Book Chapter Template

Remote Sensing of Phytoplankton Pigments

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Abstract

Pigments, as a vital part of phytoplankton, act as the light harvesters and protectors in the process of photosynthesis. Historically, most of the previous studies have been focused on chlorophyll *a*, the primary light harvesting pigment. With the advances in technologies, especially High-Performance Liquid Chromatography (HPLC) and satellite ocean color remote sensing, recent studies promote the importance of the accessory pigments within the phytoplankton. In this chapter, we will overview the technology advances in phytoplankton pigment identification, the history of ocean color remote sensing and its application in retrieving phytoplankton pigments, and the existing challenges and opportunities for future studies in this field.

Keywords: Phytoplankton, pigments, remote sensing, ocean color, satellite

1. Introduction

Phytoplankton live near the water surface to capture sufficient light for photosynthesis and act as the primary producer of the plankton community. They form the bottom levels of the marine and aquatic food webs, and their existence not only makes life in the water possible but also makes the ocean an important food source for mankind. Phytoplankton play a crucial role in the biogeochemical cycles of many important chemical elements, not only carbon but also of other elements, such as silica and nitrogen [1-4]. The release and uptake of CO_2 and CH_4, and the excretion of dimethylsulphide by phytoplankton influence the atmosphere and climate [5]. As a result of the changes in their living condition, their composition and concentration vary over space and time, which in turn can influence the whole ecosystem, such as through the changes in the size structure, formation of harmful algal blooms and development of hypoxic regions. Blooms and hypoxia can disrupt food-webs and threaten human health.

Phytoplankton pigments capture sunlight. The resulting photosynthesis and its products, especially the oxygen and organic compounds, all rely on the light energy captured by the different phytoplankton pigments [6-8]. Phytoplankton use chlorophyll *a* as their major light harvesting pigment. Accessory pigments (e.g. chlorophylls *b* and *c*, carotenoids, and phycobiliproteins) also play a significant role either in photosynthesis, by extending the organism's optical collection window, or in photoprotection, by preventing cellular damage from high irradiance levels or high ultraviolet light exposure. With the commercial availability of fluorometers, routine measurements of chlorophyll *a* became possible. That single technology to measure chlorophyll *a* fluorescence made chlorophyll *a* fluorescence a universal parameter for estimating phytoplankton biomass and productivity. As a result of improvements in culturing, microscopy, HPLC and molecular methods, rapidly separating and quantifying pigments from different phytoplankton has become possible [9-11]. These new measurements make it possible to use phytoplankton pigments as indicators to elucidate the composition and fate of phytoplankton in the world's oceans [12].

Light absorbed by phytoplankton pigments provides the initial energy for carbon cycles, and is also one of the major factors influencing the appearance of water color [13-16]. To study this important water column phenomenon, ocean color remote sensing was first proposed in late 1970s. Satellite-based remote sensing of ocean color provides unique observational capability to biological oceanographers and other Earth observation scientists interested in processes that involve phytoplankton. No other observational strategy can provide synoptic views of upper ocean optical properties with such high spatial and temporal resolution (~1 km or better, daily or better) and extent (global scales, for years to decades). Since the proof-of-concept Coastal Zone Color Scanner (CZCS) mission, the principal focus of ocean-color research has been on retrieval of information about the content of chlorophyll *a*, the major phytoplankton pigment in the upper ocean (e.g., [17]). Whereas this focus continues to the present [18-20], an evolving interest in retrieving other pigments, has emerged in recent years.

What follows, based on the most recent research findings from the ocean color community, is a brief review of how phytoplankton pigments are estimated from water samples, how pigment maps are derived from satellite measurements and what are the existing challenges and opportunities for the estimates and application of remote sensed pigments. This chapter is not meant to present a comprehensive list of all possible topics related to satellite-based pigment observations, but rather its focus is on the history of pigment retrievals with several examples showing major findings. For interested readers, a full breadth and depth knowledge in this field can be obtained by reading the refereed literature and technical reports compiled on the National Aeronautics and Space Administration ocean color website (https://oceancolor.gsfc.nasa.gov) and by International Ocean Color Coordinating Group (http://www.ioccg.org).

2. Phytoplankton and pigment properties

2.1 Optical properties

2.1.1 absorption properties

Optical properties of phytoplankton, especially the absorption coefficients of the pigments inside them (Figure 1), play a key role in determining not only the use of this radiant energy for photosynthesis, but also the penetration of the radiant energy within water. These pigment absorption coefficients were important for identifying and quantifying phytoplankton groups [12] and size class distributions (IOCCG report 15 and references therein), understanding of photosynthetic rate [11, 21], and in particular for ocean color interpretation.

Light absorption properties of phytoplankton cells from laboratory cultures as experimental materials have received a great deal of attention in fundamental photosynthesis research [22, 23]. However, the phytoplankton pigment absorption properties from natural water is the information needed in ocean color remote sensing. The collection of phytoplankton pigment information has been obtained from measurement of the spectral absorption of phytoplankton, usually through filtration onto a filter pad because of the low *in situ* concentrations of phytoplankton in the water [24].

Using data on pigment concentrations and their absorption properties, Kirkpatrick *et al.* [25] used the specific pigment absorption peaks for identification of phytoplankton types. This method has been integrated into spectral shape-based remote sensing algorithms [26, 27]. However, the absorption of phytoplankton is more complicated than a simple sum of the absorption properties of individual pigments. Differences in pigment composition and the pigment package effect influence not only the magnitude but also the shape of the spectra of phytoplankton absorption [14, 15, 28-30]. All these introduce variabilities in the specific absorption coefficients and increase the uncertainties in the application of such information.

Hoepffner and Sathyendranath [29] proposed Gaussian decomposition of phytoplankton absorption spectra. For the first time, this method decomposed the absorption spectra into Gaussian curve components and linked them to the light absorption coefficients of multiple pigments inside phytoplankton cells. Several studies followed this proxy to estimate multiple phytoplankton pigments for different water bodies [31-33] but were limited to using only *in situ* measured absorption coefficients. Wang et al. [34, 35] proposed a semi-analytical algorithm to obtain these Gaussian curves and pigment absorption coefficients from ocean color remote sensing data.

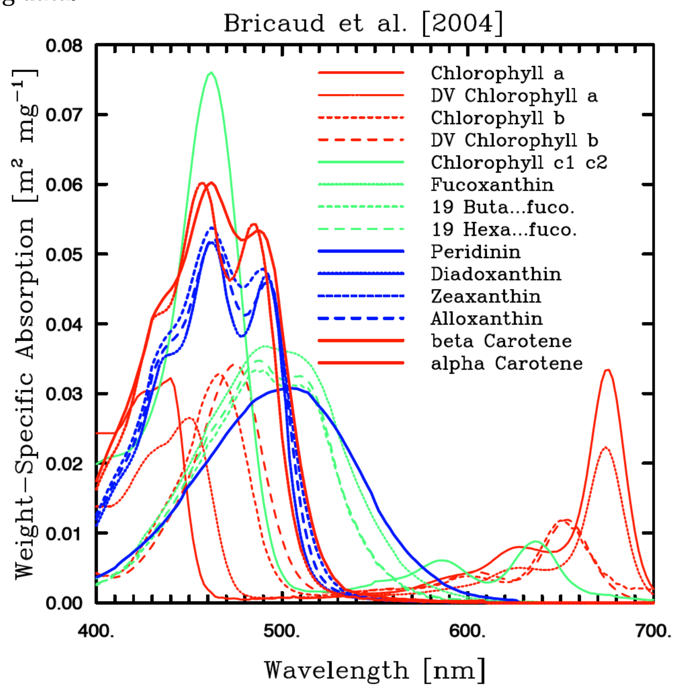

Figure 1. Weight-specific (or pigment-specific) in vitro absorption spectra of various pigments derived from measuring the absorption spectra of individual pigments in solvent and shifting the maxima of the spectra according to Bidigare et al. [14]. Data obtained courtesy of Annick Bricaud (See Bricaud et al. [15]). Credit to Moisan et al. [30].

2.1.2 fluorescence

A portion of the light absorbed by phytoplankton pigments can be emitted at a longer wavelength in a physical process called fluorescence [36]. The energy dissipated in fluorescence is secondary to that used in photosynthesis, but it is still significant enough to be observed in ocean color remote sensing data. Chlorophyll *a* fluorescence has been the most significant one (Figure 2), and the detection and products from satellite ocean color sensors have been widely used [37, 38]. Several other phytoplankton pigments (pheopigments and phycobilins) can also fluoresce.

Several factors influence phytoplankton fluorescence: nutrient conditions, stage of growth, physiological state of phytoplankton, pigment content and ratios, taxonomic position of algae, and photoadaptation [39-41]. *In situ* chlorophyll fluorescence has been the most frequent method for describing the chlorophyll and phytoplankton variation and distribution in the ocean [41], but all the uncertainties from the pigment properties make the interpretation of the chlorophyll fluorescence data a challenge.

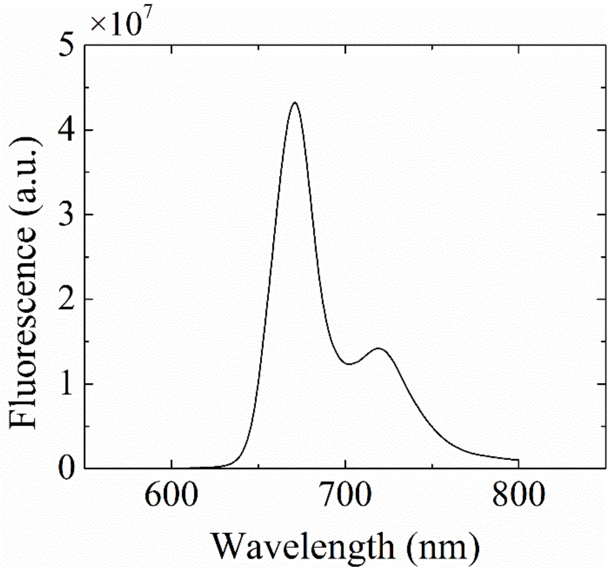

Figure 2. Chlorophyll *a* fluorescence emission. Data from Du et al. [42] and Dixon et al. [43].

2.2 Pigment measurements

Historically, chlorophyll *a* has been routinely derived from filtered fluorometric measurements following standard methods thanks to the commercial availability of fluorometers. However, even standard methods yield varying results depending on the composition of pigments within the phytoplankton, and errors can be on the order of 50% [44-46]. The presence of significant amount of chlorophyll *b* and/or chlorophyll *c*, causes fluorometric techniques to under- or over-estimate Chlorophyll *a* with respect to fluorometric measurements [44-47]. The pigment package effect is also a major source of concern.

The introduction of pigment analyses by high-pressure liquid chromatography (HPLC) [48, 49] facilitated easy and accurate separation, identification, and quantification of phytoplankton pigments. Pigment detection based on HPLC methods enables quantification of over 50 phytoplankton pigments [11,50]. Some photosynthetic pigments (e.g., fucoxanthin, peridinin, alloxanthin, chlorophyll *b*, 19′-hex-fucoxanthin, and 19′-but-fucoxanthin) can be considered diagnostic pigments (DP) of specific phytoplankton groups (diatoms, dinoflagellates, cryptophytes, chlorophytes, haptophytes, and pelagophytes, respectively) [51, 52]. Moreover, diadinoxanthin and diatoxanthin are generally found in dinoflagellates (Phylum Miozoa, Class Dinophyceae) and diatoms (Phylum Bacillariophyta, Class Bacillariophyceae), whereas lutein, prasinoxanthin, neoxanthin, and violaxanthin are found in class Chlorophyceae (Phylum Chlorophyta) and class Prasinophyceae (Phylum Chlorophyta). Chlorophyll *a*, *c*, and β-carotene are used as general indicators of total algal biomass. According to their sizes, phytoplankton are categorized into three different groups: micro-phytoplankton (20–200 μm), nano-phytoplankton (2–20 μm), and pico-phytoplankton (0.2–2 μm) [53]. The contribution of each group can also be calculated using its pigment signatures [54].

3. Ocean color remote sensing

Ocean color or aquatic remote sensing refers to the use of optical measurements made from aircraft or satellites to obtain information about the constituents of the waters.

Remote sensing can be classified as active or passive based on the energy source. Active remote sensing shots signal from the sensor platform (satellite or aircraft) to the water body and detects the return signal from it. The passive remote sensing observes the light that is reflected or emitted by the water body. The most commonly used light source for passive remote sensing is sunlight, and it detects the backscattered light towards the sensor from the water body. The launch of the first ocean color sensor Coastal Zone Color Scanner (CZCS) in 1978, started the era for passive satellite ocean color remote sensing.

Passive ocean-color remote sensing is conceptually simple (Figure 3). The signals captured by remote sensors provide information on the types and concentrations of the various constituents of the water body. The concentrations of optically-active substances present in the water can be estimated by inverting bio-optical algorithms with remote sensing data. Although this process can be fraught with difficulties, ocean color remote sensing has completely revolutionized our understanding of the oceans at local to global spatial scales and daily to decadal temporal scales.

For a better understanding of phytoplankton in the global ocean from large spatial and temporal scales, ocean color remote sensing is the most efficient tool, with the advantages of cost-free satellite imagery access from NASA and others, thus providing a guide for hypothesis testing and more efficient utilization of limited *in situ* data.

Phytoplankton pigments have a major effect on ocean color and are one of the primary reasons for studying it. Following the launch of CZCS, unprecedented data for studying the biology of the oceans have been obtained [55]. For the first time, chlorophyll *a* concentration in the surface ocean could be estimated at synoptic scales [56, 57], leading to unprecedented understanding of the biogeochemistry of the ocean, e.g., primary productivity [58]. These ocean-color observations were continued by the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) mission in 1997, which was then followed by the Moderate Resolution Imaging Spectroradiometer (MODIS on Terra in 2000, and Aqua in 2002), the Medium Resolution Imaging Spectrometer (MERIS, 2002 – 2012), the Visible Infrared Imaging Radiometer Suite (VIIRS, 2011 – present), and the upcoming hyperspectral Plankton, Aerosol, Cloud, ocean Ecosystem (PACE) mission (planned to launch in 2023).

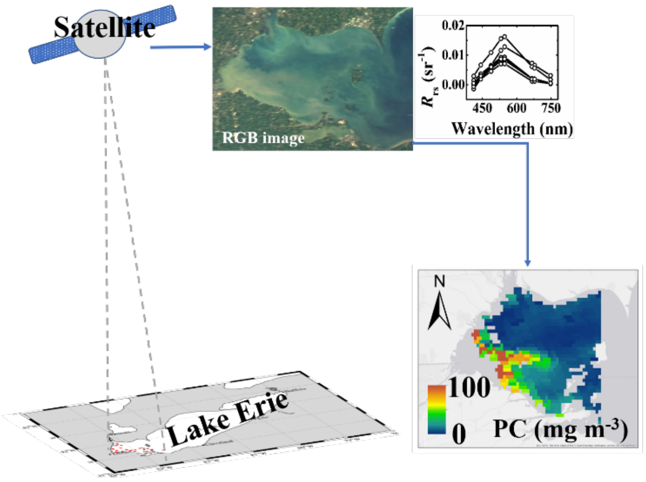

Figure 3. Conceptual figure of passive satellite ocean color remote sensing with Western Lake Erie as an example: $R_{rs}(\lambda)$ as remote sensing reflectance, PC: pigment concentration.

3.1 remote sensing of pigments

In the past decades, the identification of phytoplankton pigments from satellite remote sensing has been mainly focused on chlorophyll *a*, and the products have been widely used to represent the phytoplankton biomass in the primary productivity estimation and biogeochemical models. With the increasing recognition of the important role accessory pigments play, remote sensing of pigments from space form this rapidly advancing field. High temporal and spatial monitoring are particularly important for the study of harmful algal blooms (HABs, e.g. cyanobacteria, [59, 60]). These often-toxic blooms are a growing problem in many coastal and inland waters of the world. A review of chlorophyll *a* algorithm for global oceans has been provided in recent papers including Dierssen [61] and Hu and Campbell [62]. In general, the method to obtain phytoplankton pigments from satellite remote sensing can be classified into two different categories: empirical, and semi-analytical.

3.1.1 Empirical methods

In the process of obtaining phytoplankton pigment, especially chlorophyll *a* (Chl-a) concentrations, most effort has focused on empirical algorithms, not only because of the simplicity, but also the effectiveness. The empirical methods estimate pigments from satellite derived remote sensing reflectance ($R_{rs}(\lambda)$) through regression of pigment concentrations against $R_{rs}(\lambda)$ band ratios or band differences (e.g., [20, 63, 64]).

These methods account for regional variabilities in water properties and $R_{rs}(\lambda)$ input errors through tuning of the empirical coefficients, although the empirical design makes it prone to influences from various in-water constituents. The spectrally dependent $R_{rs}(\lambda)$ errors [65] to a large extent could be compensated through the band ratio or band difference used in empirical approaches. Thus, from the CZCS era, a set of empirical algorithms have been adopted by U.S. National Aeronautics and Space Administration (NASA) to produce the default Chl-a products from the existing ocean color satellite sensors, even though these empirical Chl-a products may contain large uncertainties [61, 66].

For remote sensing of accessory pigments, Pan *et al*. [67] proposed to retrieve 17 different phytoplankton pigments from satellite remote sensing data using empirical methods and applied the information to phytoplankton group identification [68]. This method simply used empirical relationships between pigment concentrations with the ratio of two remote sensing reflectance bands (488 or 490 to 547 or 555nm). However, same as Chl-a, in optically complicated coastal and inland waters, higher uncertainties could be introduced by the large influences from colored detrital matters (CDM) in coastal waters.

Equation 1.1 shows the polynomial algorithm for pigments, in which the blue-green band ratio was empirically related to pigment concentrations (C_{pigs}):

$$\log_{10}\left(\mathrm{C}_{\text{pigs}}\right) = a_0 + \sum_{i=1}^{N} a_i \left(\log_{10}\left(\frac{R_{rs}\left(\lambda_1\right)}{R_{rs}\left(\lambda_2\right)} \right) \right) \quad (1)$$

Where λ_1 and λ_2 represent the spectral band around blue (440-520) and green (555) region respectively, and a_0 – a_N are sensor specific regression coefficients. Details of the spectral bands and parameters used for each sensor can be found in [67] and on NASA ocean color website for Chl-a:
https://oceancolor.gsfc.nasa.gov/atbd/chlor_a/.

3.1.2 Semi-analytical algorithms

The semi-analytical algorithms obtain pigments from $R_{rs}(\lambda)$ by solving a series of equations established from simplified radiative transfer theory based on some bio-optical assumptions (e.g., [69-73]). In principle, these methods have the potential to obtain more accurate results than the empirical methods because the different water constituents affecting water color are explicitly separated. However, semi-analytical approach has its own strengths and weaknesses. The semi-analytical methods rely on tuning of the empirical parameters in the bio-optical relationships using global or local datasets. As a result of the optical properties of the constituents, the separation of them from $R_{rs}(\lambda)$ is not as explicit as expected.

Semi-analytical algorithms are relatively more complex. Based on the radiative transfer equation, remote sensing reflectance was defined as the ratio of upwelling radiance to downwelling irradiance, and its relationship with inherent optical properties of water constituents can be expressed as:

$$R_{rs}(\lambda) = G \frac{b_{bw}(\lambda) + b_{bp}(\lambda)}{a_w(\lambda) + a_{ph}(\lambda) + a_{CDOM}(\lambda) + a_{NAP}(\lambda) + b_{bw}(\lambda) + b_{bp}(\lambda)} \quad (2)$$

Where G is a parameter related to the environment and solar and sensor viewing geometry. The absorption coefficients of water ($a_w(\lambda)$), phytoplankton ($a_{ph}(\lambda)$), colored dissolved organic matter ($a_{CDOM}(\lambda)$), non-algal particles ($a_{NAP}(\lambda)$), and backscattering coefficients of water ($b_{bw}(\lambda)$) and particles ($b_{bp}(\lambda)$).

Pigment concentrations can be estimated from phytoplankton absorption coefficients from Gaussian decomposition (1.3-1.4) or by using pigment specific absorption coefficients (1.5). Figure 4 shows an example of Chl-a global distribution map obtained from MERIS ocean color data using a semi-analytical algorithm.

$$a_{\text{ph}}(\lambda) = \sum_{i=1}^{n} a_{\text{Gau}}(\lambda_i) \exp\left[-0.5 \left(\frac{\lambda - \lambda_i}{\sigma_i} \right)^2 \right] \quad (3)$$

$$\log_{10}\left(\mathrm{C}_{\mathrm{pigs}}\right)=a_0+\sum_{i=1}^{n}a_i\log_{10}\left(a_{\mathrm{Gau}}(\lambda_i)\right) \qquad (4)$$

where σ_i and $a_{\mathrm{Gau}}(\lambda_i)$ are the width and peak magnitude of the ith Gaussian curve at peak center (λ_i). As shown in Fig. 2, in the Gaussian curve assumption in Hoepffner and Sathyendranath, 1991, each Gaussian curve represents the absorption curve of a specific pigment. $\mathrm{C}_{\mathrm{pigs}}$ are pigment concentrations, with a_0 and a_{i} as empirical parameters [74].

$$a_{ph}\left(\lambda\right)=\sum_{i=1}^{N}\mathrm{C}_{\mathrm{pigi}}a^{*}_{pigi} \qquad (5)$$

With a^{*}_{pig} as the pigment specific absorption coefficients [14, 15, 75, 76].

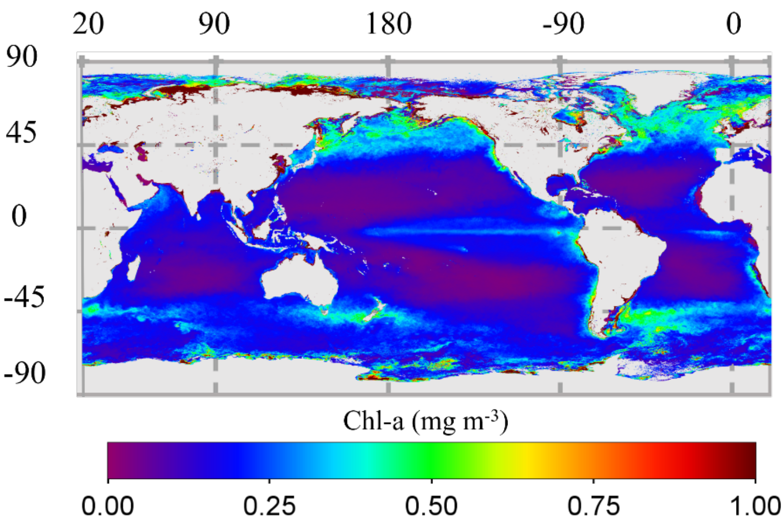

Figure 4. Chlorophyll *a* map of the global ocean from MERIS for the year of 2007 with data from Wang et al. [74].

3.2 Application of remote sensed pigments

The measuring of ocean color from space and the increasing accuracy of *in situ* pigment measurements for determining phytoplankton groups and types in the water column have greatly facilitated progress in phytoplankton research.

Empirical algorithms used to calculate chlorophyll *a* concentration from ocean color data were established for different waters (*e.g.*, [17, 19, 60, 63, 77-79]). The development and application of spectral inversion algorithms to ocean color data have further provided assessments of absorption by phytoplankton pigment absorption coefficients [34, 71, 72, 80-83]. Additional algorithm development has led to new retrievals regarding plankton community composition, including phytoplankton size fractions, the slope of the particle size distribution, and even specific phytoplankton groups, such as coccolithophores (Phylum Haptophyta, Class Coccolithophyceae), *Trichodesmium* (Phylum Cyanobacteria), and harmful algal species (e.g., [84-99] and references therein).

In recent years, the use of pigment data to map phytoplankton population and composition in the water column has become an established and convenient way of studying field phytoplankton [100]. Photosynthetic pigment biomarkers are widely used in oceanography for quantifying phytoplankton biomass and assessing the structure of phytoplankton community [52, 100]. Photosynthetic pigments also function as indicators of the physiological condition of a phytoplankton community, which may be affected by environmental and trophic conditions [101]. Photosynthetic carotenoids (PSCs) are dominant in high productivity waters, whereas photoprotective carotenoids (PPCs) are more dominant in low productivity waters [102, 103]. In addition, intensive light increases the PPC:PSC ratio [104, 105]. Thus, PPC:PSC ratio is considered a good indicator of environmental factors. Figure 5 shows the global maps of PPC and PSC from [74].

Furthermore, the sustained time series of these diverse ocean properties has provided major advances in our understanding of carbon dynamics, plankton annual cycles and their responses to climate variations. Simply, the satellite ocean color remote sensing of pigment will further improve the research revolution in oceanography.

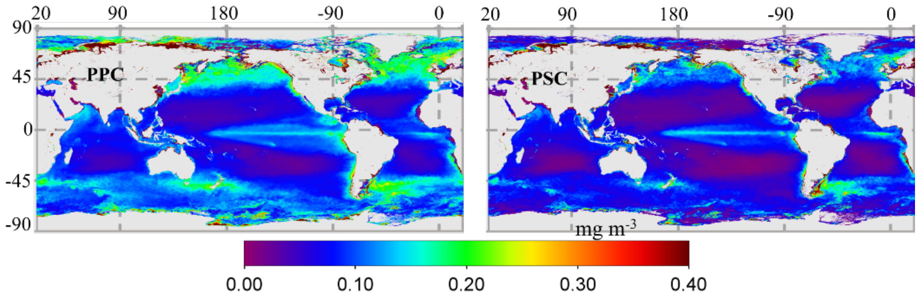

Figure 5. Global maps of photoprotective (PPC) and photosynthetic carotenoids (PSC) from Wang et al. [74].

4. Challenges and opportunities

4.1 Uncertainties in satellite remote sensing data

Despite the advances enabled through ocean color observations, the passive radiometric technique has several fundamental limitations. The major uncertainties of remote sensing pigment estimates are from atmospheric correction errors, as a result of the high signal contribution of components other than the targeted water to radiances measured by ocean color instruments, such as reflection from the ocean surface, surface foam, subsurface bubbles, and atmospheric constituents, including clouds, aerosols, and air molecules. A small error from the correction of these atmospheric contribution results in large errors in the obtained remote sensing reflectance and the associated pigment information.

Another challenge with ocean color remote sensing comes from the interferences of the optical properties of retrieved water components, including absorption by phytoplankton pigments, colored dissolved matter, and nonalgal particles, and backscattering by suspended particles. This makes the uncertainties from these properties and the derived geophysical parameters from them hard to reduce. The upcoming PACE mission is designed with expanded spectral range and resolution to address this problem.

Finally, clouds and strongly scattering aerosol layers have been significant limitation factors of the availability of satellite ocean color data. On average, about 70% of the Earth's ocean area were covered by clouds on the daily scene obtained from a sensor. For broken cloud or aerosol interfered scenes, the accuracy of ocean color retrievals can be compromised compared to clear sky pixels. In high altitude regions, specifically the polar regions, cloud conditions and low sun angles limited ocean color sampling from late fall through early spring of next year. The lack of sampling for this long period of time makes it impossible for a complete understanding of the biogeochemistry and plankton annual cycles of some of the most productive waters [106].

Other issues are from the limitation of spectral, spatial, and temporal resolutions of the existing satellite sensors: some harmful algal blooms occurring in small lakes and ponds are not able to be detected by satellite sensors with low spatial resolution (~ 1 km); while the high spatial resolution sensors (e.g., Landsat 8) cannot provide timely coverage of bloom events due to their low temporal resolution.

4.3 More accurate *in situ* measurements

The satellite ocean color remote sensing has been tasked to acquire remote sensing imagery, validate and monitor its accuracy, process the radiometric data into geophysical information using different algorithms, and apply the final products into scientific research. One of the principles of *in situ* datasets for the calibration and validation procedure is estimates of near-surface pigment concentrations [107]. Thus, accurate and complete pigment measurements are important to algorithm development as used with remote sensing of phytoplankton pigments. The application of pigment chemotaxonomy in oceanography will be more firmly established by advances in taxonomy and improved pigment analysis (e.g. greater resolution with advanced HPLC and ultra-high performance liquid chromatography – UPLC), more rapid and secure chemical identification, and further measurement and estimation of in vivo pigment absorption coefficients. With improvement in these techniques, more discoveries in pigment and taxonomic diversity and further understanding of their influences on the biogeochemical cycles of the ocean will be achieved. The current challenging environment from climate change makes this an urgent need [14, 15, 75, 76, 91].

4.4 Active remote sensing: LIDAR

Compared to passive ocean color remote sensing, lidar shows many advantages, such as operating at night and high latitudes, and can generally penetrate to the subsurface chlorophyll maximum [110, 111]. Airborne lidar is particularly useful for mapping the depth distribution of phytoplankton. The vertical distribution of phytoplankton can provide useful information as described in Moor et al. (2019) two different species of harmful Cyanobacteria in Lake Erie, USA can be identified by the differences in their characteristic depth profiles [112].

Combining the observations from lidar and ocean color sensors, especially the advanced upcoming PACE mission, would enable the achievement of greater synergies. The pairing of an ocean-optimized satellite profiling lidar with a passive ocean color sensor would provide maximized global data coverage, and enable three-dimensional reconstruction of ocean ecosystems, which would further favor the algorithm development, and expand the retrieval of geophysical properties.

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