blue
520 nm	Green
550 nm	Yellow
670 nm	Red
750 nm	Near IR

The basic principle of satellite remote sensing of watercolour is as follows. The satellite measures radiance, which consists of an atmospheric component and a waterleaving component, at the top of the atmosphere. The atmospheric component, which may be over 80% of the measured radiance even under cloud-free conditions, consists of molecular (Rayleigh) and aerosol scattered light. The Rayleigh component can be calculated and removed, and the aerosol component may be estimated from a measurement at a red or infrared wavelength where the waterleaving radiance is assumed to be zero. This process is known as atmospheric correction [Aiken et al., 1992].

Water absorbs near-infrared and middle-infrared wavelength strongly, leaving little radiation to be either reflected or transmitted. On land, vegetation or soil also reflects only a small part of the radiant flux, but this percentage is still much higher than the reflectance by water (up to 5% is reflected by water, and up to 20% by land). This results in a sharp contrast between any water and land boundaries [Curran, 1985].

Ocean colour represents mean distribution of radiant energy as a function of wavelength [Muralikrishna, 1983] and is governed by the optical properties of seawater, suspended particles and coloured dissolved organic matter. Water and its constituents affect the passage of light by scattering and absorption [Joint and Groom, 2000]. Phytoplankton absorb the sunlight required for photosynthesis using pigments such as chlorophyll (Chl) [Groom and Lavender, 1998]. The relationship between ocean colour and Chl concentration is influenced by the physical characteristics of phytoplankton populations, such as the size of the cells, and the concentration and composition of intracellular pigment [Sathyendranath, 1989]. The combined effects of pigments and physiological structure give all healthy green cells their characteristic reflectance properties: low reflectance of red and blue light, medium reflectance of green light and high reflectance of near-infrared radiation. The major differences in reflectance between species, are dependent upon algal size which affects both pigment

content and physiological structure [Curran, 1985]. Remote sensing can only visualise the size of an algal bloom, since single algal cells are too small to be measured from space.

Oligotrophic waters have a blue appearance. When phytoplankton concentrations increases, the spectral waterleaving radiance becomes darker and greener [Joint and Groom, 2000]. Therefore most of the attempts made by several ocean colour research investigators to determine concentrations of phytoplankton till now are based on the evaluation of ratio of spectral data in blue and green channels and correlation of this ratio with Chl [Muralikrishna, 1983]. The advantage of relating the pigment concentration to the ratios of radiances at various wavelengths rather than to absolute radiances is that the influence of other material in the water as well as the masking of the atmosphere is partially compensated [Gordon et al., 1980].

Most ocean colour remote sensing sensors are aboard of polar orbiting satellites follow an overhead path around the Earth so that they pass close to the North and South Poles. They orbit the Earth as it turns beneath them. By so doing, a different part of the Earth's surface is viewed on each successive orbit. In this way the entire Earth is covered, with a small amount of overlap at low latitudes, and a greater overlap at higher altitudes. Satellite orbits can be controlled so that they view the same latitude on the Earth's surface at the same local sun time (referred to as sun-synchronous).
The altitude of the satellite can affect the detail. At higher altitudes one satellite visits the same place more frequently, but the information obtained is less detailed. At lower altitudes the satellite visits less frequently, but more detailed information is acquired. It should be noted that not all sensors have the same resolution. Most ocean-colour sensors are on satellites at an altitude of around 700-800 km [http://www.ioccg.org].

- Historic Satellite Ocean Colour Sensors (CZCS, OCTS, POLDER)
- Current Satellite Ocean Colour Sensors (MOS, SeaWiFS, OCI, OCM, MODIS-TERRA, MODIS-AQUA, MISR, OSMI, MERIS)
- Scheduled Satellite Ocean Colour Sensors (MODIS-AURA, GLI, POLDER-2, S-GLI)

What is measured with remote sensing?
Satellite instruments measure ocean colour by detecting the upwelling radiance as 'seen' through the Earth's atmosphere in a number of wavebands which correspond to high, medium and low absorption by phytoplankton pigments [Joint and Groom, 2000]. The optical properties of the water constituents are converted to pigment or suspended matter concentration units [http://envisat.estec.esa.int].

Phytoplankton cells are small, with cell dimensions ranging from <1μm to a few tens or perhaps hundred μm. How can they be measured by a satellite at a distance of hundreds of kilometres? Of course, individual cells cannot be visualised but, on a typical pixel of 1-km resolution, the signal of phytoplankton pigments is readily detected in satellite images. So,

distribution patterns of those pigments are visualised and, more important, concentrations can be accurately quantified due to recent advances [Joint and Groom, 2000].

Almost all oxygenic phytoplankton contain Chl in their reaction centers, as well as in their antenna to increase the rate of photon absorption. Chl absorbs strongly in the blue-green and red regions of the light spectrum and the absorbed excitation energy is used to promote the photochemical reaction. The magnitude of the absorption of blue and blue-green photons is used to quantitatively derive the concentration of photosynthetic pigments in the upper portion of the water column and is the basis for estimating phytoplankton concentrations from space [Falkowski et al, 1998]. This absorption causes the solar radiation backscattered out of the ocean at 443 nm (blue) to decrease rapidly with increasing Chl concentration. The Chl absorption is much weaker at 520 (green) and 550 nm (yellow). Therefore, an increase in Chl causes the backscattered radiance to increase at these wavelengths as a result of the scattering associated with the phytoplankton. Thus water that is poor in Chl will appear a deep blue in sunlight, whereas water rich in Chl will appear green [Gordon et al., 1980] Phytoplankton abundance (~ Chl content) varies from less than 0.03 mg/m^3 in oligotrophic waters, up to about 30 mg/m^3 in eutrophic waters. Ocean colour responds in a non-linear way to these large changes in Chl content. It is conveniently depicted by the ratio of blue to green radiation backscattered by the ocean, with the ratio which is most sensitive based on wavelengths of 443 and 565 nm [http://envisat.estec.esa.int]. The sensitivity at 443 nm is especially very useful when one is trying to discriminate between water masses of high and low Chl content and, perhaps more important, between water masses of very low, but different, Chl concentrations, since Chl concentrations in the oceans are generally low [Hovis et al., 1980].

The wavelength-dependent, waterleaving radiance, L^λ, is proportional to b^λ_b / a^λ where b^λ_b is the backscatter coefficient (the fraction of light scattered by >90% to the incident direction) and a^λ is the absorption coefficient. The ability to detect phytoplankton from space relies on the spectral variation in phytoplankton pigment absorption [Joint and Groom, 2000].

Problems of remote sensing and their solutions
An overview of the problems that have arisen using ocean colour sensors on the basis of the development of three of the most important remote sensing sensors, namely the Coastal Zone Colour Scanner (CZCS), the Sea-viewing Wide Field-of-View Sensor (SeaWiFS) and the Moderate Resolution Imaging Spectroradiometer (MODIS) will be given in this section. An overview of the wavebands measured by these sensors is given in table 2.

CZCS was the first satellite sensor optimised for biological oceanography and was launched as a 1-year "proof of concept" mission in 1978. Although CZCS was planned to be a 1-year mission, it continued to operate until June 1986 [Aiken et al., 1992]. CZCS was designed with

a number of features specific to ocean colour observation. It viewed the Earth in four narrow wavebands in the visible located in regions of high, medium and low phytoplankton absorption with a fifth band in the near infrared for land-sea discrimination and atmospheric correction.

The atmospheric correction is important when measuring the ocean colour. The principal challenge in remote sensing was and is to overcome the influence of the atmosphere which both absorbs (reduces) the waterleaving radiance and scatters the light into the sensors field of view, so adding to the water signal [Joint and Groom, 2000]. A considerable proportion of the light, typically more than 80%, is atmospheric path radiance backscattered by molecular and aerosol particle scattering in the atmosphere [Robinson, 1990]. The approach employed for ocean colour sensors is to use measurements in the near-infrared, where the sea-water has high inherent absorption and consequently virtually zero waterleaving radiance, to characterise the aerosols and then use look up tables to extrapolate the aerosol signal to visible wavelengths [Joint and Groom, 2000]. This approach needs to be modified in turbid coastal waters where the near-infrared water signal is not negligible [Moore et al., 1999] while aerosols which absorb are potentially still a problem [Antoine and Morel, 1999].

The atmospheric correction may also fail when the solar zenith angle is high, either at high latitudes or in mid-latitude winter. Also, the ability to retrieve pigment concentrations from ocean colour is compromised when sunglint (sunlight reflected from the sea-surface) masks the waterleaving signal. CZCS had high, and variable, gain detectors to allow observation at a variety of solar elevations, and it had a mechanism to tilt the observation angle away from the sun to minimise the impact of sunlight [Joint and Groom, 2000]. A problem that was not solved using CZCS was that due to low incident irradiance, the satellite tended to overestimate the Chl concentrations from late fall until early spring [Yoder et al., 1993].

The sensor clearly demonstrated the feasibility of measuring phytoplankton pigment from space to observe spatial variations or temporal variability over weekly, monthly, seasonal, and yearly time scales [Joint and Groom, 2000].

The most familiar images from CZCS, and now from SeaWiFS and MODIS, are false-colour representations of phytoplankton pigment concentration, calculated from the radiances (light intensities) measured by the sensor. The sensors measure radiance in specific bands of the visible light spectrum, and the data are used to calculate variables as pigment concentration and light attenuation. False colour is simply used to emphasise the concentration ranges. For the CZCS, violet and blue represent low concentrations (below 1.5 milligrams per cubic meter), green and yellow are intermediate, and orange and red are high concentrations (up to 30 milligrams per cubic meter). The SeaWiFS colour scale is similar, but the improved data and better algorithms allow a better estimate of Chl, rather than pigment, concentration [http://daac.gsfc.nasa.gov], see figure 3.
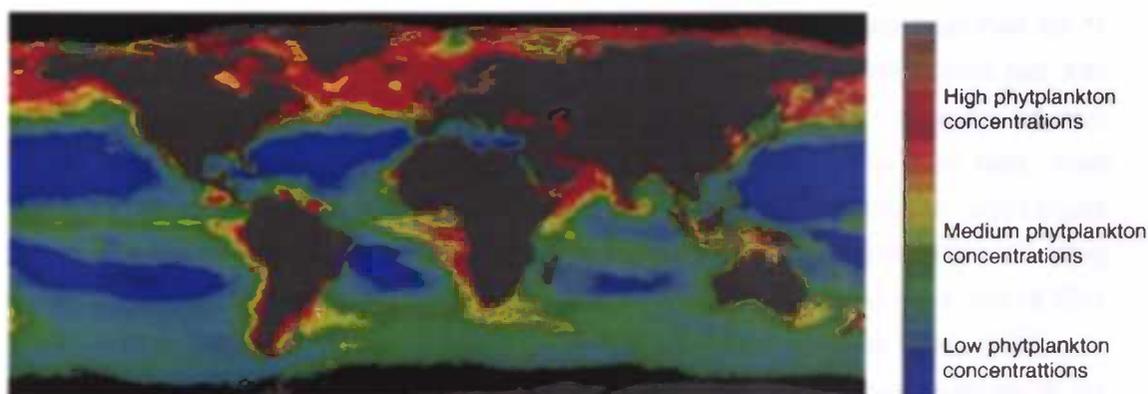
Figure 3. Summer phytoplankton concentrations measured with the Sea-viewing Wide Field-of-view Sensor's (SeaWiFS).

When a phytoplankton pigment is distributed inhomogeneously over depth, its effect on the ocean colour spectrum is not closely related to any straightforward measure of concentration. It is generally accepted that the peak of the colour spectrum of natural waters shifts toward the green in regions of high phytoplankton population and that the parameterisation of the spectrum yields a distinct relationship between Chl and spectral information [Muralikrishna, 1983].

The review of Aiken et al. (1992) of the remote sensing of oceanic phytoplankton has indicated how the CZCS, despite instrumental limitations of spectral resolution and sensitivity, has produced a wealth of new information on biomass distributions and provided the basis for new approaches to the estimation of global marine primary productivity.

In August 1997 SeaWiFS was launched on the Orbview-2 spacecraft and this sensor is still functioning. SeaWiFS operates as a follow-on sensor to the Coastal Zone Color Scanner (CZCS). Compared to CZCS the SeaWiFS instrument had been improved in a number of ways:

First, it views the Earth in six bands in the visible, including a 412-nm channel to detect coloured dissolved organic matter (CDOM), an additional blue channel at 490 nm at medium phytoplankton absorption and two bands in the near infrared to support atmospheric correction.

Second, the signal to noise ratio (S/N ratio) of SeaWiFS is much higher than CZCS. This ratio is one of the key scientific requirements and is carefully specified for ocean colour sensors, due to the fact that the oceans are quite dark. Water-leaving radiance values are commonly less than 10 percent of the total radiance measured at the sensor, and often are less than a percent.

Finally, the sensor has on-board calibration capabilities. This contrasts with the CZCS, which could not be calibrated in-orbit, and, since it was designed for a 1-year life, degradation in the system was apparent over the 8 years of the operation [Joint and Groom, 2000].

The first of a next generation of ocean colour instruments, MODIS, was launched on 18 December 1999 on-board the NASA 'Terra' satellite. Another MODIS instrument has also recently been launched (4 May 2002) aboard the Aqua satellite. MODIS represents a further leap in capability compared to SeaWiFS with more wavebands, higher S/N ratio, more complex on-board calibration, and the capability of simultaneous observation of ocean colour and sea-surface temperature [Joint and Groom, 2000], the latter being important in calculating the flux of DMS to the atmosphere. New ocean colour sensors such as SeaWiFS and MODIS, indicate a significant improvement in performance and accuracy compared to the CZCS, with only a modest change in specification in terms of the addition of sensor channels in the infrared for atmospheric corrections and visible bands for better pigment estimates (see table 2). With more and narrower visible wave bands a better distinction can be made between different algal blooms (e.g. between white, red and green algae). Gondwe et al. (2001) found that Coccolithophore, algae that form external calcium carbonate scales and are important producers of DMSP, can be detected by analysing the waterleaving radiance at 555 nm, where backscattering by ocean water is minimal, and where it is largely dominated by particulate calcite scattering when present.

In the visible region, MODIS builds upon the CZCS and SeaWiFS heritage. Two major exceptions to this are that the sensor does not tilt, in contrast to both CZCS and SeaWiFS, and the instrument is designed to provide quantitative measurements of solar stimulated fluorescence from Chl. The advantage of a tilting sensor is to achieve greater useful global coverage, because the direct specular reflection of the sun can be avoided through tilt changes. AM and PM missions give approximately equivalent global coverage frequency as a single tilting sensor. Therefore, coverage frequency of the ocean using combined data from the AM and PM sensor should be sufficient to observe the important fluctuations in phytoplankton dynamics.

Table 2. Sensor wavebands of three ocean colour sensors, which are or have been operational to date; signal to noise characteristics (*S/N*) from Esaias et al. (1998).

CZCS waveband (nm)	S/N	SeaWiFS waveband (nm)	S/N	MODIS waveband (nm)	S/N
		412 CDOM absorption	940	411 CDOM absorption	933
443	260	443	950	442	1325
High, medium		490 High, medium	1156	487 High, medium	1308
520 and low pigment	260	510 and low pigment	1055	530 and low pigment	1385
550 Absorption	233	555 Absorption	690	547 Absorption	1114
				665 Chlorophyll	1163
670	143	670	798	677 Fluorescence	1265
		765 Atmospheric	860	746 Fluorescence baseline	1077
		865 Correction	670	866 and atmospheric correction	1000

The scientific requirements for various sensors have increased from CZCS to MODIS, based on demonstrated need for higher precision and accuracy at very low Chl levels to address

vast open ocean provinces, and to accommodate improvements in atmospheric and bio-optical algorithms [Esaias et al., 1998].

The most fundamental limitation to ocean colour observation is cloud cover because it masks the sea-surface. A partial solution will be to utilise observations from ocean colour sensors passing over at different times of the day: SeaWiFS passes at local noon while MODIS on the Terra spacecraft will view the same point 90 minutes earlier, so in the presence of (moving) broken cloud a multi-sensor approach should improve retrieval of information [Joint and Groom, 2000]. The multi-sensor approach works in most cases, but is not sufficient at locations that are covered by clouds very often (e.g. the Southern Ocean).

Relation Chl en DMS

It is interesting to consider Chl-DMS relationships because of remote sensing possibilities. Remote sensing techniques could be used to estimate world ocean DMS concentrations, and surface ocean DMS concentrations could then be used in estimating the flux of DMS to the atmosphere [Cooper and Matrai, 1989]. Various attempts have been made to link Chl to DMS. Chl can be relatively easily measured by remote sensing, as it has very high characteristic light absorbing properties. Once a Chl-DMS link is established, it would be very easy to predict DMS values in the water [Kwint, 1997], but some fences have to be taken.

DMS cycling

Tight relationships between Chl and DMS are generally not expected because of the variability in DMSP production between phytoplankton species and time lag between peaks in biomass, DMSP and DMS production. The sole fact that DMS originates from a biological source implies a strong temporal and spatial variation in the formation of DMS. Can knowledge of the processes involved in DMS production and break down lead to better estimations of DMS concentration in the ocean and DMS flux to the atmosphere?

DMS is released into the water column by phytoplankton and zooplankton excretion, phytoplankton senescence, zooplankton grazing, and possibly by viral infection [Kettle et al., 1999]. In the marine mixed layer, DMS is subject to a number of removal mechanisms, including bacterial and photochemical decomposition, emission to the atmosphere, and downward mixing, with a total turnover time of one to a few days. The rates of the dominant DMS sinks, biological decomposition, photodecomposition, and ventilation, are highly variable as a function of time, place and meteorological condition, but are of comparable overall importance for the removal of dissolved DMS [Andreae and Crutzen, 1997]. Most DMS is not emitted to the atmosphere, but disappears in a different way out of the water column. Bacterial consumption of DMSP and DMS is the most important reason for the disappearance of these substances [Kwint, 1997]. The flux of a gas across the sea surface to the atmosphere is related to the difference in the chemical potential across the sea surface (a thermodynamic constraint) and wind-induced turbulence in the upper ocean (a kinetic constraint) [Kettle and Andreae, 2000], but is also related to water temperature and diffusivity of DMS: $F = K \times C$, where C is the concentration of DMS in the surface water, and K is the transfer coefficient for DMS, which is affected by temperature, salinity and wind speed.

Parameterising the processes that control DMS production and removal is far from straightforward. Simple parameterisation to assess the large-scale variability of DMS concentrations in the sea directly by linear regression from biological variables such as Chl or particulate DMSP (pDMSP) concentrations, although statistically significant, account for only 10 to 30% of DMS variability [Kettle et al., 1999].

The use of ocean colour sensor-derived Chl maps enables to observe the mesoscale variability of DMS concentrations on a weekly basis [Belviso et al., 2002]. Many current atmospheric sulphur models rely on the global database of sea surface DMS concentration measurements assembled by Kettle et al. (1999) to compute the atmospheric fluxes of DMS. This global database of sea surface DMS concentrations was updated by Kettle and Andreae (2000). With respect to DMS concentrations, the highest linear correlation was found with DMSP concentration, but the coefficient of correlation (r^2) was only 0.24. With respect to $DMSP_p$, the highest correlation was found with Chl concentration but r^2 was only 0.14. These two relationships are thus not accurate enough to estimate the sea surface distribution of DMS from the global distribution of Chl measured from space by ocean colour sensors [Belviso et al., 2002] and other methods need to be found.

Species composition

Probably the most dominant factor influencing the DMS to Chl ratio is the phytoplankton species composition, because the production of DMSP, the precursor of DMS, appears to species-specific. Some species of phytoplankton produce more DMSP than do others. As a general rule, haptophytes (including Coccolithophore and small flagellates) and small dinoflagellates produce more, or have higher intracellular concentrations of, DMSP than do diatoms [Keller et al., 1989]. Different regions of the oceans are characterised by different phytoplankton assemblages, each of which has distinctive absorption and scattering characteristics [Aiken et al., 1992]. The spectral structure of chlorophyll-specific absorption varies depending on the composition of the phytoplankton pigments present [Hoepffner and Sathyendranath, 1991] and the magnitude of absorption varies between species due to the size of the phytoplankton cells and other factors related to packaging effects [Geider and Osborne, 1992].

A complicating aspect is that within one species the relationship between DMSP and Chl may vary considerably, depending on the physiological condition of the cell which is influenced by parameters such as salinity, temperature, light and nutrient status [Stefels, 1997]. Aumont et al. (2002) made use of non-linear parameterisations to relate DMS concentration to Chl and to a community structure index (Fp-ratio). The Fp-ratio represents the proportion of diatoms and dinoflagellates (microphytoplankton) within the whole phytoplankton community and is defined as the ratio of the integrated concentrations of fucoxanthin (diatoms) and peridinin (dinoflagellates) to the sum of the integrated concentrations of diagnostic pigments of all taxa in the phytoplanctonic community [Claustre, 1994]. Claustre (1994) used the Fp-ratio as an alternate tool in identifying the trophic status of many oceanic regimes. Aumont et al. (2002) show that the use of the Fp-ratio in addition to Chl concentrations leads to much realistic estimates of the sea surface DMS concentration.

In the study of Belviso et al. (2002), the method of Aumont et al. (2002) was modified by estimating the Fp-ratio directly from Chl, so that sea surface DMS concentration can be computed solely from satellite derived ocean colour measurements. They found a non-linear relation between the Fp-ratio and Chl. Despite the good correlation coefficient ($r^2 = 0.89$), the high dispersion of Fp-ratio data for Chl lower than 0.5 mg/m^3 shows the limitation of this Chl-based approach to represent the complexity of phytoplankton communities in the open ocean. Due to the lack of high Chl data, they used a conservative relationship to compute the Fp-ratio for Chl concentrations higher than 3.5 mg/m^3. The contribution of microphytoplankton to the total concentration of Chl is assumed to be Fp x Chl.

Aumont et al. (2002) parameterised the contribution of diatoms to the sea surface distribution of DMSPp as follows: DMSPp (of diatoms) = 20 x Chl x Fp. The amount of DMS can than be estimated using *in-situ* measurements of the ratio of DMS-to-DMSPp. This way the sea surface DMS concentrations can thus be deduced directly from the surface chlorophyll concentration measured at sea or from space [Belviso et al., 2002].

DMS concentrations influenced by different factors

Different factors influence DMS concentration in the water and the flux to the atmosphere. These factors include for example temperature, salinity, wind speed, depth of the mixed layer, phytoplankton species composition and amount of phytoplankton (~Chl).

Since there is not a simple linear relation between Chl and DMS, DMS concentrations cannot be determined directly from remote sensing measurements of ocean colour, but when different factors are included in the model, a good estimation of DMS concentrations could be possible.

Belviso et al. [2000] stated that surface seawater DMS concentrations can be diagnosed at a near global scale using:

➢ Satellite observations of Chl
➢ Climatological sea surface temperature (SST)
➢ A temperature dependent index of the marine community structure
➢ Observational relationships based on cruise data

The size of the flux of DMS to the atmosphere is dependent on the amount of bacterial consumption (and other removal processes), wind speed, sea surface temperature and concentration of DMS in the atmosphere (negligible). Modelling the flux of DMS to the atmosphere would have to include all these factors. Radar is an active remote sensing system operating at the microwave wavelengths and is used to calculate wind speed. Synthetic aperture radar (SAR) images of the ocean surface often show the imprints of marine atmospheric phenomena through their effects on the near surface wind field. The higher the near surface wind speed, the rougher the ocean's surface, and the larger the radar backscatter [http://ccrs.nrcan.qc.ca].

Direct measurement of atmospheric DMS

It would be interesting when DMS could be measured directly with remote sensing. One of the latest developments in remote sensing is the Sciamachy (Scanning Imaging Absorption SpectroMeter for Atmospheric CHartographY). The Sciamachy is an UV-VIS-NIR spectrometer designed to detect a large number of trace gases in the stratosphere and troposphere relevant to ozone chemistry and the greenhouse phenomenon [http://www.sron.nl]. It measures atmospheric absorption in spectral bands from the ultraviolet to the near infrared, providing knowledge about the composition, dynamics and radiation balance of the middle atmosphere (stratosphere) and the upper part of the troposphere. Although the most important scientific goal of Sciamachy is global measurement of trace gases in the troposphere and stratosphere, it will also be possible to measure aerosols, cloud tops, fractional cloud cover and surface reflection [http://auc.dfd.dlr.de/SCIA].

Sciamachy can be applied to measure:

- concentration of trace gases:
  H_2O, O_3, CH_4, CO, N_2O, NO, NO_2, NO_3, ClO, SO_2, BrO, OClO, HCHO, and CO_2
- pressure and temperature via O2
- aerosols
- clouds: top heights

DMS concentration cannot yet be measured with Sciamachy. On the other hand, SO_2 concentrations can already be measured, and, since DMS is a very similar compound (precursor of SO_2), direct measurement of DMS should be possible in the future. Therefore more information is needed about the specific absorption spectrum of DMS.

Discussion

DMS seems to influence the global climate and therefore it is interesting to study its concentration in the ocean. The big advantage of remote sensing is that an unique image is obtained of the spatial variability of phytoplankton in the ocean which is not influenced by long-term sampling [Wernand, 1998]. The biggest problem seems to be that DMS cannot be measured directly by remote sensing and no direct link can be made between Chl and DMS concentrations. Sciamachy offers the potential for direct measurement of DMS, but this is not yet possible. Until then, estimations of DMS concentrations in water and the flux to the atmosphere have to be obtained indirectly from ocean colour measurements.

The remote sensing sensors are becoming more and more accurate. The most important limitation of remote sensing remains cloud cover. This is partly resolved by multi-sensor approaches, but not sufficient for locations with almost constant cloud cover, for example the Southern Ocean. This could be a complicating factor since, on a regional scale, the contribution of DMS to the mean annual column burden of NSS SO_4^{2-} is greatest in the Southern Hemisphere, where it is estimated at 43%. This contribution is only 9% in the Northern Hemisphere [Gondwe et al., *in press*]. The highest production of DMS thus seems to be not in the warmest part of the oceans but at locations with low temperatures.

The Chl concentrations are maximum during winter when the deep mixed layer injects nutrients into the surface. Oligotrophic conditions during summer results in very low surface concentrations [Aumont, 2002]. Vertical mixing probably also effects DMS production at longer time scales. At temperate and subpolar latitudes, seasonal changes in the stratification regime are thought to determine not only the seasonality of primary production, but also the phytoplankton succession. Thus, winter and early spring mixed waters are characterised by blooms of large diatoms and high Chl concentrations, that is, high biomass but low potential for DMS production, as most diatoms are weak DMSP producers [Simó and Pedrós-Alió, 1999]. The 'summer DMS paradox' (highest annual concentrations of DMS also found in summer, when surface Chl levels are lowest) occurs at latitudes between $10°$ and $70°$, where mixed layer Chl concentrations reach their maximum in late winter and early spring. Conversely, surface DMS generally increases from early spring with the onset of stratification, peaking in summer with concentrations higher than those of winter [Simó and Pedrós-Alió, 1999]. It seems that the succession of phytoplankton species is an important link in the measurement of DMS concentrations in the ocean. The method proposed and executed by Aumont et al. (2002) and Belviso et al. (2002) seems to be a step in the right direction of modelling DMS concentrations in the ocean.

Although coastal waters represent less than 1% of the total ocean surface, they are highly important with regard to primary production, including DMS production. The conventional atmospheric correction is based on the assumption that the water reflectance is negligible in

one or more of the infrared channels. This assumption is valid for open ocean water but not for waters that contain inorganic suspended matter that scatters strongly at both visible and near-infrared wavelengths [Frette et al., 1998]. Therefore, *in situ* measurements remain important in these coastal areas and can supplement remotely sensed data.

Conclusion

Nowadays, good estimations can be made of Chl concentrations in oceans using ocean colour remote sensing measurements. DMS concentrations would be easily determined, if there was a direct link between DMS and Chl, but this is not the case. A lot of different processes play a role in the DMS cycle in water and in the atmosphere. One of the most dominant factor influencing the DMS to Chl ratio is the phytoplankton species composition, since the production of DMSP, the precursor of DMS, appears to species-specific. Aumont et al. (2002) and Belviso et al. (2002) used models that included a community structure index (Fp-ratio) to predict DMS concentrations from ocean colour measurements. This seems to be a step in the right direction.

With Sciamachy, one of the latest developments in remote sensing, it should be possible to measure atmospheric DMS directly in the future, but until then it remains important to study the processes that are involved in the DMS cycle and make use of *in situ* measurement techniques.

In this paper I wanted to answer the question whether remote sensing can be used to determine DMS concentrations in the oceans and the flux to the atmosphere. This seems possible: at this moment indirectly via remote sensing measurements of Chl, and in future possibly directly via Sciamachy.

References

Aiken, J., Moore, G.F. and Holligan, P.M., 1992. Remote sensing of oceanic biology in relation to global climate change. *Journal of Phycology*, 28: 579-590.

Andreae, M.O. and Crutzen, P.J., 1997. Atmospheric aerosols: biochemical sources and role in atmospheric chemistry. *Science*, 276: 1052-1058.

Antoine, D. and Morel, A., 1999. A multiple scattering algorithm for atmospheric correction of remotely sensed ocean colour (MERIS instrument): principle and implementation for atmospheres carrying various aerosols including absorbing ones. *International Journal of Remote Sensing*, 20: 1875-1916.

Aumont, O., Belviso, S. and Monfray, P., 2002. Dimethylsulfoniopropionate (DMSP) and dimethylsulphide (DMS) sea surface distributions simulated from a global 3-D ocean carbon cycle model, *Journal of geophysical research*, 107(4): 101029/ 1999JC000111.

Belviso, S., Aumont, O., Bopp, L., Bréon, F.M., Couvert, P. and Monfray, P., 2000. Assessment of the marine biota-DMS-cloud-climate hypothesis using remotely sensed data and an ocean general circulation model (OGCM). *Remote Sensing of the Ocean and Sea Ice 2000*, Bostater, C.R. and Santoleri, R., Editors, pp. 102-110, Proceedings of SPIE, Vol. 4172.

Belviso, S., Moulin, C., Bopp, L. and Stefels, J., 2002. Assessment of a global climatology of oceanic dimethylsulphide (DMS) concentration based on SeaWiFS imagery (1998-2001), Manuscript prepared for the special issue of *Canadian Journal of Fisheries and Aquatic Sciences*, proceedings of the DMS(P) symposium, Rimouski, Canada.

Charlson, R.J., Lovelock, J.E., Andreae, M.O. and Warren, S.G., 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, 326: 655-661.

Claustre, H., 1994. The trophic status of various oceanic provinces as revealed by phytoplankton pigment signatures. *Limnology and Oceanography*, 39(5): 1206-1210.

Cooper, W.J. and Matrai, P.A., 1989. Chapter 9: Distribution of dimethyl sulfide in the oceans. *Biogenic sulfur in the environment*, Saltzman, E.S. and Cooper, W.J., Editors, pp. 140-149, American Chemical Society.

Curran, P.J., 1985. *Principles of remote sensing*, Longman, Harlow.

Esaias, W.E., Abbott, M.R., Barton, I., Brown, O.B., Campbell, J.W., Carder, K.L., Clark, D.K., Evans, R.L., Hoge, F.E., Gordon, H.R., Balch, W.P., Letelier, R. and Minnett, P.J., 1998. Overview of MODIS Capabilities for Ocean Science Observations. *IEEE Transactions on Geoscience and Remote Sensing*, 36(4): 1250-1265.

Falkowski, P.G., Behrenfeld, M.J., Esaias, W.E., Balch, W., Campbell, J.W., Iverson, R.L., Kiefer, D.A., Morel, A. and Yoder, J.A., 1998. Volume 42, Satellite primary productivity data and algorithm development: a science plan for mission to planet Earth. *SeaWiFS Technical Report Series*, Hooker, S.B. and Firestone E.R., Editors.

Frette, O., Stamnes, J.J. and Stamnes K., 1998. Optical remote sensing of marine constituents in coastal waters: a feasibility study. *Applied Optics*, 37(36): 8318-8326.

Gabric, A., Gregg, W., Najjar, R., Erickson, D. and Matrai, P., 2001. Modeling the biogeochemical cycle of dimethylsulfide in the upper ocean: a review. *Chemosphere - Global Change Science*, 3(4): 377-392.

Geider, R.J. and Osborne, B.A., 1992. *Algal photosynthesis*, Chapman and Hall, New York.

Gondwe, M., Klaassen, W., Gieskes, W. and Baar, H. de, 2001. Negligible direct radiative forcing of basin-scale climate by coccolithophore blooms. *Geophysical research letters*, 28(20): 3911-3914.

Gondwe, M., Krol, M., Gieskes, W., Klaassen, W. and Baar, H. de, *In press*. The contribution of ocean-derived DMS to the global atmospheric burdens of DMS, MSA, SO_2 and $NSS-SO_4^{2-}$. *Global Biogeochemical Cycles*.

Gordon, H.R., Clark, D.K., Mueller, J.L. and Hovis, W.A., 1980. Phytoplankton pigments from the Nimbus-7 Coastal Zone Color Scanner: comparison with surface measurements. *Science*, 210: 63-66.

Groom, S. and Lavender, S., 1998. Adding colour to remote sensing. *NERC News*.

Hoepffner, N. and Sathyendranath, S., 1991. Effect of pigment composition on absorption properties of phytoplankton. *Marine Ecology Progress Series*, 73: 11-23.

Hovis, W.A., Clark, D.K., Anderson, F., Austin, R.W., Wilson, W.H., Baker, E.T., Ball, D., Gordon, H.R., Mueller, J.L., El-Sayed, S.Z., Sturm, B., Wrigley, R.C. and Yentsch, C.S., 1980. Nimbus-7 Coastal Zone Color Scanner: system description and initial imagery. *Science*, 210: 60-63.

Joint, I. and Groom, S., 2000. Estimation of phytoplankton production from space: current status and future potential of satellite remote sensing. *Journal of Experimental Marine Biology and Ecology*, 250(1-2): 233-255.

Keller, M.D., Bellows, W.K. and Guillard, R.R.L., 1989. Chapter 11: Dimethyl sulfide production in marine phytoplankton. *Biogenic sulfur in the environment*, Saltzman, E.S. and Cooper, W.J., Editors, pp. 167-182, American Chemical Society.

Kettle, A.J. and Andreae, M.O., 2000. Flux of dimethylsulphide from the oceans: A comparison of updated data sets and flux models. *Journal of Geophysical Research*, 105(D22): 26793-26808.

Kettle, A.J., Andreae, M.O., Amouroux, A., Andreae, T.W., Bates, T.S., Berresheim, H., Bingemer, H., Boniforti, R., Curran, M.A.J., DiTullio, G.R., Helas, G., Jones, G.B., Keller, M.D., Kiene, R.P., Leck, C., Levasseur, M., Malin, G., Mapero, M., Matrai, P., McTaggart, A.R., Mihalopoulos, N., Nguyen, B.C., Novo, A., Putaud, J.P., Rapsomanikis, S., Roberts, G., Schebeske, G., Sharma, S., Simó, R., Staubes, R., Turner, S. and Uher, G., 1999. A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. *Global biogeochemical cycles*, 13(2): 399-444.

Kwint, R.L.J., 1997. The origin of DMS(P): a survey of the sources and sinks of the two dimethylated sulphur compounds ß-dimethylsulphoniopropionate (DMSP) and dimethylsulphide (DMS). Ph.d. thesis, Univ. of Groningen, department of microbiology, 141 pp.

Moore, G.F., Aiken, J. And Lavender, S.J., 1999. The atmospheric correction of water colour and the quantitative retrieval of suspended particulate matter in case II waters: application to MERIS. *International Journal of Remote Sensing*, 20: 1713-1733.

Muralikrishna, I.V., 1983. Ocean color studies in Arabian Sea. *Remote sensing applications in marine science and technology*, Cracknell, A.P., Editor, pp. 299-316, D. Reidel Publishing Company.

Robinson, I.S., 1990. Remote sensing – Information from the colour of the seas. *Light and life in the sea*, Herring P.J., Campbell, A.K., Whitfield, M. and Maddock, L., Editors, pp. 19-41, Cambridge University Press.

Sathyendranath, S., 1998. A three-component model of ocean colour and its application to remote sensing of phytoplankton pigments in coastal waters. *International Journal of Remote Sensing*, 10(8): 1373-1394.

Simó, R. and Pedrós-Alió, C., 1999. Role of vertical mixing in controlling the oceanic production of dimethyl sulphide. *Nature*, 402: 396-399.

Stefels, J., 1997. The smell of the sea: Production of dimethylsulphoniopropionate and its conversion into dimethylsulphide by the marine phytoplankton genus *Phaeocystis*. Ph.d. thesis, Univ. of Groningen, department of marine biology, 147 pp.

Wernand, M., 1998. Mariene optica en remote sensing, Werkgroep fysische oceanografie, NIOZ, Texel.

Yoder, J.A., McClain, C.R., Feldman, G.C. and Esaias, W.E., 1993. Annual cycles of phytoplankton chlorophyll concentrations in the global ocean: A satellite view. *Global Biogeochemical Cycles*, 7(1): 181-193.

Wepagina's

http://auc.dfd.dlr.de/SCIA
http://ccrs.nrcan.qc.ca
http://daac.gsfc.nasa.gov
http://envisat.estec.esa.int
http://seawifs.gsfc.nasa.gov
http://www.ioccg.org
http://www.sron.nl

List of used terms and abbreviations

Albedo the fraction of incident radiation that is reflected by a surface or body

CCN are cloud-condensation nuclei

CDOM is coloured dissolved organic matter

Chl is chlorophyll a

CLAW feedback hypothesis was formulated by, and named after, Charlson, Lovelock, Andreae and Warren. It states that if an increase in ocean temperature (e.g. due to global warming) leads to an increase in the production of the DMS precursor DMSP, and thus to DMS, this would result in a cooling effect of the planet due to an increase in cloud albedo

CZCS is Coastal Zone Color Scanner

DMS is dimethylsulphide, volatile sulphur compound

DMSP(p) is (particulate) dimethylsulphoniopropionate, precursor of DMS

MODIS is the Moderate Resolution Imaging Spectroradiometer

MSA is methane sulphonic acid

NSS is non-sea-salt

Rayleigh scattering is what causes the sky to have a blue colour. Sun light contains every colour, each with it's own wavelength as seen in the table above. Air molecules interacts more with shorter wavelength colours and cause it to scatter in the atmosphere

Sciamachy is SCanning Imaging Absorption spectroMeter for Atmospheric ChartographY

SeaWiFS is the Sea-viewing Wide Field-of-View Sensor

S/N ratio is signal to noise ratio