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Retrieving absorption coefficients of multiple phytoplankton pigments from hyperspectral remote sensing reflectance measured over cyanobacteria bloom waters

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Abstract

Light absorption by phytoplankton pigments plays an important role not only in photosynthesis but also in modulating the appearance of water color. Some pigments are markers of phytoplankton classes or species. To better characterize phytoplankton, an inversion model is developed to retrieve the absorption coefficients of multiple pigments from hyperspectral remote sensing reflectance. In the model, the Gaussian functions proposed by Hoepffner and Sathyendranath (1991) were refined and implemented for the estimation of the absorption coefficients of multiple pigments. Application of the inversion model to remote sensing measurements made in cyanobacteria bloom waters resulted in the absorption coefficients of *chlorophylls a, b,* and *c, carotenoid, phycoerythrin,* and *phycocyanin* with the mean absolute relative error under 32% for wavelengths between 400 nm and 700 nm. The results indicate that it is feasible to retrieve the absorption coefficients of multiple pigments from hyperspectral remote sensing reflectance as long as the pigments make adequate contributions to the total absorption coefficient.

Phytoplankton pigments act as indicators to elucidate the composition and fate of phytoplankton in the world's oceans (Schlüter et al. 2000) and are often associated with important biogeochemical cycles related to, for example, carbon dynamics in the oceans. The light absorbed by phytoplankton pigments provides the initial energy for these cycles: the photosynthetic process draws carbon dioxide out of the atmosphere, turns this inorganic carbon into organic compounds, and forms the basic energy block of the aquatic food web (Kirk 1994; Behrenfeld and Falkowski 1997; Falkowski 2002). The light absorbed by phytoplankton pigments is also one of the major factors influencing the appearance of water color (Morel and Prieur 1977; Gordon et al. 1988; Bidigare et al. 1990; Bricaud et al. 2004).

As the primary photosynthetic pigment, *chlorophyll a* has received the most attention in ocean color remote sensing, and concentration of *chlorophyll a* has been generated from satellite ocean color measurements as a standard data product for decades (O'Reilly et al. 1998, 2000; Hoge et al. 1999; Werdell and Bailey 2005; Dierssen et al. 2006; Hu et al. 2010, 2012; Mishra and Mishra 2012). In a phytoplankton cell, actually *chlorophyll a*, *chlorophyll b*, *chlorophyll c*, and

carotenoid, etc. function together as light-harvesting pigments, and all have a strong ability to capture light in the visible bands. Some accessory pigments even play a critical role in the photosynthesis process; such as the *carotenoids* have a high light-harvesting capacity (Lehman 1981; Jeffrey et al. 1997; Schitüter et al. 1997; Moisan and Mitchell 1999) and act as photoprotective pigments to protect cells from the photo-oxidation damage (Demmig-Adams 1990; Demers 1991).

With the advancement of pigment analysis techniques, such as high-performance liquid chromatography and liquid chromatography-mass spectrometry, the detection of pigment compositions, concentrations, and their influences on the absorption spectrum of phytoplankton became possible (Jeffrey et al. 1997; Kirkpatrick et al. 2000; Van Heukelem and Thomas 2001; Roy et al. 2011). Because of these techniques, pigment information has been increasingly used in in situ and remote sensing applications (Schlüter and Møhlenberg 2003; Roy et al. 2011; IOCCG Report 14 and references therein). Some pigments existing in particular groups or taxa have been recognized as their signatures, and the concentration, light absorption or scattering properties of these pigments are used as indicators for phytoplankton classes or species (Wright and Jeffrey 2006; Hirata et al.

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2008, 2011; Sarmento and Descy 2008; Brewin et al. 2010; Devred et al. 2011).

Cyanobacteria bloom, a notorious harmful ecosystem event, occurs in both fresh and salt waters. Taking advantage of the light absorption around 620 nm due to its marker pigment phycocyanin, a few methods have been developed to indicate and quantify these harmful algal blooms for inland and coastal waters (Simis et al. 2005; Wynne et al. 2008; Mishra et al. 2013; Blondeau-Patissier et al. 2014; Qi et al. 2014; Kudela et al. 2015). Based on an assumption that chlorophyll a and phycocyanin contribute equally to the phytoplankton absorption at 620 nm (Simis et al. 2005), Mishra et al. (2013) retrieved the absorption coefficient of phycocyanin from in situ remote sensing reflectance using a reparametrized quasianalytical algorithm (Lee et al. 2002; Mishra et al. 2014). Other methods, as presented in Qi et al. (2014) and Kudela et al. (2015), used spectral shapes or band ratios to get phycocyanin concentration from remote sensing reflectance.

These methods, however, retrieve the information of one more pigment other than chlorophyll a. To retrieve the information of more pigments, many efforts have been made in the past decades (Bidigare et al. 1989, 1990; Hoepffner and Sathyendranath 1991, 1993; Lohrenz et al. 2003; Bricaud et al. 2004; Ficek et al. 2004; Chase et al. 2013). Among these studies, Hoepffner and Sathyendranath (1991, 1993), Lohrenz et al. (2003), and Chase et al. (2013) used the Gaussian decomposition method to retrieve the absorption spectra of four or five different pigments. The Gaussian curves used in these studies showed the advantages of representing the in vivo pigment absorption properties. However, the input information used for the decompositions were the measured spectra of particulate absorption or phytoplankton absorption, rather than remotely sensed ocean (or water) color.

In this study, we assessed the potential of retrieving the absorption coefficients of multiple pigments from hyperspectral remote sensing reflectance collected in cyanobacteria bloom waters. Since remote sensing data could be acquired from airborne or space-borne platforms, if the approach also works with water color as the input, it will be possible to obtain information of the spatial and temporal variability of multiple pigments remotely. In this study, the Gaussian sets proposed by Hoepffner and Sathyendranath (1991) were updated for cyanobacteria dominated waters. Based on the refined parameters, a multiple pigment retrieval model was developed and applied to cocollected hyperspectral remote sensing reflectance to retrieve the magnitude of the absorption coefficient of six pigments, chlorophyll a, b, c (Chl-a, -b, -c), carotenoid (Carot), phycoerythrin (PE), and phycocyanin (PC), respectively. The proposed model was further tested with independent measurements from Taihu Lake, China to assess the effectiveness.

Data and study area

Two separate hyperspectral datasets were used for the method development and validation, and details of the datasets are provided below.

Dataset for model development

Mississippi Pond dataset (MS): This dataset includes 41 samples of remote sensing reflectance (R_{rs} , sr^{-1}) and absorption coefficients of phytoplankton (a_{ph}), detritus (a_d), and gelbstoff (a_g). A set (24 samples) of in situ measured PC concentration was also included in the dataset. This dataset (see Mishra et al. 2013 for details) was collected from a series of highly turbid and productive aquaculture ponds at various stages (initiation, peak, and senescence) of cyanobacteria bloom (Chl-a concentration varied from 59 to 1377 μ g/L), located in northwestern Mississippi, U.S.A.

The remote sensing reflectance data was acquired in the range of 400–900 nm with a sampling interval of 0.3 nm by deploying a dual sensor system with two inter-calibrated ocean optics spectroradiometers (Ocean Optics Inc., Dunedin, Florida, U.S.A.). Surface water samples were collected and filtered. A Perkin Elmer lambda 850 spectrophotometer (Perkin Elmer Inc., Waltham, Masscults, U.S.A.) was used to measure the absorption coefficient of phytoplankton, detrital matter, and gelbstoff in the 380-750 nm range at 1 nm spectral resolution. Detailed information regarding the environmental characteristics and measurement methods can be found in Mishra et al. (2013), where cyanobacteria blooms with Planktothrix agardhii as the most abundant species were happening when the in situ data were collected. A total of 41 pairs of inherent and apparent optical properties were used to refine the Gaussian curves of Hoepffner and Sathyendranath (1991) for modeling the $a_{\rm ph}$ spectrum and for the inversion model, respectively.

Dataset for validation

Lake Taihu dataset (LT): This dataset includes 45 $R_{\rm rs}$ (λ) spectra at 1.4 nm resolution, corresponding spectra of $a_{\rm d}$, $a_{\rm g}$, and $a_{\rm ph}$ (350–750 nm) at 1 nm resolution and 31 set of PC concentration collected from Lake Taihu, China, and under cyanobacteria bloom conditions (Chl-a: 10–222 μ g L⁻¹) where the dominant species was *Microcystis aeruginosa*.

Water samples and optical data of surface water were collected during two surveys in January–August 2011 and November 2011, respectively. In situ $R_{rs}(\lambda)$ was measured with a hand-held ASD (Analytical Spectral Device, Inc., Boulder, Colorado) spectroradiometer. Surface water samples were collected right after $R_{rs}(\lambda)$ measurements and analyzed on the same day in the laboratory. PC concentration was estimated based on the measurements using a spectrofluorophotometer (Shimadzu RF-5301, 620 nm excitation and 647 nm emission). The absorption spectra of particulate, detrital matter, and gelbstoff, respectively, were measured with a Shimadzu UV-2401 spectrophotometer after sample

Retrieval of absorption coefficients of multiple pigments

filtration. More information about LT and details about water sample collection, measurement protocols, and processing methods can be found in Duan et al. (2010) and Ma et al. (2006). This dataset serves as an independent source to validate the inversion scheme.

Methods

Model development

Remote sensing reflectance, $R_{rs}(\lambda)$, defined as the ratio of water leaving radiance to downwelling irradiance just above the surface, can be expressed as a function of the total absorption (a_t , m⁻¹) and the total backscattering coefficients (b_b , m⁻¹) (Gordon et al. 1988; Morel 1991):

$$R_{\rm rs}(\lambda) = F\left(\frac{b_{\rm b}(\lambda)}{a_{\rm t}(\lambda) + b_{\rm b}(\lambda)}\right) \tag{1}$$

 $a_{\rm t}$ and $b_{\rm b}$ are usually described as the sum of the primary components as:

$$a_{\rm t}(\lambda) = a_{\rm ph}(\lambda) + a_{\rm dg}(\lambda) + a_{\rm w}(\lambda) \tag{2}$$

$$b_{\rm b}(\lambda) = b_{\rm bw}(\lambda) + b_{\rm bp}(\lambda) \tag{3}$$

where a_{dg} stands for the combined absorption coefficients of detritus (a_d) and gelbstoff (a_g) , a_w is the absorption coefficients of water molecules; while b_{bw} and b_{bp} represent the backscattering coefficients of water molecules and suspended particles, respectively.

In the above equations, except the absorption and backscattering contributions from water (a_w and b_{bw}) that can be considered known (Morel 1974; Pop and Fry 1997; Zhang et al. 2009; Lee et al. 2015), the other parameters (a_{ph} , a_{dg} , and b_{bp}) are to be derived from the R_{rs} spectrum. It is impossible to get one unequivocal solution for any underdetermined system where the unknowns outnumber the equations. To be mathematically possible, spectral models have to be developed for each of these components and used in the inversion process.

The spectrum of particle backscattering coefficient was modeled following Roesler and Boss (2003) and Whitmire et al. (2007):

$$b_{\rm bp}(\lambda) = \frac{b_{\rm bp}}{b_{\rm p}} \left(c_{\rm s} - a_{\rm ph}(\lambda) \right) \tag{4}$$

where c_s represents the beam attenuation coefficient of suspended particles and was assumed spectrally independent. The $b_{\rm bp}/b_{\rm p}$ in Eq. 4 is the ratio of backscattering to scattering coefficients of particles which usually varies from 0.01 to 0.03, and was assumed a constant as 0.01 based on Whitmire et al. (2007). In the above $a_{\rm d}$ is omitted as it is very small compared with $a_{\rm ph}$ for these waters.

The spectrum of the phytoplankton absorption coefficient, a_{ph} , is modeled following Hoepffner and Sathyendranath (1991):

$$a_{\rm ph}(\lambda) = \sum_{i=1}^{n} a_{\rm gaus}(\lambda_i) \exp\left[-0.5\left(\frac{\lambda - \lambda_i}{\sigma_i}\right)^2\right]$$
(5)

where σ_i and a_{gaus} (λ_i) are the width and peak magnitudes of the *i*th Gaussian curve with peak center (λ_i). As each Gaussian curve corresponding to an absorption curve of a specific pigment (Hoepffner and Sathyendranath 1991), a_{gaus} (λ_i) could be written as $a_{pig}(\lambda_i)$.

The spectrum of the combined absorption coefficient of detritus and gelbstoff, a_{dg} , is modeled as an exponential function following Carder et al. (1991) and other semianalytical algorithms (IOCCG Report 5):

$$a_{\rm dg}(\lambda) = a_{\rm dg}(\lambda_0) \exp\left(-S(\lambda - \lambda_0)\right) \tag{6}$$

where λ_0 is taken as 440 nm and S usually varies between 0.01 nm⁻¹ and 0.02 nm⁻¹ for natural water and 0.015 nm⁻¹ was used in this study.

The above relationships form the framework of the multiple pigment inversion (MuPI) model for the retrieval of a_{pig} (λ_i) from R_{rs} (λ). To effectively derive the values of the unknowns, a spectral optimization method was employed as commonly used for the retrieval of chlorophyll concentration or water depth (Bukata et al. 1995; Roesler and Perry 1995; Lee et al. 1999; Maritorena et al. 2002; Brando et al. 2012). Spectral optimization is basically a method used to solve a complex equation (Eq. 8) numerically. The derived values are those unknowns with modeled R_{rs} spectrum best matching the input R_{rs} spectrum by minimizing the target function (Eq. 9). Specifically, define $u = b_b/(a_t + b_b)$, then there is

$$u = \frac{b_{\rm b}}{a_{\rm t} + b_{\rm b}} = \frac{b_{\rm bw} + 0.01(c_{\rm s} - a_{\rm ph}(\lambda))}{\sum_{i=1}^{n} a_{\rm gaus}(\lambda_i) \exp\left[-0.5\left(\frac{\lambda - \lambda_i}{\sigma_i}\right)^2\right] + a_{\rm dg}(\lambda_0) \exp\left(-S(\lambda - \lambda_0)\right) + a_{\rm w} + b_{\rm bw} + 0.01(c_{\rm s} - a_{\rm ph}(\lambda))}$$
(7)

Following Gordon et al. (1988) and taking into account the air–sea interface effect (Lee et al. 2002), there is

$$R_{\rm rs} = \frac{0.52(g_1 u + g_2 u^2)}{1 - 1.7(g_1 u + g_2 u^2)} \tag{8}$$



Fig. 1. The frequency distribution of each band with the first-order derivative (**A**) and second-order derivative (**B**) of a_{ph} spectrum being zero. a_{ph} data were obtained from the MS ponds.

Here, g_1 and g_2 (sr⁻¹) are model coefficients and fixed to 0.089 and 0.125 sr⁻¹ (Lee et al. 2002).

The target function to quantify the spectral closeness between measured and modeled R_{rs} spectra is defined as (Huang et al. 2013; Werdell et al. 2013)

$$\delta = \frac{\sqrt{\frac{1}{N_{\lambda}} \sum_{i=1}^{N_{\lambda}} \left(\hat{R}_{\rm rs}(\lambda_i) - R_{\rm rs}(\lambda_i)\right)^2}}{\frac{1}{N_{\lambda}} \sum_{i=1}^{N_{\lambda}} R_{\rm rs}(\lambda_i)} \tag{9}$$

with N_{λ} as the wavelength number, $R_{\rm rs}$ (λ) as the measured and $\hat{R}_{\rm rs}$ (λ) the modeled spectrum, respectively.

Refinement of the Gaussian parameters

Each Gaussian curve is determined by three parameters: width, peak center, and magnitude as shown by Eq. 5, and a set of values have been developed by Hoepffner and Sathyendranath (1991) (Table 4 in Hoepffner and Sathyendranath 1991) to model spectral $a_{\rm ph}$. This set of peak centers and widths were applied to $a_{\rm ph}$ decomposition of the MS dataset, for which a Matlab script was used to minimize the differences between the modeled (Eq. 5) and the measured $a_{\rm ph}(\lambda)$, and the magnitudes for the Gaussian curves were returned as the results. There was generally a 20% mean relative difference between the measured and Eq. 5-modeled $a_{\rm ph}$ (λ) for the 400–700 nm range, likely due to significant differences in phytoplankton groups between waters studied in Hoepffner and Sathyendranath (1991) and those in this study. More specifically, the set of parameters in Hoepffner and Sathyendranath (1991) was developed from 20 monospecific cultures, which are representative of environments dominated by three major phytoplankton groups: diatoms, chlorophyceae, and prymnesiophyceae. For cyanobacteria



Fig. 2. The mean absolute relative error (MARE, Eq. 13) between Eq. 5-modeled and measured $a_{\rm ph}$ spectrum for data obtained from the MS pond waters.

dominated waters, these parameters (peak centers, band widths, and even the number of peaks) may not be exactly applicable. We therefore refined these parameters with measurements obtained from the MS ponds for applications with cyanobacteria dominated scenarios.

Update of the Gaussian peak centers and widths

To find the parameters most suitable for a cyanobacteria abundant environment, mathematical evaluations were carried out to find the Gaussian peak centers and widths from the pool of $a_{\rm ph}$ spectra. Mathematically, the easiest way to find peaks and shoulders of a spectrum is to locate the places where the first- and second-order derivatives are zero, respectively, as demonstrated in Lee et al. (2007). Equations 10 and 11 were applied to in situ $a_{\rm ph}$ spectra obtained from the MS ponds to get the first- and second-order derivatives for each $a_{\rm ph}$ spectrum at 1 nm spectral resolution. The frequency of $a_{\rm ph}(\lambda)'$ and $a_{\rm ph}(\lambda)''$ being zeros, respectively, is shown in Fig. 1.

$$a_{\rm ph}(\lambda)' = \frac{\mathrm{d}a_{\rm ph}(\lambda)}{\mathrm{d}\lambda} \tag{10}$$

$$a_{\rm ph}(\lambda)'' = \frac{\mathrm{d}a_{\rm ph}(\lambda)'}{\mathrm{d}\lambda} \tag{11}$$

The wavelength locations with the first-order derivative as zero represent the peaks or valleys of an $a_{\rm ph}$ spectrum, while the second-order derivative as zero indicates an inflection of an $a_{\rm ph}$ spectrum. Knowing the spectral locations of these places is not only important to model the spectral variation of $a_{\rm ph}$ with a limited number of variables, but also required to derive information about specific pigments (Bidigare et al.

Table	1. Ir	nitial	guess	of the	e peak	centers	and	widths	(σ^*)	and	the o	output	mean	peak	centers	and	width	s of the	Gauss	ian c	curves.	σ^*
is relate	d to	full \	width	at ha	f max	imum (FWHM	M): FW	ΉM	$=\sigma$ >	< 2.3	55. As	a ger	neral i	ndicatio	n of	the ed	osyster	n, the	mea	n mag	,ni-
tudes o	f the	peak	s are a	also ir	cludeo	d, and t	he ca	roteno	ids a	re ma	ainly	β -caro	tenoid	s.								

Gaussian band number and associated pigment species								
		Input par	ameters (nm)	Output parameters (nm)				
Peaks	Pigment	center	width (σ^*)	center	width	Mean magnitude (m ⁻¹)		
1	Chl-a	385	15	386.6	18.8	12.8		
2	Chl-a	410	15	414	10.7	8.5		
3	Chl-a	430	15	435	12	8.3		
4	Chl-c	450	15	451.7	18.5	6		
5	Carot	480	15	484	19.6	5.8		
6	Carot	520	15	515.6	18	3.7		
7	PE	550	15	548.8	15.7	2		
8	Chl-c	580	15	584.4	17	3		
9	РС	620	15	617.6	16	3.9		
10	Chl-c	640	15	636	11.6	1.8		
11	Chl-b	650	15	653	14	2.3		
12	Chl-a	675	15	677	10.6	5.6		
13	Chl-a	695	15	693.5	20	0.7		

1989). The primary locations of these wavelengths were obtained via analyzing their distribution frequency (see Fig. 1) and they are: for the first-order derivative: 388-393, 418-426, 434-445, 555-565, 618-635, 648-658, and 674-683 nm; for the second-order derivative: 388-395, 405-413, 420-435, 444-453, 473-485, 513-523, 545-554, 573-586, 598-617, 638-647, 661-668, and 685-695 nm (Fig. 1).

It is known that the absorption curves of pure pigments isolated from particular cultures have characteristic spectral features, although the actual wavelength could vary slightly in different solutions and in vivo status (Bidigare et al. 1989, 1990; Hoepffner and Sathyendranath 1991, 1993; Jeffrey et al. 1997; Bricaud et al. 2004; Chase et al. 2013; Mishra et al. 2013). Combining this information with wavelengths where the first- and second-order derivatives of a_{ph} are zeros, an initial set of peak centers (a total of 13) for the absorption spectra of various pigments was determined. The final locations and the width of each Gaussian curve were derived by fitting the $a_{\rm ph}$ spectra obtained from the MS pond waters with Eq. 5. This was achieved via a least square optimization method embedded in MATLAB, and by minimizing the differences between the input $a_{\rm ph}$ (λ) and the Eq. 5-modeled $a_{\rm ph}$ (λ) and allowing the peak center and width vary within ± 5 nm from the initial guesses (Chase et al. 2013). The averages (finalized) of the Gaussian parameters (peak center and width, respectively) obtained from these $a_{\rm ph}$ spectra are presented in Table 1. The new set of parameters for the Gaussian curves (peak center, width, and magnitude) resulted in a mean absolute relative error (MARE, see Eq. 13) between the modeled and measured $a_{\rm ph}$ spectra generally under $\sim 2\%$ (see Fig. 2) for wavelengths in the 400–700 nm range. The higher MARE values (\sim 7%) for wavelengths around 700 nm and longer are mainly due to lower absorption at these wavelengths.

The absolute relative error (RE) and mean absolute relative errors (MARE) are calculated as:

$$\mathrm{RE}_{i} = \frac{|Y_{i} - Y_{i}|}{Y_{i}} \tag{12}$$

MARE =
$$\frac{1}{n} \sum_{i=1}^{n} \frac{|Y_i - \hat{Y}_i|}{Y_i}$$
 (13)

Here Y_i represents in situ measurement, and \hat{Y}_i for model estimates.

Compared with the results shown in Hoepffner and Sathyendranath (1991), the number of Gaussian bands (Table 1) increased slightly (11-13). One peak around 650 nm from the absorption of Chl-b and another peak at 550 nm for the absorption of PE are added. The peak around 620 nm in Hoepffner and Sathyendranath (1991) was likely a contribution from Chl-a; for waters with cyanobacteria bloom, PC also has significant contributions to absorption at this wavelength. Simis et al. (2005) assumed Chl-a and PC contribute equally to this absorption peak, but for cyanobacteria dominated water, although chlorophyll and other accessory pigments make some contributions, PC appears to be the main absorption pigment at this wavelength that contributes around 70% to the total peak height (Emerson and Lewis 1942). Compared with Hoepffner and Sathyendranath (1991), the *carotenoids* (Carot) absorption peak 5 and peak 6 shift to slightly longer wavelengths in cyanobacteria



Fig. 3. Demonstration of the correlations between $a_{pig}(\lambda)$ and examples of modeled vs measured $a_{ph}(\lambda)$ (D). (A) and (B) show linear relationships between $a_{pig}(515.6)$, $a_{pig}(584.4)$ and other $a_{pig}(\lambda)$, respectively. (C) shows the matrix of coefficient of determination (R²) between the 13 magnitudes (Table 1). (D) is an example of measured a_{ph} spectrum (black) and Eq. 5-modeled a_{ph} spectrum with 13 (blue) or 2 (red) independent magnitude variables.

dominated waters, with their widths being almost the same as shown in Hoepffner and Sathyendranath (1991). Peaks 4 and 10 at 451.7 nm and 636 nm as absorption peaks of Chlc, move to slightly shorter wavelengths and the peak at 451.7 nm becomes wider while the peak at 636 nm becomes narrower in cyanobacteria dominated waters. Peak 9 at 617.6 nm of the PC absorption is located at shorter wavelength and has a slightly broader band compared with the Chl-a in Hoepffner and Sathyendranath (1991). For the other pigment absorption peaks, the location and width are consistent with those in Hoepffner and Sathyendranath (1991).

Covariance between peak magnitudes

There are 15 unknowns (13 Gaussian magnitudes, one for $a_{\rm dg}(\lambda)$ and one for $b_{\rm bp}(\lambda)$) to be derived from the spectral optimization scheme (Eq. 9). When inverting an $R_{\rm rs}$ spec-

trum for information of water constituents, it is always useful and important to have fewer variables. In particular, although there are 13 Gaussian curves to form one $a_{\rm ph}$ spectrum, it does not mean the magnitudes among the Gaussian curves are independent of each other, especially for those from the same pigments. Further, for a specific phytoplankton group the composition of pigments could be stable, thus dependencies between pigments may exist, therefore it is necessary to diagnose to what extent the 13 Gaussian peaks are independent, at least for such cyanobacteria dominated waters.

Intercorrelation between the 13 peaks of $a_{pig}(\lambda)$ derived from measured $a_{ph}(\lambda)$ was evaluated and a correlation matrix was developed (see Fig. 3). It is found that there is a very high coefficient of determination ($R^2 > 0.9$) among many mangitudes of $a_{pig}(\lambda)$, and two magnitudes at 515.6 nm

(peak 6) and 584.4 nm (peak 8) show the highest correlations with others (Fig. 3A,B).

Based on the above analyses (see Table 2 for results of linear regression analysis), apparently the magnitudes of the other Gaussian peaks could be estimated from a_{Carot} (515.6) (representing the absorption coefficient of Carot) and $a_{\text{Chl-c}}(584.4)$ (representing the absorption coefficient of Chl-c). Consequently an a_{ph} spectrum could be constructed with Eq. 5 with just two independent variables (a_{Carot} (515.6) and $a_{\text{Chl-c}}(584.4)$), and the resulted a_{ph} spectrum is only slightly worse (the maximum MARE in the 400–

Table 2. Relationships between the magnitudes of a_{pig} (λ) and a_{Carot} (515.6) and a_{Chl-c} (584.4), respectively. Values of R^2 are also included. x_1 for a_{Carot} (515.6) and x_2 for a_{Chl-c} (584.4).

	Gaussian bands and pigment relationships							
Peaks	Pigment	Peak (nm)	relationship	R ²				
1	Chl-a	386.6	$y = 2.80 \times x_1$	0.96				
2	Chl-a	414	$y = 1.78 \times x_1$	0.98				
3	Chl-a	435	$y = 2.23 \times x_1$	0.98				
4	Chl-c	451.7	$y = 1.65 \times x_1$	0.99				
5	Carot	484	$y = 1.63 \times x_1$	0.99				
6	Carot	515.6	<i>x</i> ₁	1				
7	PE	548.8	$y = 0.60 \times x_1$	0.95				
8	Chl-c	584.4	<i>x</i> ₂	1				
9	PC	617.6	$y = 1.24 \times x_2$	0.99				
10	Chl-c	636	$y = 0.52 \times x_2$	0.99				
11	Chl-b	653	$y = 0.81 \times x_2$	0.98				
12	Chl-a	677	$y = 1.52 \times x_2$	0.94				
13	Chl-a	693.5	$y = 0.39 \times x_2$	0.97				

700 nm range increased to ~ 10%) compared with that modeled with 13 independent magnitudes (see Fig. 3D for an example). Therefore, the two variables for an $a_{\rm ph}$ spectrum along with $c_{\rm s}$ for the particle backscattering coefficient (Eq. 4) and $a_{\rm dg}$ (λ_0) for the detritus–gelbstoff absorption coefficient (Eq. 6) form a four parameter model for an $R_{\rm rs}$ spectrum.

Results and discussion

Performance of MuPI for the MS dataset

Evaluation of the MuPI scheme was conducted by comparing the magnitudes of a_{pig} derived from measured R_{rs} spectra and those a_{pig} magnitudes from a_{ph} spectra of the MS dataset. The value of the target function (Eq. 10) is under 10% for the entire dataset. The MARE at each wavelength between the optimized and measured $R_{\rm rs}$ (λ) is generally less than 10% for the 400-700 nm range. For some samples the maximum RE at wavelength 610-680 nm runs to \sim 20%, a result of the slight variance between relationships of pigment absorption magnitudes and the likely fluorescence of PC around 650 nm (Gregor et al. 2007). An example of the optimized R_{rs} vs. the measured R_{rs} is shown in Fig. 4A, where a closure between the output and input R_{rs} spectra is achieved with the value of the target function as 0.047. Figure 4B further provides the corresponding spectra of a_{pig} $a_{\rm ph}$, $a_{\rm dg}$, $a_{\rm t}$, and $b_{\rm b}$ resulted from the MuPI model. The $a_{\rm ph}$ spectrum from sample measurements is also included for a comparison.

The MARE of two independent variables ($a_{\text{Carot}}(515.6)$) and $a_{\text{Chl-c}}(584.4)$) derived from R_{rs} are 30% and 26%, respectively. The absorption coefficients of the other 11 pigments are calculated from the $a_{\text{Carot}}(515.6)$ and $a_{\text{Chl-c}}(584.4)$ values



Fig. 4. An example of results from the MuPI scheme. (**A**) is the input and optimized R_{rs} spectrum (the value of the target function is 0.047 (Eq. 9); and (**B**) presents the corresponding (retrieved) spectra of the absorption coefficients of pigments (a_{pig}), total phytoplankton (a_{ph}), detritus and gelbst-off (a_{dq}), bulk water (a_t), and the spectrum of backscattering coefficient (b_b). Also included is the measured a_{ph} spectrum.



Fig. 5. Comparison between the absorption coefficients (a_{pig}) of Chl-a, Chl-b, Chl-c, carot, PE, and PC retrieved from R_{rs} and those derived from a_{ph} for the MS dataset.

following the relationships shown in Table 2. It is found that the MARE values are in a range of 22-31% when comparing $a_{pig}(\lambda)$ derived from R_{rs} with those derived from a_{ph} (see Table 3 and Fig. 5). The MuPI derived a_{pig} matches the values from $a_{\rm ph}$ decomposition well (MARE \leq 32%) for these pigments, especially for Chl-a (MARE = 22%). For the entire dataset, the MARE of a_{pig} is 30% for $a_{Carot}(515.6)$, 31% for $a_{\rm PE}(548.8)$, 26% for $a_{\rm Chl-c}(584.4)$, 25% for $a_{\rm PC}(617.6)$, 32% for $a_{\rm Chl-b}(653)$, and 22% for $a_{\rm Chl-a}(677)$ (see Table 3). These results indicate comparable or better results in retrieving the absorption coefficients of other pigments as that of Chl-a via the empirical ratio algorithm (O'Reilly et al. 1998). Also included in Table 3 is the root mean square error in log scale (RMSE, Eq. 14) between the $R_{\rm rs}$ derived and $a_{\rm ph}$ -derived $a_{\rm pig}$ (λ) values, which is calculated as

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left(log_{10}\left(\hat{A}_{i}\right) - log_{10}\left(A_{i}\right) \right)^{2}}$$
(14)

where, A_i is a_{ph} -derived a_{pig} (λ) and \hat{A}_i the R_{rs} -derived a_{pig} (λ). RMSE provides a more balanced evaluation of both higher and lower values when the dynamic range is orders of magnitude; and the RMSE values of these pigments are equivalent to that of band-ratio derived chlorophyll-a concentration (O'Reilley et al. 1998).

Application to LT dataset

The MuPI scheme was further applied to the LT dataset to test its applicability, with a_{pig} retrieved from a_{ph} and R_{rs} spectra separately. Figure 6 compares the two sets of retrieved a_{pig} values and it is found that the a_{pig} derived

Table 3. Mean (and medium) absolute relative error between a_{pig} derived from R_{rs} and those decomposed from a_{ph} for the MS dataset. Also include are the RMSE values for each a_{piq} peak.

Peaks (nm)	Mean RE (%)	Medium RE (%)	RMSE
386.6	30	29	0.19
414	28	29	0.18
435	27	27	0.17
451.7	29	32	0.18
484	30	32	0.19
515.6	30	33	0.19
548.8	31	29	0.15
584.4	26	19	0.15
617.6	25	16	0.14
636	26	16	0.15
653	32	27	0.17
677	22	15	0.13
693.5	22	15	0.12

RE, absolute relative error; RMSE: root mean square error.

from $R_{\rm rs}$ is generally in agreement with those derived from $a_{\rm ph}$ (see Table 4). In particular, the MARE values are 22.4% and 24% for $a_{\rm Chl-c}(584.4)$ and $a_{\rm PC}(617.6)$, respectively, although higher (~ 40%) for $a_{\rm Carot}(515.6)$ and $a_{\rm PE}(548.8)$.

The slightly lower performance of the MuPI scheme for the LT data is likely a result of different phytoplankton species. P. agardhii was the most abundant species in the MS dataset, together with other species of Raphidiopsis brookii (cf. Cylindrospermopsis raciborskii), Planktothrix perornata and Anabaena circinalis (Mishra et al. 2013); however, M. aeruginosa was the dominant species in the LT dataset (Qi et al. 2014). The difference in phytoplankton communities could result in different pigment compositions, which would then bring in some differences in the covariance among the absorption coefficients of the pigments. Besides, the dominant particles in the MS dataset are phytoplankton, and their contribution to the total absorption coefficient is higher than 70%. However, for LT, beside phytoplankton, non-phytoplankton particles also make high contributions to the total absorption coefficient (> 40% for wavelengths shorter than 550 nm) (Fig. 7). Consequently the model of $b_{\rm bp}$ spectrum (Eq. 4) could have larger errors where the effect of a_d is omitted. Because a_d and a_g have similar spectral shapes, it is still a research subject in adequately separating these two in ocean color remote sensing (Dong et al. 2013). Nevertheless, a smaller than 42% MARE for a_{pig} retrieval from R_{rs} for the independent LT dataset suggests reasonable results of the MuPI scheme, and future studies should focus on incorporating the $a_{\rm d}$ variability in the inversion process.

In addition to comparison of the absorption coefficients of specific pigments, the $a_{\rm ph}$ values obtained from the MuPI scheme were also compared with measured $a_{\rm ph}$ (see Fig. 8). The MARE between measured and retrieved $a_{\rm ph}$ at 410, 440, 510, 560, 660, and 680 nm are 30.1%, 31.9%, 31.8%, 27.7%, 32.3%, and 35.8%, respectively. Further, Fig. 8B compares the $a_{\rm ph}$ spectra of a randomly selected station, where an underestimation of $\sim 20\%$ for wavelengths shorter than 550 nm is found. To identify the likely error sources, the measured $a_{\rm ph}$ spectrum was compared with the twoparameter modeled $a_{\rm ph}$ (based on Eq. 5 and parameters in Table 2). It appears that there are disagreements for wavelengths longer than 550 nm (Fig. 8B), e.g., an overestimation of the absorption coefficient of PC at 617.6 nm and an underestimation of the absorption coefficient of Chl-a at 677 nm. This is mainly due to the different cyanobacteria groups in the two datasets as mentioned above. Different cyanobacteria groups usually have different absorption and concentration ratios of PC to Chl-a (Roy et al. 2011; Kudela et al. 2015). This suggests that it is likely necessary to expand the two-parameter $a_{\rm ph}$ model to more parameters, which will require a more inclusive database to optimize such spectral models.

Estimation of PC concentration

As a signature pigment of cyanobacteria bloom, the retrieval of PC concentration ([PC]) has been the focus of many studies (Simis et al. 2005; Wynne et al. 2008; Mishra et al. 2013; Mishra and Mishra 2014; Qi et al. 2014; Kudela et al. 2015), and all these methods have tried to use the information of PC absorption at around 620 nm. In the MuPI scheme, $a_{PC}(617.6)$ represents the in vivo absorption coefficient of pigment PC and can be obtained from the R_{rs} specttum. Previous studies (Hoepffner and Sathyendranath 1993; Bricaud et al. 1995; Chase et al. 2013) have shown that there is a strong relationship between absorption coefficients and pigment concentration, such as the linear relationship in Hoepffner and Sathyendranath (1993) and Chase et al. (2013) and the power law relationship in Bricaud et al. (1995).

In this study, a power law relationship between [PC] (77–3032 μ g L⁻¹) and $a_{\rm pc}$ (617.6) from the MS dataset was developed (see Eq. 15 and Fig. 9A)

$$y=31.2x^{1.78}$$
 (15)

where *y* is [PC], and *x* is a_{pc} (617.6).

From the retrieved $a_{\rm PC}$ (617.6) from $R_{\rm rs}$ and apply the relationship of Eq. 15, the [PC] was estimated remotely for the LT dataset. This estimated [PC] was then compared with the measured values (Fig. 9B). The MARE between the estimated and measured [PC] for these 31 samples is 43.7% ($R^2 = 0.96$), with [PC] in a range of ~ 1–300 µg L⁻¹. Despite a 30% underestimation, these evaluations show quite encouraging results in estimating PC concentration with a spectral optimization scheme.



Fig. 6. Comparison between the absorption coefficients (a_{pig}) of Chl-a, Chl-b, Chl-c, carot, PE, and PC retrieved from R_{rs} and those derived from a_{ph} for the LT dataset.

Improvement of a_{ph} retrieval over traditional approaches

There are two parameters (a_{Carot} (515.6) and $a_{\text{Chl-c}}$ (584.4)) used in MuPI to model the a_{ph} spectrum, whereas most ocean color remote sensing algorithms (e.g., Lee et al. 1999, 2002; Maritorena et al. 2002; Werdell et al. 2013) use just one parameter for this purpose. To evaluate the impact in retrieving a_{ph} with added variables, the hyperspectral optimization process exemplar (HOPE) developed in Lee et al. (1999) and the quasi-analytical algorithm (QAA) developed in Lee et al. (2002) were also applied to the MS and LT datasets to retrieve the spectrum of a_{ph} . In Lee et al. (1999), the spectra of a_{ph} and b_{bp} are described as:

$$a_{\rm ph}(\lambda) = \left\{ a_0(\lambda) + a_1(\lambda) \ln \left[a_{\rm ph}(\lambda_0) \right] \right\} a_{\rm ph}(\lambda_0) \tag{16}$$

$$b_{\rm bp}(\lambda) = b_{\rm bp}(\lambda_0) \left(\frac{\lambda_0}{\lambda}\right)^{\eta} \tag{17}$$

where $a_{\rm ph}$ (λ_0) and $b_{\rm bp}$ (λ_0) are two independent variables with λ_0 as 440 nm. The values of a_0 (λ) and a_1 (λ) are provided in Lee et al. (1998). Both MuPI and HOPE use a spectral optimization method to retrieve $a_{\rm ph}$, while QAA is a step-wise method which uses a series of equations to derive $a_{\rm ph}$ analytically. To make it suitable for highly turbid and algal bloom waters, Mishra et al. (2014) reparameterized QAA based on measurements in the MS pond waters. And, the $R_{\rm rs}$ data of the MS and LT datasets were reduced to 10 nm spectral resolution in order to match the spectral resolution of HOPE.

A comparison of the performance of the three inversion methods is shown in Fig. 10, where the MARE values vary in a range of 30–57%, 23–89%, and 23–34% in the 400–700 nm range, for HOPE, QAA, and MuPI, respectively. Apparently it is spectrally stable with the MuPI model, while both HOPE and QAA show spectrally selective performances, at least for the MS dataset. Specifically for $a_{\rm ph}$ (440), MuPI resulted $a_{\rm ph}$ (440) is around the 1:1 line, while HOPE and QAA derived $a_{\rm ph}$ (440) values are somewhat underedtimated (see Fig. 10B,D). These results suggest a necessity to refine both HOPE and QAA for such extreme waters, while the MuPI scheme

Table 4. Average (and medium) absolute relative error between a_{pig} derived from R_{rs} and those decomposed from a_{ph} for the LT dataset. Also include are the RMSE values for each a_{pig} peak.

Peaks (nm)	Mean RE (%)	Medium RE (%)	RMSE
386.6	42	41	0.35
414	41	41	0.35
435	36	28	0.29
451.7	40	38	0.34
484	42	41	0.36
515.6	39	35	0.31
548.8	43	40	0.35
584.4	22	18	0.15
617.6	24	18	0.14
636	39	30	0.28
653	31	30	0.22
677	35	31	0.24
693.5	29	23	0.16

RE, absolute relative error; RMSE: root mean square error.

worked quite well in retrieving $a_{\rm ph}$ spectrum, at least for this dataset.

Analysis of model development and application

When selecting independent parameters for $a_{\rm ph}$ modeling, peak 6 (515.6 nm) and peak 8 (584.4 nm) were used based on regression analysis. However, there are some peaks which show higher correlations with other pigments than these two (Fig. 3). For example, peak 12 (677 nm) has a higher correlation with peak 3 (435 nm) ($R^2 = 0.97$) than with peak 8 $(R^2 = 0.94)$. To test the impact of selecting free variables for $a_{\rm ph}$ modeling on the optimization retrievals, different combinations and number of peaks used to model a_{ph} : such as 3 peaks ($a_{\text{Carot}}(484)$ or $a_{\text{Carot}}(515.6)$, $a_{\text{Chl-c}}(584.4)$ and $a_{\text{Chl-c}}(584.4)$ $_{a}(693.5)$) and 4 peaks ($a_{Carot}(515.6)$, $a_{Chl-c}(584.4)$, $a_{PC}(617.6)$ and $a_{\text{Chl-a}}(677)$). No significant improvements in the a_{pig} retrieval were found when additional parameters were applied to the MS dataset. It appears that $a_{\text{Carot}}(515.6)$ and $a_{\text{Chl-c}}(584.4)$ are adequate parameters for a_{ph} modeling, at least for this dataset.

But it is necessary to keep in mind that the model developed in this study was based on measurements from cyanobacteria bloom waters where the absorption coefficient of phytoplankton is very strong. This dataset is far from representative in dynamic range, especially to many, normal and healthy, lake and coastal waters, thus the applicability of the MuPI scheme to such waters are unknown, although the general framework seems encouraging. More tests with data measured from other ecosystems are desired and required for the validation and improvement of MuPI.

Separately, although hyperspectral R_{rs} spectrum was used for a_{pig} retrieval, the total number of unknowns in the MuPI scheme is only four, which suggests that such a fine



Fig. 7. Mean percentage contributions of a_{ph} , a_d , a_g , and a_w to a_t for the MS (left) and LT (right) datasets.



Fig. 8. (A) Comparison bewteen measured and R_{rs} -derived a_{ph} at 410, 440, 510, 560, 660, and 680 nm for the LT dataset. (B) A comprison of a_{ph} spectrum of a randomly selected station of the LT dataset, with black from sample measurements, red from the MuPI scheme, and blue from the two-variable (a_{Carot} (515.6) and a_{Chl-c} (584.4)) model.



Fig. 9. (A) A power law relationship between a_{PC} (617.6) (derived from a_{ph} decomposition) and PC concentration ([PC]) obtained from the MS pond waters. (B) A comparison between measured PC concentration and that estimated from R_{rs} using the MuPI model for the LT dataset.

hyperspectral resolution (1 nm) may not be necessary to obtain satisfactory a_{pig} results. This is supported with the good results when MuPI was applied to R_{rs} data with a spectral resolution of 10 nm (see Fig. 10). Mathematically, it might be workable of MuPI if the number of spectral bands are greater than four and are spread enough to contain independent spectral information. The lower requirement of spectral resolution shows that the MuPI scheme has the potential (after refinement) to be implemented to past (e.g., SeaWiFS, MERIS) or current (e.g., MODIS) multispectral satellite data or future hyperspectral data (e.g., HyspIRI) (Devred et al. 2013). However, for better or more reasonable retrievals it should be cautious for the reduction of spectral bands, especially for optically complex bloom waters as some bands, like the one around 695–715 nm, play critical roles for the retrieval environmental properties from $R_{\rm rs}$ (Lee and Carder 2002; Lee et al. 2007; Mouw et al. 2015).

Conclusion

In this study, the MuPI model that combined Gaussian decomposition and spectral optimization was used to retrieve the absorption coefficients of multiple pigments from hyperspectral remote sensing reflectance. In particular, the absorption coefficients of two representative pigments were derived from R_{rs} via spectral optimization, which were then used to estimate the absorption coefficients of other 11 peaks that represent six different pigments (*chlorophyll a, b, c, carotenoid, phycoerythrin,* and *phycocyanin*). It is found that the absorption coefficients of these pigments retrieved from



Fig. 10. Performances of three methods in retrieving a_{ph} from R_{rs} for the MS (**A** and **B**) and LT (**C** and **D**) datasets. (**A** and **C**) The distribution of MARE in the 400–700 nm range for a_{ph} derived from HOPE (black), QAA (red) and MuPI (blue). (**B** and **D**) A scatter plot compares measured and retrieved a_{ph} (440) from the three methods.

 $R_{\rm rs}$ are quite consistent with those decomposed from $a_{\rm ph}$ spectra (MARE $\leq \sim 32\%$ for a dataset used for the model development). This is further demonstrated with an independent dataset where the MARE ranges between 22% and 42% for wavelengths of 400–700 nm.

The results of this effort indicate the possibility of retrieving absorption coefficients of multiple phytoplankton pigments from hyperspectral remote-sensing reflectance, especially for waters where the contribution from phytoplankton dominates the total absorption coefficient. However, the boundary of the applicability of such a scheme is not yet fully known and its performance when applied to past or current satellite ocean color data remains to be determined.

Author Contributions

Zhongping Lee framed the research question and helped the interpretation of the results; Deepak Mishra and Ronghua Ma provided in situ data and helped in data analyses; Guoqing Wang carried out the study, analyzed the data and inversion results, and drafted the manuscript. All co-authors provided critical revisions to the manuscript.

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Acknowledgments

We thank Charles Kovach for the grammar proof and comments and suggestions from two anonymous reviewers which greatly improved this manuscript. The support by the National Aeronautics and Space Administration (NASA) Ocean Biology and Biogeochemistry and Water and Energy Cycle Programs, the National Oceanic and Atmospheric Administration (NOAA) JPSS VIIRS Ocean Color Cal/Val Project, the National Natural Science Foundation of China (No. 41431176, Ma), and the University of Massachusetts Boston is greatly appreciated.

> Submitted 10 September 2015 Revised 4 February 2016 Accepted 3 March 2016

Associate editor: Paul Kemp