Quantifying cyanobacterial phycocyanin concentration in turbid productive waters: A quasi-analytical approach

Sachidananda Mishra a,⁎, Deepak R. Mishra b, Zhongping Lee c, Craig S. Tucker d

a Geosystems Research Institute and Department of Geosciences, Mississippi State University, Mississippi State, MS 39762, USA
b Department of Geography, University of Georgia, Athens, GA 30602, USA
c Department of Environmental, Earth, and Ocean Sciences, University of Massachusetts Boston, Boston, MA 02125, USA
d United States Department of Agriculture-Agricultural Research Service, Catfish Genetics Research Unit, Stoneville, MS 38776, USA

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ABSTRACT

In this research, we present a novel technique to monitor cyanobacterial bloom using remote sensing measurements. We have used a multi-band quasi analytical algorithm that determines phytoplankton absorption coefficients, \( a_\lambda (\lambda) \), from above surface remote sensing reflectance, \( R_{\text{rs}} (\lambda) \). In situ data including remote sensing reflectance, phytoplankton pigment concentration, and absorption coefficients of optically active constituents in the water were collected from highly turbid and productive aquaculture ponds. These shallow (<1.5 m) ponds in northwestern Mississippi, USA, were used for channel catfish Ictalurus punctatus aquaculture and had high nitrogen and phosphorus loading rates from manufactured feeds added to ponds to promote rapid fish growth. These practices resulted in high phytoplankton biomass (chlorophyll-\( a \) = 1376.6 mg m\(^{-2}\)) with communities dominated by filamentous, gas-vacuolate cyanobacteria. A novel technique was developed to further decompose the \( a_\lambda \) to obtain phycocyanin absorption coefficient, \( a_{\text{PC}} \), at 620 nm, a primary peak of phycocyanin absorption spectrum. Validation of the model produced mean and median absolute relative errors of 36.2% and 22.0%. Overall, the model performance was higher in the higher range of PC concentration (>150 \( \mu \)g l\(^{-1}\)). Results demonstrate that the new approach will be suitable for quantifying phycocyanin concentration in cyanobacteria dominated turbid productive waters.

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1. Introduction

Cyanobacteria, also known as blue-green algae, can be important in aquatic and marine food chains and in biogeochemical cycling of nutrients. Under certain conditions, however, plankton communities may comprise relatively large colonial or filamentous species, many of which have the ability to regulate their position in the water column through light-regulated changes in cell buoyancy. These communities often dominate the phytoplankton of warm, nutrient-enriched fresh and brackish waters and are often undesirable components of the ecosystem. Bloom-forming cyanobacteria are a relatively poor base for aquatic food chains and have the obnoxious habit of forming unsightly surface scums under calm conditions (Paerl et al., 2001). Many cyanobacteria also produce intensely odorous compounds such as geosmin and 2-methylisoborneol (MIB) that cause earthy or musty odors and flavors in drinking water (Juttner & Watson, 2007). These compounds can also be absorbed from the water across fish gills and deposited in fatty tissues, giving fish undesirable ‘off-flavors’ (Tucker, 2000).

Because of health risks and economic impacts, cost-effective monitoring solutions should be developed to study water bodies subject to cyanobacterial blooms. Remote sensing can be a viable option for this kind of environmental monitoring because of low cost, synoptic, and temporally repetitive nature of monitoring capabilities. Optical properties of phycocyanin (PC), the characteristic cyanobacterial photosynthetic pigment, in the visible wavelength range can be used to develop algorithms to detect and quantify cyanobacterial biomass in natural waters. PC has a very distinct absorption characteristic at 620 nm which is prominent in the reflectance spectra acquired from cyanobacteria dominated water bodies (Glazer, 1989; Richardson, 1996). When the cyanobacterial biomass dominates the water body, the reflectance spectrum shows an absorption maximum around 600–625 nm and a reflectance maximum around 650 nm (Dekker, 1993; Kutser et al., 2006; Mishra et al., 2009) which can be used to identify cyanobacteria in remotely sensed data.

Most research pertaining to the detection and mapping of cyanobacteria from in situ remote sensing spectra have used the local minimum and maximum features at 620 and 650 nm to develop relationships between remote sensing reflectance (\( R_{\text{rs}} \))
and PC concentrations. To date, four broad types of algorithms have been proposed to quantify PC based on its absorption feature (transfers to a valley in reflectance) at 620 nm: 1) single band ratio empirical algorithm (Mishra et al., 2009; Schalles & Yacobi, 2000), 2) semi-empirical baseline algorithm (Dekker, 1993); 3) multiple band linear regression algorithm (Vincent et al., 2004), and 4) a nested semi-analytical band ratio algorithm (Simis et al., 2005). From the above algorithms, Dekker (1993), Schalles and Yacobi (2000), and Mishra et al. (2009) were designed for optimized bands and Vincent et al. (2004) and Simis et al. (2005) were designed for use with satellite sensors. Ruiz-Verdu et al. (2008) evaluated the performances of all existing algorithms until 2008 and reported that different algorithms perform differently based on the strengths and weaknesses of the algorithms, such as, ease of use, spectral band availability, and other methodological biases (Ruiz-Verdu et al., 2008).

It is known that chlorophyll-a (chl-a) and other accessory photosynthetic pigments act as confounding constituents while retrieving PC concentration from \( R_{\text{rs}} \) data (Mishra et al., 2009; Simis et al., 2005). In addition to PC, chl-c and other accessory pigments also absorb light at the PC absorption maximum (≈620 nm) and thus affect the accuracy of PC prediction algorithms. In order to minimize the influence of chl-a absorption, Simis et al. (2005) semi-analytically subtracted the chl-a absorption component \( (a_{\text{chl}}(\lambda)) \) from the phytoplankton absorption at 620 nm, \( a_{\text{chl}}(620) \). Steps of the Simis et al. (2005) algorithm are provided below to highlight the chl-a correction to PC retrieval.

\[
a_{\text{chl}}(665) = \left( \left\{ \frac{R_{\text{rs}}(708)}{R_{\text{rs}}(665)} \right\} - a_{\text{w}}(708) + b_1 \right) - a_{\text{w}}(665) - b_1 \right) \gamma^{-1} \tag{1}
\]

Similarly absorption by PC at 620 nm is derived as:

\[
a_{\text{PC}}(620) = \left( \left\{ \frac{R_{\text{rs}}(708)}{R_{\text{rs}}(600)} \right\} - a_{\text{w}}(708) + b_1 \right) - a_{\text{w}}(665) - b_1 \right) \gamma^{-1} \tag{2}
\]

where, \( a_{\text{w}}(\lambda) \), \( a_{\text{PC}}(\lambda) \) and \( a_{\text{chl}}(\lambda) \) represent absorption coefficient of pure water, PC, and chl-a respectively. Model coefficients \( \gamma \) and \( \delta \) empirically relates the model retrieved \( a_{\text{chl}}(665) \) and \( a_{\text{PC}}(620) \) to the measured ones from quantitative filter-pad technique (QFT); and \( \varepsilon \) relates the \( a_{\text{chl}}(620) \) and \( a_{\text{w}}(665) \). Simis et al. (2005) estimated backscattering coefficient, \( b_\lambda(\lambda) \) as (Gordon et al., 1988):

\[
b_\lambda(\lambda) = \frac{a_{\text{w}}(779)aR_{\text{rs}}(779)}{0.82 - aR_{\text{rs}}(779)} \tag{3}
\]

where, \( \alpha \) accounts for refraction at the water surface (≈0.68), and the factor 0.82 accounts for the average cosine of downward irradiance (Gordon et al., 1988).

It should be noted that Simis et al. (2005) used two empirically derived coefficients, \( \gamma \) and \( \delta \), to relate model derived non-water absorption coefficients, \( a_{-w}(665) \) and \( a_{-w}(620) \) with pad-measured \( a_{\text{w}}(665) \) and \( a_{\text{w}}(620) \) to estimate the proxies for \( a_{\text{chl}}(665) \) and \( a_{\text{PC}}(620) \). If the relative proportion of \( a_{\text{w}} \) and absorption by colored detrital matter (colored dissolved organic matter + detritus), \( a_{\text{DM}} \) varies outside the optimized range, the model could estimate erroneous PC values especially in turbid waters. In addition, the model does not consider \( a_{\text{PC}}(665) \) before subtracting the chl-a contribution at 620 nm which may also increase the estimation error. Mishra et al. (2009) suggested to use the spectral information at 600 nm in simple band ratio algorithms even though the PC absorption maximum is centered around 620 nm, because light absorption efficiency of chl-a is comparatively less at 600 nm than at 620 nm. However, 600 nm could also be contaminated by \( a_{\text{TM}}(600) \) and add uncertainties to PC estimation using empirical models in highly turbid waters.

In this study, we develop a quasi-analytical algorithm to retrieve cyanobacterial PC concentration in turbid and productive waters. The specific objectives of this research are: 1) develop an algorithm to retrieve PC concentration in cyanobacteria, 2) optimize the model parameters using optical and pigment measurements from turbid productive waters dominated by cyanobacterial biomass, and 3) validate the algorithm for accuracy assessment. Two field campaigns were carried out in the catfish aquaculture ponds at the National Warmwater Aquaculture Center, located near Stoneville, MS, USA during 13–16 July, 2010 and 28–29 April, 2011. These shallow, nutrient-enriched ponds were ideal sites for this study because their eutrophic to hypereutrophic status favors high phytoplankton standing crops (chl-a concentration exceeding 1000 mg m\(^{-3}\) in summer months) often dominated by cyanobacteria (Paearl & Tucker, 1995).

2. Algorithm development

2.1. The inversion method

The quasi-analytical algorithm (QAA) (Lee et al., 2002) is a multi band inversion algorithm that inverts total absorption coefficients, \( a(\lambda) \), and particulate backscattering coefficients, \( b(\lambda) \), from an \( R(\lambda) \) spectrum. Unlike other semi-analytical algorithms (e.g., Hoge & Lyon, 1996; Maritorena et al., 2002), QAA retrieves \( a(\lambda) \) first and then decomposes it into individual absorption components. In addition, it does not require spectral models for \( a(\lambda) \) but retrieves it independently from \( R(\lambda) \). The model has been extensively validated using simulated and field datasets from different geographic regions (Craig et al., 2006; Le et al., 2009; Lee & Carder, 2004; Lee et al., 2002; Zhu et al., 2011). These studies have shown that the model was able to retrieve \( a(\lambda) \) with a percentage difference of <20% between the measured and inverted data within 413–665 nm range. Recently, the algorithm was parameterized to retrieve \( a(\lambda) \) in extremely turbid and cyanobacteria dominated hypereutrophic waters, where, \( a(443) \) (3.44–37.67 m\(^{-1}\)) contributes >54% of the \( a(443) \) (4.99–47.21 m\(^{-1}\)) (Mishra, 2012). The model was able to retrieve \( a(\lambda) \) with an average percentage error of 27.2% within 413–665 nm range. A brief description of the parameterized QAA algorithm including the mathematical steps is provided in Appendix A.

2.2. Decomposition of \( a(620) \) for PC retrieval

In this research, we further decompose the QAA derived \( a(\lambda) \) to retrieve PC absorption at 620 nm. \( a(\lambda) \) provides information about the absorption by all intracellular phytoplankton pigments. The proposed novel decomposition method is based on the simple assumption, as in Simis et al. (2005), that \( a(620) \) is approximately equal to the sum of chl-a and PC contributions at those wavelengths; and \( a(665) \) is dominated by chl-a. However, we also include PC contribution at 620 nm. In other words, contribution of pigment absorption other than chl-a and PC to the \( a(620) \) and \( a(665) \) was considered negligible.

\[
a(665) = a_{\text{chl}}(665) + a_{\text{PC}}(665) \tag{4}
\]

\[
a(620) = a_{\text{chl}}(620) + a_{\text{PC}}(620) \tag{5}
\]

where, \( a_{\text{chl}}(\lambda) \) and \( a_{\text{PC}}(\lambda) \) are the absorption coefficients of chl-a and PC, respectively. These two simple algebraic equations can be solved to retrieve \( a_{\text{PC}}(620) \) as:

\[
a_{\text{PC}}(620) = \frac{\psi_1 a_{\text{PC}}(620) - a_{\text{chl}}(620)}{\psi_1 - \psi_2}, \tag{6}
\]

where, \( \psi_1 = a_{\text{chl}}(665)/a_{\text{chl}}(620) \) and \( \psi_2 = a_{\text{PC}}(665)/a_{\text{PC}}(620) \) and their values can be empirically modeled. Further, if the specific absorption
coefficient of PC at 620 nm, \(a_{PC}(620)\), is known, concentration of PC can be estimated as:

\[
PC(\mu g \cdot L^{-1}) = \frac{a_{PC}(620)}{\sigma_{PC}(620)}.
\]  (7)

However, \(a_{PC}\) significantly varies with season, variability in cell morphology, and pigment concentrations. Any uncertainties associated with \(a_{PC}(620)\) estimation will introduce error in predicting PC concentration. In this study an empirical approach has been used to estimate \(a_{PC}(620)\) from a reflectance band ratio.

The major advantage of this algorithm is that unlike the existing semi-analytical model (Simis et al., 2005) this method does not neglect the \(a_{C(DM)}(620)\). It also does not assume the \(b_{sp}(\lambda)\) to be spectrally neutral. In addition, it considers the PC absorption at 665 nm and incorporates that information to algebraically retrieve \(a_{PC}(620)\).

3. Data and methods

3.1. Study site

Twenty-four channel catfish I. punctatus aquaculture ponds located at the Thad Cochran National Warmwater Aquaculture Center, Stoneville, MS, were sampled over 2 years. Ponds were 0.4–3 ha in area and 1.1 m average depth and constructed on fine montmorillonitic clay soils of the Yazoo-Mississippi River floodplain. Water was supplied from a well pumping from the Mississippi River Alluvial Aquifer, which is the water source for all catfish aquacultures in northwest Mississippi. Total alkalinity and total hardness of pond waters varied between 100 and 200 mg/L as CaCO\(_3\) with about 70% of the hardness contributed by calcium. Pond construction, soil type, water supply, water management, and aeration practices were typical of those used in channel catfish aquaculture in northwest Mississippi (Tucker, 1996). During the sampling period, fish were fed a commercial manufactured feed at 75 to 150 kg ha\(^{-1}\) d\(^{-1}\), resulting in net loading rates of 200 to 400 mg m\(^{-2}\) d\(^{-1}\) for nitrogen and 40 to 80 mg m\(^{-2}\) d\(^{-1}\) for phosphorus. These management practices result in high concentrations of total nitrogen (4–8 g m\(^{-3}\)) and total phosphorus (0.5–0.8 g m\(^{-3}\)), and high phytoplankton biomass with communities dominated by large buoyancy-regulating species of filamentous and colonial cyanobacteria (Paerl & Tucker, 1995).

These management practices result in high concentrations of total nitrogen (4–8 g m\(^{-3}\)) and total phosphorus (0.5–0.8 g m\(^{-3}\)) and high phytoplankton biomass with communities dominated by bloom-forming cyanobacteria (Paerl & Tucker, 1995).

3.2. Remote sensing reflectance \((R_{rs})\)

A dual sensor-system with two inter-calibrated Ocean Optics spectroradiometers (Ocean Optics Inc., Dunedin, FL, USA) was deployed to acquire remote sensing reflectance data in the range 400–900 nm with a sampling interval of 0.3 nm as described in Dall’Olmo and Gitelson (2005). Radiometer 1, equipped with a 25° field-of-view optical fiber measured the upwelling radiance just below the air-water interface, expressed in digital numbers as \(D_{Nrad}(\lambda)\); whereas, radiometer 2, equipped with an optical fiber and cosine diffuser (yielding a hemispherical field of view) acquired above surface downwelling irradiance, expressed in digital numbers as \(D_{Nref}(\lambda)\). To match their transfer functions, inter-calibration of the radiometers was accomplished by measuring the upwelling radiance of a white Spectralon reflectance standard (Labsphere, Inc., North Sutton, NH, USA) simultaneously with incident irradiance. The two radiometers were inter-calibrated immediately before and after measurements in each field site. After the data acquisition, \(R_{rs}(\lambda)\) was calculated as follows:

\[
R_{rs}(\lambda) = \frac{t}{\pi} \frac{D_{Nrad}(\lambda)}{D_{Nref}(\lambda)} \frac{D_{Nref}(\lambda)}{D_{Nrad}(\lambda)} F_{i}(\lambda) \]  (8)

where, \(t\) is the transmittance at the air–water interface (0.98); \(n\) is the refractive index of water (1.34); \(D_{Nrad}(\lambda)\) and \(D_{Nref}(\lambda)\) are digital numbers representing upwelling radiance and downwelling irradiance over the white Spectralon panel; \(I_{ref}(\lambda)\) is the irradiance reflectance of the Spectralon panel; and \(F_{i}(\lambda)\) is the spectral immersion factor (Ohde & Siegel, 2003). For each station 6 consecutive scans were recorded and further averaged to calculate a representative \(R_{rs}(\lambda)\) spectrum (Fig. 1a).

3.3. Water quality parameters

3.3.1. Phytoplankton

Water samples for phytoplankton identification and enumeration were collected in a 1-L Niskin bottle and immediately transported to the laboratory. Subsamples (50 ml) were preserved with Lugol’s iodine and phytoplankton were concentrated by settling and enumerated at 150× in a Sedgewick-Rafter counting chamber (Eaton et al., 2005). Cell counts for colonial forms were estimated by multiplying mean colony size by previously determined conversion factors.

3.3.2. Chlorophylls

Water samples for chl-\(a\) and chl-\(b\) analyses were simultaneously collected in 1 L Niskin bottles and immediately filtered onto GF/F
filters (Whatman, 0.7 μm pore size) under low vacuum (<5 in of Mercury). Samples were extracted in triplicates using acetone extraction procedure and concentrations were measured using HPLC as in Environmental Protection Agency method 447 (Arar, 1997).

3.3.3. Phycocyanin

Water samples for PC analysis were filtered immediately after collection through 0.2 μm nucleopore membrane filters (Millipore) under low vacuum. Filters were placed into a 15 ml falcon tube then frozen at −80°C until analysis. Prior to the analysis, filters were transferred to a 50 ml polycarbonate centrifuge tubes, allowed to reach ambient room temperature, and then suspended in 5 ml of 50 mM phosphate buffer. Samples were homogenized as in Sarada et al. (1999) using a sonicator. Ice-bath was included while on the process of homogenization to avoid destruction of pigments from local heating. Tip of the sonicator was rinsed twice with 5 ml of 50 mM phosphate buffer each time and collected in the centrifuge tube. Samples were centrifuged at 5 °C, 27,200 g for 25 min. Samples were again homogenized and the tip of the sonicator was rinsed with 5 ml of buffer and collected in the centrifuge tube and again centrifuged in the same settings. Finally, supernatant was collected and absorbance was measured using a Perkin Elmer lambda 850 spectrophotometer (Perkin Elmer Inc., Waltham, MA, USA) (Fig. 2). Concentration of PC was calculated using the equation from Bennett and Bogorad (1973).

3.3.4. Measurement of absorption coefficients

Surface water samples were collected in 1 L Niskin bottles and immediately filtered onto 0.7 μm Whatman GF/F filters under low vacuum (<16.9 kPa). The volume of water filtered varied from 50 to 100 ml depending on the load of particulate matter in the sample. Particulate absorption coefficient, $a_p(\lambda)$, and absorption coefficient of detrital matter, $a_d(\lambda)$, were determined using standard QFT as described in Mitchell et al. (2003). A Perkin Elmer lambda-850 spectrophotometer with an integrating sphere was used to measure absorbance of the samples within a spectral range from 400 to 800 nm. While measuring absorption coefficients through QFT, path-length of photons increases due to multiple scattering by the glass fibers in the filter paper. To correct for this effect, path-length amplification factor (β-factor) needs to be derived empirically relating the optical density of samples on filters (ODf) and the optical density of samples in suspensions (ODs). In this research, we used the β-factor developed by Dall’Olmo (2006) for similar turbid productive waters in eutrophic inland lakes and reservoirs in Nebraska, USA. The β-factor ($OD_s = 0.7348 OD_f^{1.7221}$, $R^2 = 0.95$) in Dall’Olmo (2006) was developed from a dataset (n = 15) that contained samples from eutrophic waters and dense algal cultures of Microcystis and Synechococcus. Further, $a_p(\lambda)$ was computed by subtracting $a_d(\lambda)$ from $a_p(\lambda)$. Finally, $a_d(\lambda)$ was corrected for residual scattering by subtracting $a_d(800)$ from all wavelengths (Tassan & Ferrari, 2003). Water samples for colored dissolved organic matter (CDOM) analysis were filtered immediately after collection through 0.2 μm nucleopore membrane filters under low vacuum. A detailed description of the methods of absorption measurements from the aquaculture ponds was provided in Mishra et al. (2013). Absorbance of CDOM, $a_{CDOM}(\lambda)$ was measured following the standard protocol (Mitchell et al., 2003) as described in Mishra et al. (2013). The $a_{CDOM}(\lambda)$ (m$^{-1}$) for path length, l (m$^{-1}$) was calculated as:

$$a_{CDOM}(\lambda) = \frac{2.303[a_{CDOM}(\lambda)]}{l},$$

3.4. Error analysis

PC concentration varied within about 2–3 orders of magnitude in the current dataset. Therefore, it is more meaningful to assess the uncertainty of model retrieved PC by providing mean and median relative errors (%) instead of root mean square error (RMSE). We calculated the relative error (RE) and absolute relative error (ARE) as:

$$RE_i = \frac{Y_i - \bar{Y}_i}{\bar{Y}_i},$$

$$ARE_i = \frac{|Y_i - \bar{Y}_i|}{\bar{Y}_i},$$

where, $Y_i$ and $\bar{Y}_i$ are the measured and model retrieved pigment concentration in ith sample.

We also use the slope and $R^2$ of least-square fit between measured and model retrieved parameters to report the consistency of the algorithm retrievals whenever needed.

4. Results and discussion

4.1. Water quality parameters

Filamentous, gas-vacuolate cyanobacteria constituted more than 90% of the standing crop in all ponds. With the exception of one pond,
Planktothrix agardhii was the most abundant species in the community, with standing crops ranging from 3.8 × 10^5 to 5 × 10^6 cells ml^-1. In one pond, Raphidiopsis brookii (cf. Cylindrospermopsis raciborskii) was most abundant, at 7.5 × 10^5 cells ml^-1. Populations of two odor-producing species, Planktothrix perornata and Anabaena circularis, were present as minor components of the community in four and seven ponds, respectively. P. perornata produces 2-methylisoborneol and is the most common cause of off-flavors in farmed catfish in west Mississippi (Tucker, 2000). Populations of A. circularis produce geosmin—a less common cause of fish off-flavors in the region (Schrader & Dennis, 2005). The two odor-producing species did not co-occur in communities sampled in this study, although co-occurrence of MB- and geosmin-producing species is not uncommon in catfish pond phytoplankton communities (Schrader & Dennis, 2005). Diatoms (primarily Aulacoseira spp. and Stephanodiscus sp.), euglenophytes (Euglena spp. and Trachelomonas spp.) and chlorophytes (primarily Closterium spp., Pediastrum spp., and Schroederia sp.) were minor community components. Total non-cyanophyte standing crops ranged from 0 to 2.1 × 10^5 cells ml^-1. In general, pond communities were typical of nutrient-enriched, warmwater aquaculture ponds: they had high phytoplankton standing crops due to the package effect, and therefore, cannot be assumed as abundant, at 7.5 × 10^5 cells ml^-1. The presence of cyanobacterial species that produce the odorous compounds 2-methylisoborneol (MIB) or geosmin.

Analysis of water samples from the aquaculture ponds showed a wide range of pigment concentration (Table 1). PC concentration varied from 68.13 to 3032.47 μg l^-1 with an average value of 431.26 μg l^-1. The high values indicate the abundance of PC containing cyanobacteria in the waters during the sampling period. Chl-a concentration varied within 59.4–1376.6 mg m^-3 with an average of 302.06 μg l^-1. PC-chl-a ratio varied from 0.3–3.29 (mean = 1.27) reinforcing the cell-count data in the previous paragraph indicating cyanobacterial dominance in the phytoplankton community structure (Table 1). Strong dependence was found between chl-a and PC concentration in the entire dataset (R^2 = 0.84). Similarly, a strong positive correlation was found between chl-a and PC in the 2010 dataset (R^2 = 0.89, Fig. 3) further corroborating the fact that the algal community was mostly dominated by cyanobacterial biomass. However, a weak relationship was found between those two parameters in the 2011 dataset, indicating a mixed algal community. Chl-b concentration varied in a range 1.57–13.71 with a mean value of 4.36 μg l^-1. Strong positive correlation was found between chl-a and chl-b (R^2 = 0.63).

Absorption measurements show that the water samples were collected from highly turbid and productive waters where a_{chla}(443) (5.24–37.67 m^-1) contributes >50% towards the a_{chl}(443) (8.85–47.21 m^-1) (Table 1). a_{CDM}(620) varied within 0.09–1.12 m^-1 with a mean value of 0.32 m^-1 supporting the fact that it cannot be assumed negligible in semi- and quasi-analytical algorithms to retrieve PC in turbid and productive waters. In our dataset, a_{CDM}(620) was ~3–11% of a_{chl}(620). An uncertainty of this magnitude may introduce considerable amount of error in the analytical estimation of PC especially in waters with low PC concentration. For example, a simple calculation using Simis et al. (2005) showed that the residual a_{CDM}(620) may overestimate the final PC retrieval up to 38% and 114% in waters with PC concentration of 150 μg l^-1 and 50 μg l^-1, respectively. The overestimation can go as high as 150–447% in case of high CDM waters. It should be noted that the average value of a_{CDM}(620) (0.32 m^-1), and a_{CDM}(665) (0.19 m^-1) from this study, average ε(0.24) from Simis et al. (2005), and average a_{chl}(620) from this study (0.0048 m^-2 ng^-1) were used in the above calculation. Mean relative contribution of a_{CDM} to a_{chl} at 665 and 708 nm was found to be 3.4% and 3.8%, respectively.

### Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean</th>
<th>Std</th>
<th>Min</th>
<th>Max</th>
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<tr>
<td>Pigment concentrations</td>
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<tr>
<td>PC (μg/l)</td>
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<td>68.13</td>
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<td>Chl-a (μg l^-1)</td>
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<td>Chl-b (μg l^-1)</td>
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<td>3.29</td>
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<td>Total absorption coefficients, α_i (m^-1)</td>
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<tr>
<td>a_{443}(443) (m^-1)</td>
<td>16.42</td>
<td>8.26</td>
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<td>a_{620}(620) (m^-1)</td>
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<td>a_{665}(665) (m^-1)</td>
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<td>a_{708}(708) (m^-1)</td>
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<td>a_{443}(443)/a_{443}(665)</td>
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<td>a_{620}(620)/a_{620}(665)</td>
<td>0.87</td>
<td>0.04</td>
<td>0.78</td>
<td>0.94</td>
<td>24</td>
</tr>
<tr>
<td>Absorption coefficients of CDOM and detritus, a_{CDM} (m^-1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a_{CDM}(443) (m^-1)</td>
<td>3.71</td>
<td>1.65</td>
<td>2.08</td>
<td>9.54</td>
<td>24</td>
</tr>
<tr>
<td>a_{CDM}(620) (m^-1)</td>
<td>0.32</td>
<td>0.21</td>
<td>0.19</td>
<td>1.12</td>
<td>24</td>
</tr>
<tr>
<td>a_{CDM}(665) (m^-1)</td>
<td>0.19</td>
<td>0.13</td>
<td>0.04</td>
<td>0.67</td>
<td>24</td>
</tr>
<tr>
<td>a_{CDM}(708) (m^-1)</td>
<td>0.07</td>
<td>0.06</td>
<td>0.01</td>
<td>0.30</td>
<td>24</td>
</tr>
<tr>
<td>a_{CDM}(620)/a_{CDM}(665)</td>
<td>0.07</td>
<td>0.03</td>
<td>0.04</td>
<td>0.12</td>
<td>24</td>
</tr>
<tr>
<td>PC absorption coefficients, α_{PC} (m^-1)</td>
<td>1.94</td>
<td>2.96</td>
<td>0.30</td>
<td>13.94</td>
<td>24</td>
</tr>
</tbody>
</table>

Fig. 3. Relationship between measured PC and chl-a concentration in the samples. Solid and empty circles represent data from 2010 and 2011 respectively. Dotted line is the least-square fit line using all samples.

4.2 Retrieval of a(λ) spectrum from R_σ(λ)

QA retrieved a_{chl}(λ) values were compared with filter-pan measured values for accuracy assessment (Fig. 4). In this paper, we have shown the retrieval accuracy of a_{chl}(620) and a_{chl}(665) because the proposed algorithm uses retrieved a_{chl} values only at those band centers. A detailed parameterization and validation of the QAA to retrieve a_{chl}(λ) in highly turbid and productive water can be found in Mishra et al. (2013). Mean ARE (%) for a_{chl}(620) and a_{chl}(665) of all samples was 16.2% and 14.7% respectively; whereas the median ARE of a_{chl}(620) and a_{chl}(665) retrieval was 11.6 and 12.7% respectively. Two samples showed relatively high error for both a_{chl}(620) (~60%) and a_{chl}(665) (30%). Overall, the relative error of retrieved a_{chl}(620) and a_{chl}(665) was <30%.

4.3 Retrieval of a_{PC}(620) from a_{chl}(620)

4.3.1 Using ψ_{i} and ψ_{r} measured from experimental data

Newly proposed method (Eq. (6)) was used to retrieve a_{PC}(620) from a_{chl}(620) and a_{chl}(665). It should be noted that the biggest challenge of this method was to tune the values of ψ_{i}, [a_{chl}(665)/a_{chl}(620)], and ψ_{r}, [a_{chl}(665)/a_{PC}(620)], from K_λ band ratios because they vary considerably due to the package effect, and therefore, cannot be assumed as...
samples in 2010 dataset and the data were used to calculate (Eq. (6)).

\[ \psi_1 (\text{chl-a}, \lambda) = aPC_1(\lambda) \]

should be close to zero. In this case, a linear retrieved

\[ a_{PC} \]

lower range of chl-concentration were also used to calculate \( \psi_2 \).

Strong dependence (power fit) was found between \( \psi_1 \) and chl-a concentration \( (R^2 = 0.93, \text{Fig. 5a}) \). After including \( \psi_1 \) values for the lower range of chl-a concentration from literature (Bidigare et al., 1990; Bricaud et al., 2004), \( R^2 \) of the power fit increased to 0.96 indicating its validity even in the lower chl-a (5–50 mg m\(^{-3}\)) range (relative to very high concentration in this study) (Fig. 5a). Considering sub-surface reflectance ratio \( \psi_2 \) as a proxy of chl-a concentration, an empirical model was established between the band ratio and \( \psi_1 \). A logarithmic fit showed strong relationship between the two \( (R^2 = 0.89, \text{Fig. 5b}) \). This newly developed empirical model was used to retrieve \( \psi_1 \) for all samples in the dataset for further analysis. Similarly, \( \psi_2 \) was empirically modeled from \( r_{560}/r_{665} \) band ratio. A power fit explained about 50% variance in the dataset \( (R^2 = 0.5, \text{Fig. 5c}) \).

\[ a_{PC}(620) \]

values were calculated from \( a_{\text{chl-a}}(665) \) and \( a_{\text{chl-a}}(620) \) using empirically retrieved \( \psi_1 \) and \( \psi_2 \) values in Eq. (6). For accuracy assessment, retrieved \( a_{PC}(620) \) values were compared with in vitro measured \( a_{PC}(620) \) (Fig. 6). It should be noted that there was a systematic overestimation of model retrieved \( a_{PC}(620) \). If the model retrieved \( a_{PC}(620) \) was close to the measured values, it is logical to think that the intercept of the best-fit line between PC and \( a_{PC}(620) \) should be close to zero. In this case, a linear fit produced an intercept of 1.76 (Fig. 6) which may indicate that experimentally measured (in vitro) \( \psi_1 \) values were larger than the corresponding in vivo \( \psi_1 \) values that could retrieve \( a_{PC}(620) \) closer to the measured ones.

4.3.2. Using \( \psi_1 \) derived by optimization

Taking into account the difficulties involved in carrying out in vivo measurements of \( a_{\text{chl-a}}(\lambda) \), \( \psi_1 \) values were also retrieved by optimization. For each sample, \( \psi_1 \) was solved using in vitro measured \( a_{PC}(620) \) and \( \psi_2 \), and filter-pad measured \( a_{\text{chl-a}}(620) \) and \( a_{\text{chl-a}}(665) \) (Eq. (6)). \( \psi_1 \) was varied iteratively within 0.8–2 with a 0.001 increment and the \( \psi_1 \) value that returns the most accurate \( a_{PC}(620) \) was selected. To assess the accuracy of the decomposition, we evaluated the method in an ideal case where the parameters \( \psi_1 \) and \( \psi_2 \) are known. \( a_{PC}(620) \) was estimated from model retrieved \( a_{\text{chl-a}}(620) \) and \( a_{\text{chl-a}}(665) \) using optimized \( \psi_1 \) and measured \( \psi_2 \) values. The model retrieved \( a_{PC}(620) \) values were compared with measured \( a_{PC}(620) \) (Fig. 7a). Retrieved \( a_{PC}(620) \) matched very well with the measured values with an average relative error of ~10% (Fig. 7a). A linear fit between model retrieved and measured \( a_{PC}(620) \) produced a slope of 1.02 and an intercept of 0.005 \( (R^2 = 0.99) \).

This newly developed method produced high retrieval accuracy when sample by sample optimized \( \psi_1 \) and measured \( \psi_2 \) values were used; however, this method is not practical for a remote sensing mapping protocol. Therefore, we developed another empirical model establishing a power fit between optimized \( \psi_1 \) values and \( r_{560}/r_{665} \) \( (R^2 = 0.53, \text{Fig. 8}) \). Later, modeled \( \psi_1 \) and \( \psi_2 \) values were used to retrieve \( a_{PC}(620) \). Fig. 9a shows the comparison of model retrieved \( a_{PC}(620) \) with measured \( a_{PC}(620) \). Excluding 2 samples, all other samples matched well with the measured ones.
relative errors of the model retrieval were 33.3% and 27%. Two samples produced considerably high error (74.3% and 87.0%) in this dataset. Further investigation revealed that the two points were also associated with the highest ψ2 errors. ψ2 model errors for those two points exceeded 90% (not shown). After excluding the points with high ψ2 model errors, the mean and median relative errors decreased to ~29% and 23% respectively. Overall, accuracy of ψ1 retrieval depends on the accuracy of modeled ψ1 values as the errors for all samples other than two samples strongly correlated with the ψ1 model errors ($R^2 = 0.63$). In future studies, it is expected that fine-tuning of ψ1 and ψ2 empirical models will improve the retrieval accuracy of $a_{PC}(620)$.

### 4.4. Retrieving PC concentration from $a_{PC}(620)$

PC concentration can be calculated if $a_{PC}(620)$ and $a_{PC}^* (620)$ are known (Eq. (7)). Values of $a_{PC}^* (620)$ do not highly vary within different species of cyanobacteria (Simis & Kauko, 2012). However, it widely varies with nutrient and light conditions (Tandeau de Marsac, 1977). Retrieving in vivo $a_{PC}^* (620)$ for samples collected from a mixed phytoplankton community is also a difficult task due to the presence of non-chlorophyllous absorption at 620 nm. Because of the variability in $a_{PC}^* (620)$ from non-chlorophyllous absorption at 620 nm, Simis et al. (2005) used a sample-by-sample $a_{PC}^* (620)$ and ε information to retrieve PC concentration in lake Loosdrecht, The Netherlands and were able to retrieve PC with better accuracy (RMSE=6.5 mg m$^{-3}$ or 19%; $R^2=0.94$). However, the accuracy considerably decreased when a constant $a_{PC}^* (620)$ and a mean ε were used to retrieve PC concentration. In this study, we retrieved PC concentration in three different ways, such that the effects of $a_{PC}^* (620)$ on final PC retrieval can be analyzed. The three methods are: 1) using known $a_{PC}^* (620)$ values, 2) using the mean $a_{PC}^* (620)$ value, and 3) using modeled $a_{PC}^* (620)$ values. We analyzed the three different cases using $a_{PC}(620)$ retrieved from: 1) optimized ψ1 and measured ψ2, and 2) modeled ψ1 and ψ2.

#### 4.4.1. PC from optimized $\psi_1$ and measured $\psi_2$

PC concentrations were estimated from $a_{PC}(620)$ derived by using optimized ψ1 and measured ψ2 values. Therefore, final estimation errors of PC can only be attributed to $a_{PC}^* (620)$. First, sample-by-sample measured values of $a_{PC}^* (620)$ were used and compared with the measured PC values (Fig. 7b). The mean and median ARE of PC estimation were 10.6% and 6.2%. Slope and $R^2$ of the straight line fit between measured and retrieved PC concentrations were 1.03 and 0.99 highlighting high retrieval accuracy. However, using sample-by-sample $a_{PC}^* (620)$ is not feasible in remote sensing. Therefore, we used the mean value of $a_{PC}^* (620)$ of all samples in this study (0.0048 m$^2$ mg$^{-1}$) to estimate PC. When compared, estimated PC values matched very well with the measured ones ($R^2=0.98$, slope = 0.96, Fig. 7b). However, the mean and median ARE error increased to 22.3% and 15.9% (Table 2). We also noticed that $a_{PC}^* (620)$ linearly increased with $r_{rs} (665)/r_{rs} (620)$ ($R^2=0.4$) and explained the variability to some extent. The use of modeled $a_{PC}^* (620)$ brought the mean relative error down to 20.4%. In all three cases, mean relative error of PC estimation varied from 10 to 22%.
4.4.2. PC from modeled $\psi_1$ and $\psi_2$

PC estimation error was minimal when it was calculated using the aforementioned optimization process. However, this is impractical to be used in remote sensing, therefore, PC concentration was estimated from $a_{PC}(620)$ that was retrieved from modeled $\psi_1$ and $\psi_2$. PC concentrations were retrieved in three different ways by changing $a^{a}_{PC}(620)$:

- PC concentrations were estimated by using sample-by-sample measured $a^{a}_{PC}(620)$ (Fig. 9b). The mean and median ARE of PC estimation were 37.2% and 27.2% respectively.
- PC retrievals using mean $a^{a}_{PC}(620)$ produced mean and median ARE of 34.9% and 26.0% respectively.
- PC retrievals using modeled $a^{\ast}_{PC}(620)$ produced mean and median ARE of 36.2% and ~22% respectively (Table 2).

4.5. Model performance comparison

We compared the performance of the newly developed algorithm with the widely used semi-analytical algorithm (Simis et al., 2005) for performance evaluation. We used the same values of model parameters $\gamma$ and $\delta$ reported in Simis et al. (2005). However, the algorithm produced severe underestimation of $a^{a}_{PC}(620)$ and $a^{a}_{PC}(665)$. The values reported by Simis et al. (2005) did not hold true in our dataset because of optically different waters in our study area. Therefore, values of $\gamma$ and $\delta$ for our dataset were estimated by least-square regression technique. The new values of $\gamma$ and $\delta$ were found to be 0.5 and 0.67 and used in the model (Mishra, 2012). The mean value of $a^{a}_{PC}(620)$ for various lakes in Spain and Netherlands ($=0.007 \text{ m}^2 \text{ g}^{-1}$) and $\epsilon$ reported by Simis et al. (2006) ($=0.24$) were used to retrieve PC. Estimation errors from the semi-analytical algorithm were considerably higher than the newly developed quasi-analytical approach. The mean relative error of model estimation was 68.39%, whereas, the median error was ~46% (Table 2). Slope and $R^2$ of the regression line between measured and modeled PC were 0.6 and 0.73 showing the deviation of modeled values from the 1:1 line (Fig. 10). The semi-analytical algorithm severely overestimated the model estimation in the lower PC range and severe underestimation was also observed in the higher PC range (Fig. 10). However, PC model error increased with decrease in PC:chl-a ratio which is consistent with Simis et al. (2005). Obtaining high estimation accuracy of PC algorithm in lower PC (~50 $\mu g \text{l}^{-1}$) range is still an existing issue. Simis et al. (2005) reported as high as 2.5 to ~15 fold overestimation when PC is less than 15 $\mu g \text{l}^{-1}$. In this study, we evaluated the performance of the new approach with Simis et al. (2005) in relatively lower PC range (<150 $\mu g \text{l}^{-1}$). Accuracy of the new approach was considerably higher than the semi-analytical algorithm (Simis et al., 2005). The mean relative error of the semi-analytical algorithm was 100%. Comparison of $a^{a}_{PC}(620)$ derived from the semi-analytical algorithm with the measured $a^{a}_{PC}(620)$ confirmed the overestimation $a^{a}_{PC}(620)$ which can be attributed to selection of a smaller $\epsilon$ than the true value (Fig. 10a). In addition, residual $a^{\text{CNDL}}(620)$ could be contributing to the overestimation of $a^{a}_{PC}(620)$ as well. On the other hand, the new algorithm produced a mean relative error of 45% in the lower PC range. Better performance of the new algorithm in the lower PC range can be attributed to two unique characteristics of the algorithm: 1) the new approach considers the variability in $\psi_1$ and $\psi_2$, and 2) it does not assume the $a^{\text{CNDL}}(620)$ and $a^{a}_{PC}(665)$ as negligible.

4.6. Algorithm uncertainties

As the samples were collected from shallow aquaculture ponds in this study, there could be a possibility of the contamination of measured $R_{\lambda}(\lambda)$ by bottom reflectance. Unfortunately, we do not have enough data to analytically derive euphotic depth. However we used a chl-a based empirical relation that was developed for fresh water lakes in FL, USA to retrieve Secchi depth from field measured chl-a values (Hoyer et al., 2002). Analysis showed that the model retrieved Secchi depth varied from 0.19 m$^{-1}$ to 0.88 m$^{-1}$ with an average value of 0.46 m$^{-1}$ in our dataset. Note that the model derived Secchi depths are very conservative estimates as the model does not account light attenuation attributed to inorganic suspended solids and CDOM. Retrieved Secchi depth values are lower

![Image](98x581 to 489x741)
than the depth of the ponds and therefore, it implies that the measured \( R_{\psi}(\lambda) \) data are not contaminated by bottom reflectance.

Even if we assume that the in situ \( R_{\psi} \) measurements were completely error free; there are still multiple sources of uncertainties at different steps of the above developed procedure. Lee et al. (2010) have systematically studied the sources of uncertainties of inverted inherent optical property products from QAA. For coastal waters, errors from the modeled \( a_{\psi}(\lambda \mathrm{a}) \) at the reference wavelength will have larger effect, as compared to \( b_{\psi}(\lambda) \) modeling errors on the \( a_{\psi}(\lambda) \) estimation. It was found that for strongly absorbing waters, when \( a_{\psi}(440) \) approaches 0.5 m\(^{-1}\), uncertainty in retrieving \( a_{\psi}(440) \) could be up to ±37% (Lee et al., 2010). There could be even considerably higher uncertainties in \( a_{\psi}(\lambda) \) and \( c_{\psi}(\lambda) \) estimations because of the physics nature of the decomposition of \( a_{\psi}(\lambda) \) signal into their individual components. In this research, we have even added another step to decompose the \( a_{\psi}(620) \) for retrieving \( a_{\psi}(620) \) using algebraic methods, where the coefficients, \( \psi_1 \) and \( \psi_2 \), were modeled from \( R_{\psi} \) band ratios. Therefore, uncertainties with those values will introduce errors in the final estimation of \( a_{\psi}(620) \) as well.

Another critical source of error in PC concentration is from the variability of \( a_{\psi}(620) \). As discussed earlier, \( a_{\psi}(620) \) could vary based on the response of the cyanobacteria species to the environmental and optical conditions. Grossman et al. (1993) reported that a number of phycoerythrin (PE) and PC hexamers in phycobilisome structure (PBS) change based on the quality of light availability. More PC pigments are synthesized in cyanobacteria cells when exposed to red light, whereas, more PE pigments are synthesized in cyanobacteria cells when exposed to green light. Hence, the intracellular PC and PE concentrations are sensitive to the quality of light availability and can have corresponding effect on \( a_{\psi}(620) \) from pigment packaging. It has also been reported that the cell morphology and photo adaptation may cause variability in \( a_{\psi}(620) \) (Bricaud et al., 1995; Sathyendranath et al., 1987). Similar reasons may cause variability in \( a_{\psi}(620) \) as well. In this study, \( a_{\psi}(620) \) varied from 0.003 to 0.006 m\(^{-1}\) mg\(^{-1}\) with an average value of 0.0048 m\(^{-1}\) mg\(^{-1}\). If the mean \( a_{\psi}(620) \) is used as a constant, the model will have 25% underestimation for the sample with highest \( a_{\psi}(620) \) and 37.5% overestimation for the sample with lowest \( a_{\psi}(620) \). However, the use of the modeled \( a_{\psi}(620) \) values addresses the variability to some extent and somewhat reduces the estimation error. Model uncertainties also depend on the relative contribution of cyanobacteria in the water supporting the findings in Simis et al. (2005). Results show that the relative errors were higher for samples with PC:Chl-a > 0.5 (Fig. 11). Samples with lower \( a_{\psi}(620) / a_{\psi}(440) \) and \( a_{\psi}(620) / a_{\psi}(665) \) values also showed higher relative errors.

Another source of error could have been from the analytical measurement of PC concentration. Sarada et al. (1999) reported that extraction procedures can affect the quality of extracted PC and hence the final accuracy of PC estimation. The samples extracted by homogenization using a sonicator showed a minor secondary peak at 678 nm, in addition to the major peak at 620 nm, indicating some chlorophyll contamination while disintegrating the cells (Sarada et al., 1999). In this study, homogenization procedure was used for the extraction of PC. Hence samples with high chl-a and chl-b concentrations will have higher chance of inaccuracy. Similarly, extraction efficiency of PC samples also affects the final PC concentration as well as the \( a_{\psi}(620) \). For example, a lower (higher) extraction efficiency could over (under) estimate \( a_{\psi}(620) \) and will eventually affect the final estimation accuracy. Although ice-bath was used to avoid local heating (under the tip of the probe) during the process of homogenization, some pigment degradation could have occurred and contributed to errors from PC extraction efficiency as well.

5. Conclusions

A novel method has been developed to quantify PC based on the multiband quasi-analytical algorithm (Lee et al., 2002). In a parallel study, QAA was parameterized to retrieve \( a_{\psi}(\lambda) \) in extremely turbid and hypertrophic waters (Mishra et al., 2013). The newly developed

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**Fig. 10.** Validation of the semi-analytical algorithm (SA) (Simis et al., 2005): a) Comparison of model retrieved PC concentrations with measured ones. Solid line is the 1:1 line and the dashed line is the linear regression line; comparison between measured and modeled \( a_{\psi}(620) \) from the semi-analytical algorithm (circles) and quasi-analytical algorithm using modeled \( \psi_1 \) and \( \psi_2 \) (stars) is also provided in the inset; and b) comparison of model errors from the SA with errors from QAA. Stars and circles represent errors from the newly developed quasi-analytical approach (QAA-PC) and from the semi-analytical algorithm (SA) (Simis et al., 2005) respectively.

**Fig. 11.** Relationship between PC:chl-a and relative error of PC estimation. Empty and filled circles represent the model errors from the PC retrievals using: 1) optimized \( \psi_1 \) and measured \( \psi_2 \) and 2) modeled \( \psi_1 \) and \( \psi_2 \).
method was successful in decomposing the $a_{Q}(620)$ to $a_{w}(620)$ with a mean ARE of ~28%. Magnitude of $a_{Q}(620)$ varied widely (0.003–0.006 m$^{-2}$ mg$^{-1}$) in this dataset. To reduce the uncertainty in PC estimation because of $a_{Q}(620)$ variability, an empirical model was developed to retrieve $a_{Q}(620)$ from $r_{rs}(620)/r_{rs}(665)$. The mean and median ARE of PC estimation were 36.2% and 22% respectively when modeled $\psi_{1}$ and $\psi_{2}$ were used. Overall, performance was lower in the lower range of PC concentration (>150 μg l$^{-1}$). The mean and median ARE in the lower PC range were 45.2% and 44.7%, whereas, the errors in the higher PC range (>150 μg l$^{-1}$) were 27.9% and 19.9%. We also compared the newly developed method with the best existing semi-analytical algorithm (Simis et al., 2005). The mean and median relative errors from the semi-analytical algorithm (68.4% and 46.0% respectively) were much higher than those of the current approach. The newly developed method shows a strong potential of quantifying and mapping PC in optically complex turbid productive waters. Findings from this research are based on a small dataset ($n=24$) with a wide range and because of the same reason the robustness of the new empirical steps to retrieve $\psi_{1}$ and $\psi_{2}$ has not been fully assessed. Future work will focus on using a large dataset for a robust optimization of the coefficients and validation of the proposed model. Results demonstrate that the new approach presented in this study will be suitable for quantifying PC concentration in cyanobacteria dominated turbid productive waters such as inland lakes and estuaries.

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Appendix A. Steps of quasi-analytical algorithm

QAA takes above surface remote sensing reflectance as input and first calculates sub-surface remote sensing reflectance $r_{rs}$ as:

$$r_{rs} = R_{rs}/(0.52 + 1.7R_{aw}). \hspace{1cm} (A1)$$

$r_{rs}$ is a function of $u$, the ratio of back scattering coefficient $b_{b}$ to the sum of total absorption coefficients and backscattering coefficients.

$$u(\lambda) = \frac{b_{b}(\lambda)}{a(\lambda) + b_{b}(\lambda)} \hspace{1cm} (A2)$$

$u$ can be empirically derived from $r_{rs}$ as in Gordon et al. (1988):

$$u(\lambda) = \frac{-g_{0} + \sqrt{(g_{0})^{2} + 4g_{1} * r_{rs}(\lambda)}}{2 * g_{1}} \hspace{1cm} (A3)$$

where $g_{0} = 0.089$ and $g_{1} = 0.125$. Further, the QAA estimates total absorption coefficients at a reference wavelength, $\lambda_{0}$. In the native form, QAA uses 555 or 650 nm as $\lambda_{0}$ based on the level of turbidity. However, in another study, Mishra et al. (2013) have parameterized the QAA for extremely turbid and productive water where the $\lambda_{0}$ was moved to 708 nm because of strong absorption by non-water optical constituents even at 650 nm.

$$a(\lambda_{0}) = a_{w}(709) + 10^{0.8125-2.3404 x + 1.24 x^{2}} \hspace{1cm} (A4)$$

where $x = \log_{10}(0.01 * r_{rs}(442) + r_{rs}(620)) \hspace{1cm} (A5)$

The QAA then analytically retrieves particulate backscattering coefficients at the reference wavelength, $b_{bp}(\lambda_{0})$.

$$b_{bp}(\lambda_{0}) = u(\lambda_{0})a(\lambda_{0}) - \frac{b_{bp}(\lambda)}{1 - u(\lambda)} \hspace{1cm} (A6)$$

Knowing $b_{bp}(\lambda_{0})$ and $\eta$, the QAA estimates $b_{bp}(\lambda)$ at other wavelengths from:

$$b_{bp}(\lambda) = b_{bp}(\lambda_{0}) \left( \frac{\lambda}{\lambda_{0}} \right)^{n} \hspace{1cm} (A7)$$

The spectral power, $\eta$, is empirically estimated from:

$$\eta = 2.0 \left( 1 - 1.2 \exp \left( -0.5 \frac{r_{rs}(443)}{r_{rs}(555)} \right) \right) \hspace{1cm} (A8)$$

The total absorption coefficient is then calculated as:

$$a(\lambda) = (1 - u(\lambda)) \left( b_{bp}(\lambda) + b_{bp}(\lambda_{0}) \right) \hspace{1cm} (A9)$$

The QAA further decomposed the total absorption spectrum into 1) $a_{Q}(\lambda)$, a combined absorption by colored dissolved organic matter (CDOM) and detrital matter, and 2) $a_{w}(\lambda)$.

$$a_{Q}(\lambda) = \left[ a(\lambda) - a_{w}(\lambda) \right] - a_{w}(411) - \zeta a_{w}(411) \hspace{1cm} (A10)$$

where

$$\zeta = \frac{a_{w}(411)}{a_{Q}(\lambda)} = 0.74 + 0.8 \frac{r_{rs}(443)/(r_{rs}(555))}{0.2} \hspace{1cm} (A11)$$

Absorption coefficients by phytoplankton is then calculated as:

$$a_{Q}(\lambda) = a_{Q}(\lambda) - a_{w}(\lambda) - a_{Q}(\lambda) \hspace{1cm} (A12)$$

References
