Chapter 5

Biogeochemical Cycles

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The ocean contains the largest active pool of carbon near the surface of the Earth. Important carbon-related processes include exchange of CO_2 with the atmosphere through the sea surface; conversion of CO_2 into organic carbon by phytoplankton photosynthesis in the sunlit upper layers; and sequestration of carbon into the deeper aphotic zone, either by settling of particulate matter or by diffusive or advective transport of carbon in organic or inorganic form. An inorganic long-term cycle driven by water alkalinity and the formation of calcium carbonate is also a component of the overall oceanic carbon cycle.

Knowledge of the magnitude of the carbon pools and fluxes in the ocean is a prerequisite to gaining a better understanding of the biogeochemical cycles, and is also a requirement for the construction of models to improve prediction of atmospheric pCO_2 concentrations, a major contributor of global warming (Fasham, 2003; Le Quéré *et al.* 2005; Behrenfeld *et al.*, 2006; Doney *et al.*, 2006). In this domain, satellite ocean-colour radiometry (OCR) has emerged as an essential tool to understanding and quantifying several aspects of the biogeochemical cycles of carbon as well as other elements.

The radiance reflected from the upper layer of the ocean (*i.e.* the water-leaving radiance) in the visible domain determines ocean colour and it varies with the concentration and composition of optically-active components in the water. These constituents span a broad size range from water molecules and dissolved matter to large zooplankton particles, and include a variety of material such as bacteria, viruses, phytoplankton, organic detritus, minerals, and more. The water-leaving radiances result from the additive contribution of these constituents to absorption and scattering of light. Remote observations of ocean colour from space are therefore directly related to various components of biogeochemical cycles and associated processes, and complement traditional ship observations in the global assessment of the flux of material through the water column.

5.1 Assessment of Carbon Reservoirs

5.1.1 Particulate Organic Carbon (POC)

Particulate organic carbon (POC) in the ocean represents an assemblage of living particles (bacteria, phyto- and zooplankton) and non-living material (detritus, fecal pellets, aggregates) that contribute to the biological pump (transfer of carbon from the upper layers to the deeper ocean by biological processes). POC sinks from surface waters to deeper layers, removing carbon from the surface layer and supplying food to mesopelagic and benthic organisms. Despite its importance, POC concentrations and its variability over basin or global scales have been poorly assessed. All components of POC are optically active and thus modify the light path through their absorption and scattering properties. Several attempts have been made to characterize POC in the ocean using optical measurements such as the beam attenuation coefficient at 660 nm (Bishop, 1999; Claustre *et al.*, 1999; Mishonov *et al.*, 2003), and the scattering or backscattering coefficient (Balch *et al.*, 1999; Twardowski *et al.*, 2001; Boss *et al.*, 2004; Loisel *et al.*, 2007; Stramski *et al.*, 2007). Relationships linking POC and chlorophyll have also been proposed (Legendre and Michaud 1999; Sathyendranath *et al.*, 2008) for application in remote sensing. Interestingly, these bio-optical variables are potentially retrievable from satellite OCR (Stramski *et al.*, 1999; Loisel and Stramski, 2000; Lee *et al.*, 2002; Roesler and Boss, 2003; IOCCG, 2006; Doron *et al.*, 2007).

POC concentrations and its seasonal variations have been estimated at regional (Stramski *et al.*, 1999; Loisel *et al.*, 2001) and global (Loisel *et al.*, 2002) scales using ocean-colour sensors (Fig. 5.1), based on the relationships linking particle concentrations to backscattering, on the one hand, and remote sensing reflectance (R_{rs}) and backscattering, on the other hand. In all cases, sensor wavebands around 555 nm (*e.g.* SeaWiFS) appear to be most suitable in retrieving the particle backscattering coefficient, where the effect of phytoplankton absorption on the remote-sensing reflectance is often small. Recently, algorithms based on ratios of $R_{rs}(443)/R_{rs}(555)$ and $R_{rs}(490)/R_{rs}(555)$ have been proposed for a standard processing of ocean-colour satellite data to map POC distribution at the ocean surface (Stramski *et al.*, 2007).

So far, remote sensing of POC relies very much on a few contemporary studies, but it is gaining interest and momentum from these promising results. Theoretically, backscattering is related to the total suspended particulate matter (SPM) of which POC is just a component. Global and basin-scale mapping of POC (Fig. 5.1) from satellite-derived optical properties requires the assumption that POC is dominant within SPM, or that the POC contribution to SPM is known over different conditions. Field measurements tend, however, to demonstrate substantial variability of the POC: SPM ratio even in the open ocean (Stramski *et al.*, 2007), which would impact the relationships between POC and bulk optical properties. More field investigations

with concurrent measurements of POC and optical variables in different marine environments and improvements in our understanding of the relationships between SPM and POC will certainly improve the performance of the algorithms for retrieval of POC using satellite data.

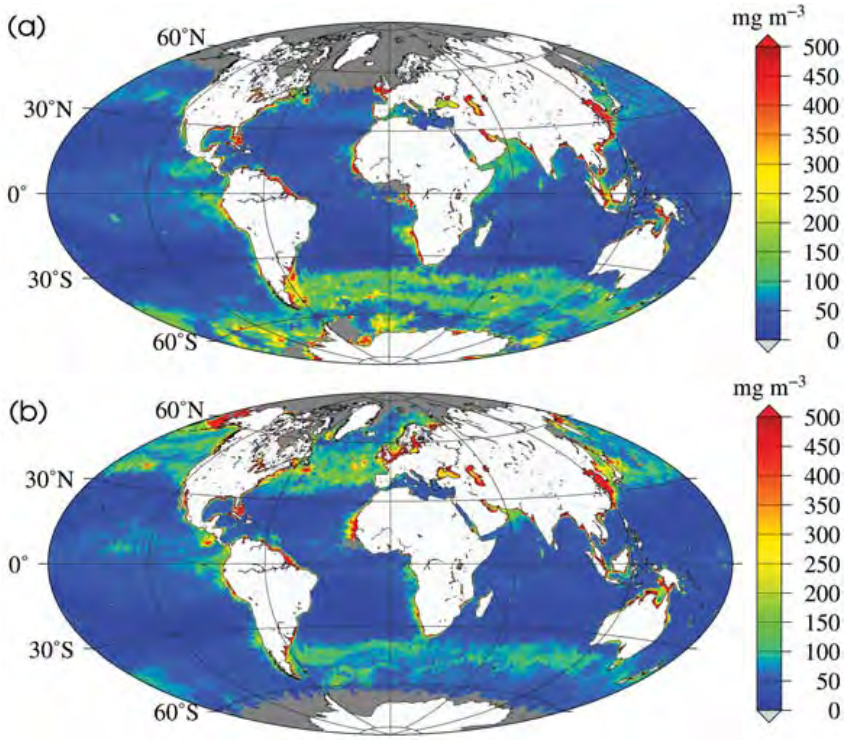

Figure 5.1 Maps of global POC in (a) January 2001 and (b) April 2001. (Image provided by David Dessailly, Université du Littoral Côte d'Opale, France).

5.1.2 Phytoplankton Carbon

Since the advent of OCR three decades ago, the global distribution of phytoplankton biomass, expressed as the surface concentration of chlorophyll-a, has been analysed extensively at time scales of a few days to weeks, to multi-annual time series (Yoder, 2000; Gregg *et al.*, 2005). In marine biogeochemistry studies, the biomass of any population is often required in carbon units. Facing difficulties in directly measuring phytoplankton carbon in the field, biogeochemical studies rely on a carbon:chlorophyll ratio to transform chlorophyll concentration to phytoplankton carbon biomass. Although known to vary over a wide range (10 to >200 g C:g Chl; Taylor *et al.*, 1997; Lefèvre *et al.*, 2003; Marañón, 2005), the C:Chl ratio is often treated as a constant, with typical values ranging from 30 to 60 (Eppley, 1972; Fasham *et al.*, 1990). This can result in unrealistic estimates of primary production rates and the carbon stock of plant biomass in the marine environment and its contribution to the

global carbon budget (Faugeras *et al.*, 2004). A more accurate assessment of this factor could also lead to improved parameterisation of photosynthetic rates and insights into physiological processes (*e.g.* growth rate).

The variability of the C:Chl ratio has been investigated primarily in laboratory settings (Banse, 1977; Laws and Bannister, 1980; Geider, 1987; Geider *et al.*, 1997). It has been shown, experimentally, to be regulated by light level, temperature, and nutrient availability (Geider, 1987; Cloern *et al.*, 1995). The C:Chl ratio is also tightly linked to phytoplankton growth (Landry and Hassett, 1982; Geider, 1987), and has been used in the calculation of the light-saturated photosynthetic rate (Geider *et al.*, 1998) and in the interpretation of widely used temperature-growth relationships (Eppley, 1972). Under nutrient-replete conditions and at balanced growth, C:Chl increases linearly with increasing irradiance levels (at constant temperature), and decreases exponentially with increasing temperature (Geider, 1987). Nutrient limitation also impacts growth rate which translates into changes in cellular C:Chl (Sakshaug *et al.*, 1989).

Accordingly, empirical relationships have been established for C:Chl ratio as a function of temperature, daily irradiance, and nutrient-limited growth rate (Cloern *et al.*, 1995). Their model includes both light-limited and nutrient-limited conditions. Using this model and input variables from ocean-colour radiometry and other satellite-derived data sets or atlases, it is possible to generate global fields of C:Chl (Moore and Dowell, 2004). From another angle, Behrenfeld *et al.* (2005) provided an initial attempt to map phytoplankton biomass in carbon units, and the C:Chl ratio of phytoplankton on the global scale using the particulate backscattering coefficient at 440 nm retrieved from OCR. The assumptions associated with this study are more speculative than in the algorithms for retrieval of POC from space, and must be carefully considered for any application of this method. More recently, Sathyendranath *et al.*, (2008) have used a large number of observations on POC and chlorophyll, along with simple ecological considerations, to propose a method of retrieving phytoplankton carbon from ocean colour. These recent investigations are encouraging, and the knowledge of the phytoplankton C:Chl ratio from satellite data may lead to improved calculations of the flow of carbon and energy through the marine system and may also provide additional insight into the physiological status of phytoplankton.

5.1.3 Particulate Inorganic Carbon (Calcium Carbonate)

Calcification is an integral component of the ocean carbon cycle and calcium carbonate, whether in the form of calcite or aragonite, represents an important constituent of the total marine particulate inorganic carbon (PIC). Calcification, as described by the reaction:

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + H_2O + CO_2, \tag{5.1}$$

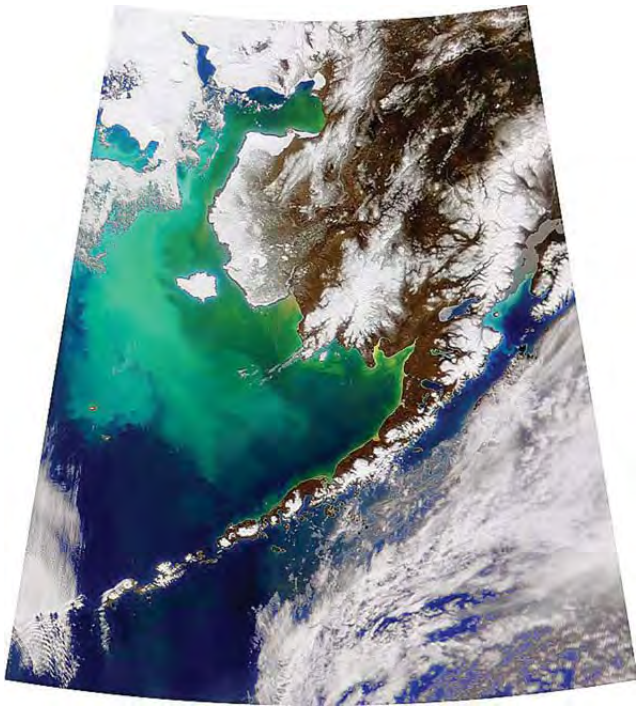

Figure 5.2 Turquoise shades indicate the spatial extent of a coccolithophore bloom in the Bering Sea captured by the SeaWiFS sensor on 25 April 1998 (Credit: NASA/GSFC SeaWiFS Project and GeoEye).

leads to a disequilibrium in the ocean carbonate system that can drive an outgassing of CO_2 to the atmosphere. Specifically, calcification depletes surface CO_3^{2-}, reduces alkalinity, and tends to increase pCO_2. The effect of $CaCO_3$ formation on fluxes of pCO_2 (surface water and air-sea) is therefore counter to the effect of organic carbon production through photosynthesis. On the other hand, the biogenic production and subsequent sedimentation of calcite promotes a long-term carbon export into the deep ocean, acting as 'ballast' for more efficient sinking of associated organic matter as well as increasing overall particle density (Armstrong, 2002).

The annual calcite production in the global ocean varies from 0.8 to 1.4 Gt C yr^{-1} (Feely *et al.*, 2004), most of it being derived from calcification by planktonic organisms. Coccolithophorids are small phytoplankton that synthesize small plates or 'liths' (coccoliths) of pure calcium carbonate covering the external surface of the cell. The shape and style of the liths identify particular species. These organisms create massive blooms in the ocean, and during the later stages of the blooms, the cells shed their liths. Calcium carbonate, being white, strongly reflects light, lending a turquoise-blue-white colour to the ocean. The blooms are easily observed in the pseudo-true-colour images from satellites (Fig. 5.2), meaning that their distribution, both temporally and spatially, can be monitored using ocean-colour radiometry (Brown and Yoder, 1994; Brown, 1995). It has been determined that *Emiliania huxleyi*,

a well-known and abundant coccolithophore, has increased its geographic range, blooming with greater frequency in northern waters, such as the Bering Sea (Iida *et al.*, 2002) and the Barents Sea (Smyth *et al.*, 2004a).

More importantly, specific algorithms have been elaborated to retrieve quantitatively calcite concentration and PIC standing stocks at regional and global scales (Fig. 5.3) from ocean-colour data (Gordon *et al.*, 2001; Balch *et al.*, 2005). An averaged, global total of euphotic PIC, derived from MODIS data, has been estimated at 18.8 Mt, with systematically higher concentrations at latitudes greater than 30° (Balch *et al.*, 2005). It is possible that these values may be contaminated by other suspended mineral compounds, *e.g.* opal from diatom populations (Broerse *et al.*, 2003). More verification with field measurements of PIC concentrations, PIC turnover time, and the opal:PIC ratio are therefore necessary to optimize the use of ocean-colour radiometry in models of the marine carbonate cycle.

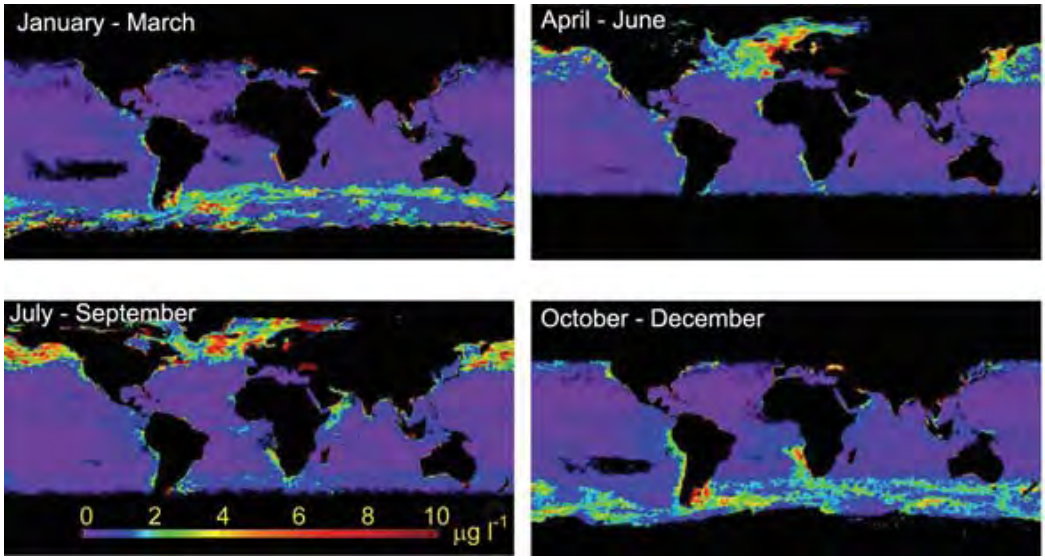

Figure 5.3 Global composite images of seasonal suspended particulate inorganic carbon (PIC) concentration in 2002, as derived from MODIS/Terra data using a two-band calcite algorithm (adapted from Balch *et al.*, 2005).

With increasing concern about marine acidification, it is not clear if coccolithophores and other carbonate-dependant organisms can survive or adapt to a high CO_2 world. Substitution by other species will modify the overall ecosystem, as well as the carbon budget in unknown ways. Long time-series of coccolithophore blooms and PIC concentrations will be essential in studies on the impact of ocean acidification on the marine ecosystem.

5.1.4 Coloured Dissolved Organic Matter

One of the largest reservoirs of carbon on Earth is the organic matter dissolved in the ocean (see review by Hansell and Carlson, 2002). The distribution, sources and sinks of dissolved organic matter (DOM) in the ocean remains insufficiently known. Obstacles to progress include the fact that DOM comprises a complex array of molecules that are difficult to analyze and identify chemically. In practice, DOM is defined operationally as the fraction of suspended material that goes through a sub-micrometre filter (usually 0.2 µm). A fraction of DOM strongly absorbs light in the UV-blue region of the spectrum, such that its presence turns the water yellow. This is why it was originally called 'gelbstoff' or 'yellow substance' by oceanographers. The term in common usage today for this component of DOM is chromophoric (or coloured) dissolved organic matter, or CDOM. Its abundance in sea water can be assessed through its optical properties, particularly the absorption coefficient at blue wavelengths (Bricaud *et al.*, 1981; Blough and Del Vecchio, 2002, and references therein; Twardowski *et al.*, 2004) which can be retrieved from space by ocean-colour radiometry (Carder *et al.*, 1999; Lee *et al.*, 2002; Maritorena *et al.*, 2002; Fichot *et al.*, 2008). However, the similarity between the absorption spectra of CDOM and detrital matter, which decrease exponentially with wavelength, makes it impossible to distinguish between the two using remote sensing. The retrieved absorption coefficient is thus representative of some 'coloured detrital material' (CDM) combining CDOM and detritus (IOCCG, 2006). Assuming a negligible contribution of detritus in the open ocean, the global distribution of CDOM has been derived from ocean-colour radiometry (Siegel *et al.*, 2002; 2005). Obviously, the interpretation of these data becomes more difficult in coastal waters where the contribution of organic detrital matter could be significant. Most remote sensing algorithms treat the absorption coefficient of CDM as a measure of its concentration. To convert absorption into carbon units remains problematic. It is also not easy to establish the relationship between the total detrital material and the coloured component.

In general, CDOM concentrations are higher in coastal areas compared with the open ocean, pointing towards river and coastal runoff as being a major source of CDOM in these areas. The source of CDOM in open ocean waters needs an improved characterization (Nelson and Siegel, 2002), although its occurrence following bloom peaks suggests a local origin from decaying phytoplankton cells, zooplankton grazing, and microbial activity (Hu *et al.*, 2006). In any case, CDM is an important element in determining the light field in marine waters, which is required in the analysis of photobiological and photochemical processes. CDOM has an important role in the production of dissolved inorganic carbon (see section 5.2.2). Moreover, the variability in CDM concentration affects the penetration of harmful UV radiation within the surface layer with consequences for the surrounding ecosystem and biogeochemical cycles. Finally, CDM can also be used as a tracer of water masses, particularly freshwater inputs. CDM and salinity have often been found to vary inversely as river

water mixes with ocean water; thus, CDM can help to understand the interactions between rivers and the coastal ocean (Ferrari and Dowell, 1998; Chen *et al.*, 2007a). Systematic observations of CDM over regional and basin scales using ocean-colour radiometry are essential to gain a better understanding of the biogeochemical cycles and to reduce uncertainties in the marine carbon cycle.

5.2 Carbon Fluxes

5.2.1 Calculating Phytoplankton Productivity from Ocean Colour

Ocean colour from satellite sensors offers the possibility of providing global estimates of the most important transformation occurring in the ocean carbon cycle: the conversion of inorganic carbon to organic carbon through photosynthesis, termed primary production. This marine component of carbon fixation represents approximately half the global total, making it a critical element of the Earth's carbon budget and biogeochemical cycles (Longhurst *et al.* 1995; Antoine *et al.*, 1996; Falkowski *et al.*, 1998). Moreover, synoptic estimates of algal biomass and primary production, as descriptors of the first trophic level, provide insights into the dynamics of marine ecosystems. Access to estimates of primary productivity at spatial scales of about one kilometre, and at time scales of about one week (average time required to obtain clear skies for satellite observations) has thus become a considerable asset in ocean sciences (*e.g.*, Platt and Sathyendranath, 1988).

Primary productivity, P, at any particular location, depth (z), and time (t) in the ocean is determined by chlorophyll-a concentration $B(z,t)$ and a function ($f(E)$) which describes the photosynthetic response of phytoplankton to the available irradiance $E(z,t)$, as follows:

$$P(z,t) = B(z,t) \times f(E;z,t). \tag{5.2}$$

In Equation 5.2, chlorophyll-a concentration is used as an index of phytoplankton biomass, since it is the main data product derived from ocean-colour remote sensing, and is also at the heart of the photosynthetic process. Another possibility is to use phytoplankton carbon, but these methods require further research and validation as mentioned previously. The irradiance, E, refers to that part of the electro-magnetic spectrum between 400 and 700 nm, *i.e.*, the photosynthetically available radiation (PAR), expressed as a spectrally-resolved or integrated quantity. Surface PAR can be derived directly from satellite ocean-colour radiometry (Frouin *et al.*, 2003), or using various spectral approaches based on remote sensing (Frouin and Pinker, 1995; Bouvet *et al.*, 2002). Other relevant environmental variables such as SST (which appear in some implementations of the function f) are also available from remote sensing. Thus, in principle, we can retrieve the major elements required to calculate primary productivity from satellite data.

In reality, satellite ocean-colour radiometry is only sensitive to constituents in the ocean upper layer, whereas biological and chemical processes such as photosynthesis extend to deeper zones (*e.g.* 1% or 0.1% surface light level). The application of Equation 5.2 therefore requires additional knowledge on the vertical structure of the phytoplankton biomass (Platt *et al.*, 1988; Morel and Berthon, 1989), and the attenuation of irradiance with depth (Sathyendranath and Platt, 1989). Integration of Equation 5.2 over depth and day-length provides an aerial daily rate of primary production. Primary-production models may vary from each other depending on how E is expressed (spectral or non-spectral), on how vertical structure of phytoplankton is specified and on how the function $f(E; z, t)$ in Equation 5.2 is specified (Platt *et al.*, 1977; Platt and Sathyendranath, 1993; Sathyendranath and Platt 1993; Behrenfeld and Falkowski, 1997a; Sathyendranath and Platt 2007). Spectral models account for the wavelength-dependent characteristics of the propagation and absorption of light, whereas non-spectral models use total PAR. Time-integrated models express the daily integrated productivity from daily averaged inputs. Depth-integrated versions of models are also in use. Figure 5.4 shows an example of global primary production calculated using a wavelength and depth-resolved primary production model.

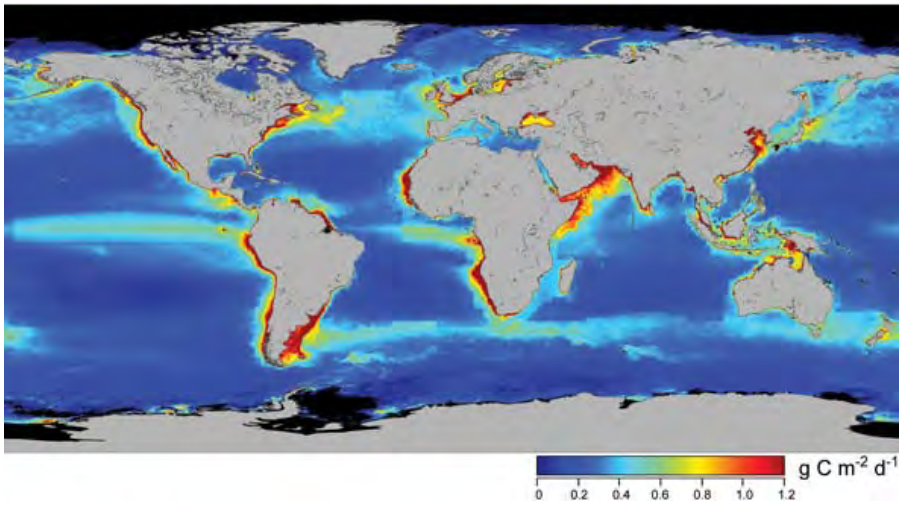

Figure 5.4 Global primary production computed using MODIS-Aqua data from July 2002 to June 2005 with a wavelength, depth-resolved, primary production model down to the 0.1% light-level. (Credit: Frédéric Mélin, Joint Research Centre, EC, unpublished data. MODIS data provided by NASA/GSFC).

Regardless of the complexity of the model formulation, a critical aspect of estimating productivity is specifying the photosynthetic parameters that are contained in the term f in Equation 5.2. In particular, we need to know the rate of photosynthesis per unit B, a property sometimes known as the photosynthetic index, P^B. The relationship between P^B and E, the photosynthesis-irradiance ($P - E$) curve, is well known empirically and can be described using two parameters: the

slope of the curve at the origin, and the maximum photosynthetic rate at saturating light levels. As for the shape of the vertical biomass profile, this information is not accessible directly from space, although P^B at saturating light levels has been shown to vary with temperature (Eppley 1972; Bouman *et al.* 2005), a relationship at the heart of some models of productivity based on satellite data (*e.g.*, Antoine *et al.*, 1996; Behrenfeld and Falkowski, 1997b). Another approach has been to identify biogeochemical provinces for which a comprehensive data set of field measurements enables the definition of representative photosynthetic parameters (Longhurst *et al.*, 1995; Sathyendranath *et al.*, 1995). This method acknowledges the existence of oceanographic regions characterized by distinct physical forcing and variability, as well as the primary importance of the physical forcing in regulating algal processes (Longhurst, 2006). Both implementation methods can be combined in various ways. In any case, satisfactory representation of algal physiology at the global scale by simple relationships applicable to remote sensing has so far proved elusive, though regional approaches are promising (Bouman *et al.*, 2005).

Several years ago, NASA established the Primary Productivity Working Group (PPWG) to investigate the various issues surrounding the calculation of productivity from ocean-colour radiometry. Campbell *et al.* (2002) reported the first results of a comparison between different models using a database of *in situ* primary production. The model results were generally within a factor of two of the observations. A similar exercise conducted more recently by the PPWG (Carr *et al.*, 2006) showed that most models yielded an annual global primary production estimate in the range 35-60 Gt C y^{-1}. Breaking down the results by season or region can lead to larger differences between the models. In the description of the approaches adopted for deriving primary productivity from ocean-colour data, some of the assumptions, limitations and difficulties have already been highlighted (Platt *et al.*, 1988; Platt *et al.*, 1995). The discrepancies between satellite-derived products and field observations may be grouped into the following sources of uncertainties: (1) the input fields from ocean colour, mainly the surface concentration of Chl-a or the phytoplankton absorption coefficient, and the optical properties of the other constituents, (2) the explicit or implicit definition of a vertical structure for the algal biomass and the inherent optical properties, (3) the propagation of the light field, and (4) the rate at which the photons absorbed by the phytoplankton are used for photosynthesis.

The immense value of primary production estimates based on ocean-colour radiometry and other remote-sensing data products is unquestionable. The limitations noted above call our attention to the fundamental aspects of the functioning of marine ecosystems and the challenges in their faithful representation in models. Primary production models are continuously improving, owing to advanced characteristics of on-going ocean-colour sensors, and significant progress in bio-optical algorithms. A third exercise of the PPWG (Friedrichs *et al.*, 2008) demonstrated a reduction by 58% of the differences between ocean-colour derived primary production and *in situ* data when compared with the first series of round-

robin experiments by the PPWG to evaluate and compare primary productivity algorithms. Another conclusion from this exercise is that algorithm performance is not always related to model complexity (Campbell *et al.*, 2002; Friedrichs *et al.*, 2008). This is not surprising considering the comprehensive knowledge on physiology and optics required by all algorithms. However, the continuing development of more elaborate, wavelength-resolved and depth-resolved models have the potential to create new parameterizations and to provide better quality estimates as new insights of the various processes involved are ascertained. At present, the greatest uncertainty in production estimates arises from uncertainty in the estimate of Chl-a from satellite data (Platt *et al.* 1995). As improved ocean-colour sensors lead to better estimates of Chl-a and other bio-optical properties, one anticipates immediate improvements in primary production estimates as well.

5.2.2 Photochemistry in the Upper Ocean

Both biogeochemistry of marine dissolved organic matter (DOM) and photochemistry have shown impressive developments in recent years (Hansell and Carlson, 2002). Deciphering the complex interactions of DOM with microorganisms and the radiation regime is important in understanding the oceanic system and its relation with climate, and the fate of terrestrial input of DOM into the oceans. As stated previously, the absorption of coloured dissolved organic matter (CDOM) increases exponentially towards the blue and ultraviolet wavelengths, a spectral domain that is very energetic for photochemical reactions. The CDOM absorption of blue and UV light modifies chemical species to more reactive forms (free radicals, other reactive species), that will then take part in biochemical processes. The availability of CDOM absorption maps from ocean colour (see section 5.1.4) thus opens new perspectives for quantifying a complex array of biogeochemical rates. Some parallels can be made between the framework of primary production modelling and photochemistry through the definition of absorbed photochemically usable radiation, and quantum yield or action spectra of photochemically-driven rates.

The direct production (through photo-oxidation) of carbon monoxide (CO) and dissolved inorganic carbon (DIC) from terrestrial organic matter may be a major term in the cycle of organic carbon (Miller and Zepp, 1995). The photochemical degradation of DOM may also lead to eventual remineralisation of nitrogen-rich, biologically available compounds (Bushaw *et al.*, 1996). A major decomposition process of the terrestrial inputs of DOM is the transformation into lower-molecular-weight, more biologically-labile, organic substances. Various studies have shown how this pathway modifies the availability of substrates for the microbial loop (Mopper and Kieber, 2002). Photobleaching, the loss of colour and fluorescence properties due to the degradation of chromophores induced by radiation, is a 'visible' manifestation of these phenomena. This process has been well documented, particularly for coastal waters. Far from land, the dynamics of CDOM is heavily conditioned by bleaching,

especially in the top layer of the water column (Nelson *et al.*, 1998). Quantum yields have been documented for photochemical production of DIC (Johannessen and Miller, 2001), CO (Zafiriou *et al.*, 2003), hydrogen peroxide (H_2O_2, Yocis *et al.*, 2000), biologically labile photoproducts (Miller *et al.*, 2002) and CDOM photobleaching (Del Vecchio and Blough, 2002). Global estimates of CO photoproduction using SeaWiFS data have been presented by Miller and Fichot (2004). Organic compounds and photochemical reactions are also part of the marine cycle of trace metals (*e.g.*, Barbeau *et al.* 2001), important for phytoplankton populations.

Photochemical processes are also important drivers of the oceanic sulfur cycle and DOM is an element of many of the related transformations. For instance in the upper ocean, DOM is involved in the production (by photolysis) of carbonyl sulfide, an important gas for stratospheric processes (Weiss *et al.*, 1995). A similar involvement of DOM also appears for the photolysis of dimethyl sulfide (DMS, *e.g.*, Toole *et al.*, 2003), a cycle that has received particular attention since the description of possible climate feedbacks (Charlson *et al.*, 1987). Also relevant to ocean-colour radiometry is the use of Chl-a maps in association with physical variables to derive surface concentrations of DMS at the global scale through empirical relationships (Simó and Dachs, 2002).

That short-wavelength radiation is efficient for photosensitizing dissolved organic compounds, and thus enhancing the overall reactivity of the medium, opens the door to all sorts of processes and it is clear that many of those mentioned above interact. For instance, photodegradation of DOM and microbial activity are intertwined. Photobleaching of CDOM deepens the euphotic zone, and results in increased PAR in the water, as well as increased potentially damaging, UV radiation. From the point of view of carbon fluxes, photosynthesis is enhanced by a greater availability of light and of macro- and micro-nutrients, whereas photochemical production of DIC reinforces the source terms of CO_2. Therefore, these various processes should be analyzed in an integrated way. The extrapolation of local measurements to regional and global scales will certainly require a better understanding of the complex photochemical pathways. Ocean colour has an emerging role to play, by providing information on the distribution of optically significant constituents, thus contributing to a better definition of the light field in the ocean, but also more specifically to an assessment of the CDOM dynamics.

5.3 Ocean Colour and Nitrogen Cycling

Total primary production in the ocean is partitioned into recycled production, which is dependent on recycled nutrients in the upper layer, usually ammonia, and new production, which is fuelled by allochtonous nitrogen supply (Dugdale and Goering, 1967). The paradigm in biological oceanography is that the vertical upwelling of nitrate from the deep drives new production in the nutrient-limited regions of the

surface ocean (Lewis *et al.*, 1986). This process is well documented, particularly in the equatorial ocean where surface chlorophyll increases with shoaling of the thermocline, bringing more nutrients to the surface (Chavez *et al.*, 1998; Siegel *et al.*, 1999; Ryan *et al.*, 2002; Wilson, 2003). Nitrate is assumed to be the limiting nutrient on short time scales (Lewis *et al.*, 1986), outside of high-nutrient, low-chlorophyll (HNLC) regions, where iron becomes a factor. Since transport of nitrogen from the deep, cool waters to the surface is typically accompanied by a decrease in surface temperature, it has been possible to use sea-surface temperature data to track the supply of new nitrogen into the surface waters, and to use a combination of ocean-colour and thermal infra-red remote sensing to measure new production in the ocean (Dugdale *et al.*, 1989; Sathyendranath *et al.*, 1991; Goes *et al.*, 2000). Campbell and Aarup (1992) used information on the nitrate concentrations in oceanic waters prior to the spring bloom, and mixed-layer depths at the time of the collapse of the bloom, to derive consumption of nitrate by new production. In this study, CZCS data were used to estimate the time of collapse of the blooms. Since only new nitrogen can be responsible for phytoplankton growth in nitrogen- limited areas, primary production integrated over the spring bloom can be used to infer a lower limit on new production over that time interval (Platt and Sathyendranath, 2008).

Figure 5.5 Photograph of a *Trichodesmium erythraeum* bloom in the North East Arabian Sea (off the Gulf of Khambhat), taken from the research vessel "ORV Sagar Kanya", April 2000. (Credit: Image provided by Shailesh Nayak, Space Applications Centre, ISRO, India).

Nitrogen fixation is another mechanism responsible for new production in the ocean. Diazotrophs, organisms that fix nitrogen gas, can thrive in nitrate-depleted waters, and might even shift the ocean from nitrogen to phosphorus limitation (Karl *et al.*, 1997; Cullen, 1999; Tyrrell, 1999). The most well-known oceanic diazotroph is *Trichodesmium* (Fig. 5.5) but nitrogen fixation occurs in a number of organisms,

including unicellular cyanobacteria (Zehr *et al.*, 2001; Montoya *et al.*, 2004), and the endosymbiotic *Richelia* that is found within several species of diatoms (Venrick, 1974; Villareal, 1992).

Recent studies have shown that nitrogen gas assimilated by nitrogen fixation could form a significant proportion of the total oceanic new production (the fraction of total primary production fuelled by nitrate) (Michaels *et al.*, 1996; Karl *et al.*, 1997; Zehr *et al.*, 2001). This source of new production could have an important impact on the overall global carbon cycle since, unlike nitrate brought to the surface from upwelling, N_2-fixation is not coupled to fluxes of dissolved carbon from the deep ocean, and can potentially drive a net uptake of atmospheric CO_2 and export of carbon (Hood *et al.*, 2000). Another biologically mediated process that increases surface nitrate is the vertical migration of *Rhizosolenia* diatom mats. These mats use carbohydrate ballasting to migrate vertically between the nutricline, where they uptake nitrate, and the surface, where they photosynthesize (Villareal and Carpenter, 1989; Villareal *et al.*, 1999). Similar to nitrogen fixation, this process results in new production without a flux of deep carbon to the surface, and so can result in more efficient removal of carbon from surface waters (Richardson *et al.*, 1998).

However, it remains difficult to quantify these processes because ship-based observations can provide only limited coverage over large spatial scales. The high spatial and temporal coverage of satellite chlorophyll data supports improved assessments of these processes at regional and global scales. Two different methodologies have been used to identify nitrogen fixation from ocean-colour data. Genera-specific optical properties have been used to develop an algorithm to identify *Trichodesmium* from analysis of satellite measured water-leaving radiances. Initial algorithms only worked on significantly dense blooms, with chlorophyll values >1 mg m^{-3} (Subramaniam *et al.*, 1999, Subramaniam *et al.*, 2002), and therefore could not be applied globally, as chlorophyll levels do not approach this threshold in the oligotrophic ocean, where nitrate-deplete waters will favour nitrogen fixation. Recently, a new algorithm has been developed that appears promising for detecting *Trichodesmium* globally (Westberry *et al.*, 2005). Such algorithms, however, are genera specific, and will not identify production stimulated by other forms of nitrogen fixation, or by migrating mats.

An alternative approach to identifying nitrogen fixation from satellite data takes into account the oceanic conditions conducive to nitrogen fixation (and mat migration) that are very different from conditions leading to upwelling-derived production. Populations of *Trichodesmium* and *Rhizosolenia* mats are generally found in stable, stratified waters, with low winds (Capone *et al.*, 1997; Villareal and Carpenter, 1989; Subramaniam *et al.*, 2002). *Trichodesmium* is usually not present in waters colder than 20°C, and rarely blooms below 25°C (Carpenter and Capone, 1992; Capone *et al.*, 1997; Subramaniam *et al.*, 2002). Culture studies indicate an ideal temperature range of 24 to 30°C for *Trichodesmium* (Breitbarth *et al.*, 2007).

Chlorophyll blooms in the southwest Pacific, observed by both CZCS and SeaWiFS,

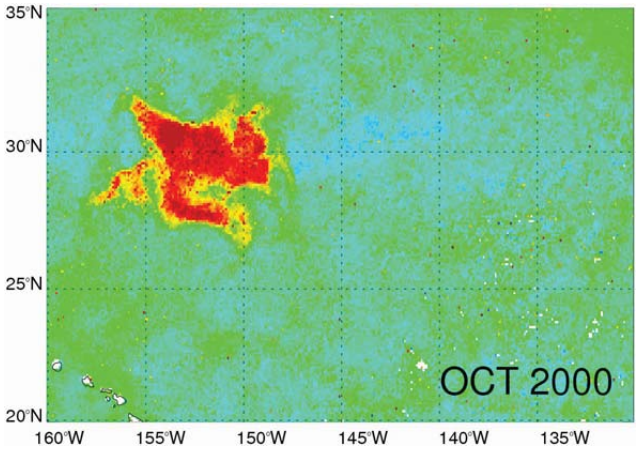

Figure 5.6 Monthly SeaWiFS composite of chlorophyll for October 2000, showing a large chlorophyll bloom northeast of Hawaii in the oligotrophic Pacific. The bloom developed at the end of August and lasted into December. It has been speculated that the bloom was driven by nitrogen fixation or vertically migrating diatom mats (adapted from Wilson, 2003).

have been identified as *Trichodesmium*, based on previous reports of *Trichodesmium* in the area, especially in summer when the surface water is warm and stratified (Dupouy*et al.*, 1988; Dupouy *et al.*, 2000). Chlorophyll blooms which develop in late summer in the oligotrophic Pacific, northeast of Hawaii, have been observed by CZCS, OCTS and SeaWiFS, as seen in Figure 5.6 (Wilson, 2003; Wilson *et al.* 2008). The cause of these blooms has been attributed to either nitrogen fixation (although not necessarily *Trichodesmium*) or vertically migrating *Rhizosolenia* diatom mats, based on concurrent SSH and SST data, and previous biological observations in the area (Wilson, 2003; Wilson *et al.*, 2008). Since diatom blooms are important mechanisms for sequestering carbon into the deep ocean (Goldman, 1988), the carbon export from these blooms could be significant given their size and duration: they can become as large as the state of California and can last up to 5 months. A similar analysis of satellite data (Coles *et al.*, 2004) has identified an annual summer chlorophyll bloom in the western tropical Atlantic as attributable to nitrogen fixation. Coles *et al.* (2004) showed further that the seasonal cycle of satellite chlorophyll for this area could only be reproduced in a biological model that explicitly simulated nitrogen fixation.

The approach of using multiple satellite measurements to identify production under conditions favouring diazotrophy (stratified, low nutrient, high light, sufficient iron) can provide a means for estimating patterns of nitrogen fixation on global scales. If diazotrophs have the potential to shift the ocean from nitrogen to phosphorus limitation (Karl *et al.* , 1997) and alter global climate through changes in the biological pump (Michaels *et al.*, 2001; Sañudo-Wilhelmy *et al.*, 2001), then improving our understanding of their spatial and temporal patterns and production is essential.

5.4 Future Directions

Optical remote sensing aims at quantifying optical properties in the surface layer of the oceans. Algorithms have been steadily increasing and diversifying in the remote-sensing era. Nevertheless, there is a demand for even better descriptions of marine absorption and scattering properties, especially those associated with phytoplankton stocks or CDOM absorption. This is particularly true in coastal waters, which are also areas of intense biogeochemical cycling. In turn, better optical descriptions may lead to more accurate derived information on dissolved and particulate organic carbon or particle size spectra that can be used in studies of biogeochemistry. Also, the detection of phytoplankton functional groups has been proposed by Sathyendranath *et al.* (2004), Alvain *et al.* (2005) and Aiken *et al.* (2008) among others, and such techniques would favour a better representation of algal physiology in satellite-based models of primary production.

Moreover, an improved retrieval of optical properties will improve the modelling of radiative transfer in the water column. The importance of an accurate, spectral, three-dimensional depiction of the light field in the ocean cannot be understated for studies of biogeochemical cycles, because of its effects on physics, biology and chemistry. Clearly, the potential of ocean colour in the field of biogeochemistry will be enhanced if links between other remote-sensing products and dynamic models are improved. Besides accurate bio-optical measurements, applications of ocean colour to biogeochemical cycles will benefit from data sets gathered by field measurements. For example, the progress of Fast Repetition Rate Fluorometer (FRRF)-based techniques to determine *in situ* primary productivity or photosynthetic parameters (*e.g.* Smyth *et al.*, 2004b) will help primary production modelling, while autonomous sensors (Bishop *et al.*, 2002) will complement studies of particles and carbon dynamics in the ocean. Finally, understanding biogeochemical cycles relies on long-term data series, and the existence of an ocean-colour record that now exceeds 10 years will give more weight to studies addressing time scales beyond the seasonal cycle.