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RESEARCH ARTICLE

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Key Points:

- A color-index algorithm for estimating POC is proposed
- The performance of the algorithm is compared with the band-ratio algorithm
- Optical proxies for POC estimation are discussed

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A Color-Index-Based Empirical Algorithm for Determining Particulate Organic Carbon Concentration in the Ocean From Satellite Observations

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Abstract An empirical algorithm for estimating particulate organic carbon (POC) concentration in the surface ocean from satellite observations is formulated and validated using in situ POC data and remote-sensing reflectance (R_{rs}) data obtained from match-up satellite ocean color measurements. The algorithm builds upon the band-difference algorithm concept, which was originally developed for estimating chlorophyll-a concentration in clear waters. This algorithm utilizes three spectral bands centered approximately at 490, 550, and 670 nm to determine a color index (CI_{POC}), from which POC can be estimated from satellite measurements. For comparison, the blue-green band-ratio algorithm is also formulated using the same data set of in situ POC and satellite-derived R_{rs} . Results show that the statistical parameters characterizing the differences between the satellite-derived POC and matchup in situ POC are similar when the CI_{POC} and band ratio algorithms are applied to open ocean waters where the values of CI_{POC} are relatively low. In coastal waters where the values of CI_{POC} are generally higher, the statistical parameters of algorithm performance are better for the CI_{POC} algorithm. In addition, because the CI_{POC} algorithm is less sensitive to errors and noise in the satellite-derived R_{rs} , the image quality obtained with this algorithm can be improved for both open-ocean and coastal waters.

Plain Language Summary Particulate organic carbon (POC) in the global ocean is linked to many important ocean biogeochemical processes and is responsible for large carbon fluxes. POC variations occur over a broad range of spatial (from regional to global) and temporal (from seasonal to decadal) scales due to various factors. Ocean color data acquired from satellite sensors, such as Sea-viewing Wide-Field-of-view Sensor (SeaWiFS), Moderate Resolution Imaging Spectroradiometer (MODIS), and Medium-Resolution Imaging Spectrometer (MERIS), can be used to quantify POC, with the capability for uninterrupted long-term observations and global coverage. This study demonstrates that the color-index (band-difference) approach is applicable to the POC retrieval from remote-sensing reflectance in both open ocean and coastal waters.

1. Introduction

Particulate organic carbon (POC) in the global ocean is linked to many important ocean biogeochemical processes and is responsible for large carbon fluxes. The marine biological carbon pump is dominated by vertical transfer of POC from the surface to the interior part of the ocean (Falkowski et al., 1998). The efficiency of this transfer is crucial in controlling the amount of atmospheric carbon sequestered in the deep ocean (Longhurst & Harrison, 1989; Volk & Hoffert, 1985). Changes in the efficiency of biological carbon pump can affect atmospheric CO_2 (Kwon et al., 2009). The knowledge of total POC in the surface ocean and subsequent inference of the phytoplankton portion of POC are also essential to the development of methods for estimating phytoplankton growth rates and carbon-based net primary production from satellite observations (Behrenfeld et al., 2005).

POC concentration (in mg/m^3) in surface waters is highly dynamic and its variability results from various factors, such as biological production, POC transformations (e.g., remineralization), sinking of POC to the interior of the ocean, physical mixing, and horizontal transport by currents (Field et al., 1998; Omand et al., 2015; Le et al., 2017; Marsay et al., 2015). These factors cause POC variations to occur over a broad range of spatial (from regional to global) and temporal (from seasonal to decadal) scales (Allison et al., 2010a;

Duforêt-Gaurier et al., 2010; Gardner et al., 2006; Loisel et al., 2002; Lutz et al., 2007; Martiny et al., 2013; Stramska, 2009; Stramska & Cieszyńska, 2015; Stramska & Stramski, 2005; Stramski et al., 1999). Thus, the POC variations in the global upper ocean cannot be fully characterized by measurements obtained solely from ships or other in situ observation platforms. Ocean color data acquired from satellite sensors, such as Sea-viewing Wide-Field-of-view Sensor (SeaWiFS), Moderate Resolution Imaging Spectroradiometer (MODIS), and Medium-Resolution Imaging Spectrometer (MERIS), can be used to quantify POC on an almost daily basis, with the capability for uninterrupted long-term observations and global coverage (Allison et al., 2010a; Duforêt-Gaurier et al., 2010; Stramska, 2009; Stramska & Cieszyńska, 2015; Stramska & Stramski, 2005; Stramski et al., 1999).

Several two-step algorithms have been developed in the last two decades to estimate POC in the surface ocean from satellite measurements (Gardner et al., 2006; Loisel et al., 2002; Stramska & Stramski, 2005; Stramski et al., 1999; Stramski et al., 2008). These algorithms use the relationship between remote-sensing reflectance (R_{rs} , in sr^{-1}) and particle inherent optical properties (IOPs), such as particulate backscattering (b_{bp} , in m^{-1}) and particulate beam attenuation (c_p , in m^{-1}) coefficients, and the relationships between these IOPs and POC to estimate the concentration of POC. However, the particulate IOPs are sensitive to particle abundance and composition through variations in particle refractive index, size, shape, and internal structure (e.g., Babin et al., 2003; Neukermans et al., 2012); thus, their relationships with POC can vary significantly (Gardner et al., 2006; Stramska & Stramski, 2005; Stramski et al., 1999). For example, a variation in POC-specific b_{bp} can introduce uncertainty in a two-step algorithm that includes the relationship between POC and b_{bp} (Loisel et al., 2002; Stramski et al., 1999; Stramski et al., 2008). The covariation of POC and chlorophyll-*a* (Chl*a*) concentration has also been used to construct a two-step algorithm to derive POC from satellite measurements (Sathyendranath et al., 2009), but the POC:Chl*a* ratio exhibits significant variations and is difficult to predict (Morel, 1988).

The empirical algorithms for estimating POC directly from the spectral remote-sensing reflectance, $R_{rs}(\lambda)$, where λ is light wavelength, have also been developed and evaluated in the past (Allison et al., 2010b; Stramska & Stramski, 2005; Stramski et al., 2008). Evaluation and comparisons of performance of different types of POC algorithms show that simple empirical algorithms based on the input data of blue-to-green (BG) band ratio of reflectance generally outperform two-step algorithms in the applications on large ocean basin and global scales (Allison et al., 2010b; Evers-King et al., 2017; Stramska & Stramski, 2005). Currently, the National Aeronautics and Space Administration (NASA) Ocean Biology Processing Group uses the BG band-ratio algorithm to generate the standard global POC data product from ocean color data, and this product has been made available on the OB.DAAC website (<http://oceancolor.gsfc.nasa.gov>). This BG algorithm utilizes the band ratio of R_{rs} at light wavelengths of 443 and 555 nm, $R_{rs}(443)/R_{rs}(555)$, and the power function relating POC to $R_{rs}(443)/R_{rs}(555)$. This algorithm has been developed by Stramski et al. (2008) using open-ocean in situ data of POC and $R_{rs}(\lambda)$ collected in the Pacific and Atlantic waters covering ~20-fold range of surface POC from about 12 to 270 mg/m^3 . Thus, the formulation of this BG algorithm does not account for waters characterized by high POC and optically complex coastal waters. We also note that this type of algorithm can be referred to as “in-water” algorithm because its formulation is based entirely on concurrent in situ data.

Recent evaluation of POC algorithms using a large satellite-in situ matchup data set (3,891 matchups utilizing satellite data from SeaWiFS, MODIS/Aqua, and MERIS) indicated a reasonably good performance of the standard BG algorithm in open ocean waters at global scale with an overall median absolute percent difference of 25% ($\pm 37\%$ interquartile range) between the satellite-derived POC and in situ POC matchups (Evers-King et al., 2017). In another recent study evaluating the standard BG algorithm with satellite-in situ matchups of POC (satellite data from SeaWiFS and MODIS/Aqua), Świrgoń and Stramska (2015) reported an overall mean absolute percent difference of 33% when GAC, MLAC, and LAC satellite data were included in the analysis of 260 matchups and 37% when only LAC data were included (99 matchups). These investigators also reported that this difference can range from about 8 to 74% when matchup data from different oceanic basins and field experiments are analyzed separately.

Although these evaluation results indicate that the standard BG algorithm for estimating POC has comparable performance to the standard empirical algorithm for estimating Chl*a* concentration, the individual satellite retrievals of POC in various specific cases of oceanic waters including coastal regions can differ by more

than 50% or even 100% from the in situ matchups (Evers-King et al., 2017). It must be emphasized, however, that such algorithm evaluation based on satellite-in situ matchups does not reflect just the uncertainties in the formulation of the “in-water” algorithm itself, but it also includes other potentially significant sources of uncertainties associated with satellite retrievals of R_{rs} , such as atmospheric correction, calibration, and measurement noise of satellite radiometer, as well as spatial and temporal mismatch issues in the generation of matchup data sets. It has been recognized, for example, that the application of “in-water” Chla band-ratio algorithms to satellite data in clear and very turbid waters are affected by digitization noise-induced and atmospheric correction errors, which may result in patchiness and speckling noise in the spatial distributions of satellite data product and possible bias in long-term trends (Hu et al., 2001, 2012).

Recently, a novel algorithm concept was proposed to estimate surface Chla in oligotrophic oceans on the basis of a three-band reflectance difference (i.e., Color Index or CI) involving blue, green, and red bands (Hu et al., 2012). An advantage of this concept over the band-ratio algorithm concept is that the color-index approach can reduce the impact of errors induced by satellite instrument noise and imperfect atmospheric correction (including sun glint and whitecap corrections), thereby leading to improved Chla data product for clear waters. After extensive evaluation, this algorithm was accepted by NASA as the default clear-water Chla algorithm for ocean color sensors, while for more productive waters the traditional band-ratio algorithm (O'Reilly et al., 2000) or a combination of both algorithms is used. The National Oceanic and Atmospheric Administration also made similar changes in global processing of VIIRS (Visible Infrared Imaging Radiometer Suite) data to include the color-index Chla algorithm (after appropriate tuning of the algorithm coefficients; Wang & Son, 2016). Recently, the same algorithm concept was extended to green-red-near infrared bands to estimate concentrations of particulate inorganic carbon (PIC; Mitchell et al., 2017). The new PIC algorithm demonstrated better performance than the look-up-table approach from the combined algorithms of Gordon et al. (2001) and Balch et al. (2005).

Considering the demonstrated advantages of color-index (the three-band-difference) algorithm approach to estimating Chla and PIC, it is useful to examine whether the same approach can be extended to the estimation of POC from satellite observations in the global ocean. The objective of this study is to develop and evaluate an empirical color-index POC (CI_{POC}) algorithm on the basis of satellite-in situ matchup data set. For this purpose, we use in situ POC data in the period 1998–2015 acquired from NASA's SeaWiFS Bio-optical Archive and Storage System (SeaBASS) and a matchup satellite data set obtained from different ocean color sensors. The performance of CI_{POC} algorithm is compared with the BG band-ratio algorithm that is parameterized with the same satellite-in situ matchup data set.

2. Data and Methods

2.1. In Situ POC Data Set

In situ POC data within the ocean surface layer (depth < 10 m) were obtained from the NASA SeaBASS archive (<https://seabass.gsfc.nasa.gov/>), which is a database of measurements collected by many research groups to develop and validate satellite ocean color algorithms. The POC data set contains samples collected from areas ranging from oligotrophic oceans to coastal waters during the period 1998 to 2015 (Figure 1). POC was measured following the protocols of the Joint Global Ocean Flux Study (Knap et al., 1996). Briefly, samples were collected on precombusted (450 °C) GF/F filters and dried overnight at 65 °C before analysis. The filters were acidified either by adding low-carbon HCl directly or by overnight exposure to the fumes of a concentrated HCl solution in a desiccator to remove PIC. The filters were then dried at 55 °C, packed in precombusted tin capsules, and combusted at 960 °C in an elemental analyzer. The POC concentration was calculated by subtracting the average mass of organic carbon determined on blank filters from the mass of carbon determined on sample filters and then dividing the result by the measured volume of the filtered sample. POC values less than 10 mg/m³ were considered invalid in this study because they may possess substantial bias due to adsorption of dissolved organic carbon onto the filters (Cetinić et al., 2012; Stramski et al., 2008).

2.2. Satellite-In Situ Matchup Data Set

Daily 1 km SeaWiFS (GAC) and MODIS/Aqua Level-2 R_{rs} products and MERIS full-resolution Level-2 R_{rs} products were obtained from the NASA website (<http://oceancolor.gsfc.nasa.gov/>) in May 2017. The images

Figure 1. Geographical distribution of in situ particulate organic carbon (POC) sampling stations used to develop and validate the blue-green band-ratio algorithm and the three-band difference (color index Cl_{POC}) algorithm. The insert shows the relative frequency distribution of in situ POC values.

were reprocessed (version 2014.0) using the SeaWiFS data analysis system software (Version 7.0) with up-to-date calibration coefficients and algorithms. The Level-2 R_{rs} products were extracted for matching the locations and times with in situ POC samples to develop and validate the empirical algorithms. The details for matching satellite and in situ data have been presented in Le et al. (2013). Briefly, a time window between in situ-satellite data of ± 3 hr was used, and a median value of a 3×3 satellite pixel box centered at each field sampling site was employed to filter the satellite sensor and algorithm-related noise. Comparisons between in situ and satellite-derived POC were performed only when the number of valid pixels (i.e., after discarding pixels that failed quality control flags) in the box was >4 and the coefficient of variation for R_{rs} among pixel values was <0.4 . A total of 455 satellite-in situ pairs of matched data were obtained for SeaWiFS and used to develop and evaluate the Cl_{POC} algorithm and also to parameterize and evaluate the BG band-ratio algorithm. A total of 899 and 72 satellite-in situ pairs of matched data were acquired for MODIS and MERIS, respectively, and used to evaluate the performance of the Cl_{POC} algorithm and to compare it with the performance of the BG algorithm.

2.3. Algorithm Formulation

Figure 2 shows the concept of the formulation of the Cl_{POC} algorithm for the two R_{rs} spectra extracted from SeaWiFS images in open ocean waters (Figure 2a) and coastal waters (Figure 2b) with POC values of 52.6 and 375.2 mg/m^3 , respectively. The R_{rs} for open ocean waters exhibits typical clear water reflectance spectrum characteristics. R_{rs} decreases with increasing wavelength from the blue (412 nm) to the red (670 nm). The R_{rs} for coastal waters shows a reflectance peak at 555 nm, which is typical for turbid waters. The ocean color index for POC (Cl_{POC}) was created based on the three-band-difference concept. Considering that satellite-derived R_{rs} at 412 and 443 nm may have relatively high uncertainties (Wang et al., 2009), we formulated the three-band-difference algorithm by using R_{rs} at 490, 555, and 670 nm (red line in Figure 2) as follows:

$$Cl_{POC} = R_{rs}(555) - (R_{rs}(490) + (555 - 490) / (670 - 490) \times (R_{rs}(670) - R_{rs}(490))) \quad (1)$$

MODIS bands centered at 547 and 678 nm and MERIS bands centered at 560 and 665 nm were used to replace 555 and 670 nm in the formulation of Cl_{POC} for MODIS and MERIS, respectively. The satellite-derived Cl_{POC} data were used with concurrent and co-located (i.e., matchup) in situ POC data to develop the empirical relationship between these variables, which serves as the Cl_{POC} algorithm. Likewise, the satellite-derived data of the BG band ratio $R_{rs}(443)/R_{rs}(555)$ were used with matchup in situ POC data to develop the parameterization of the BG empirical algorithm.

Figure 2. Illustration of the approach for calculating the color index, Cl_{POC} (the magnitude of color index is indicated by the red line), from spectral remote-sensing reflectance, $R_{rs}(\lambda)$, for two example cases: (a) open-ocean waters with particulate organic carbon (POC) of 52.6 mg/m^3 and (b) coastal waters with POC of 375.2 mg/m^3 . The data of $R_{rs}(\lambda)$ were derived from satellite measurements with Sea-viewing Wide-Field-of-view Sensor (SeaWiFS).

2.4. Evaluation of the Algorithm Performance

The performance of the two algorithms was evaluated with several statistical parameters, which are similar to those used in the evaluation analysis of POC algorithms presented in Allison et al. (2010b). Specifically, for comparisons of satellite-derived POC obtained by applying the algorithms to satellite-derived R_{rs} with matchup data of in situ POC, we use the following parameters:

1. Correlation coefficient between the satellite-derived and in situ values, R .
2. Slope of the principal axis of Model II linear regression between the satellite-derived and in situ values, *Slope*.
3. Median ratio of satellite-derived to in situ values, MR.
4. Median absolute percent difference (MAPD in %) calculated as the median of the individual absolute percent differences $PD = 100 \times |(y_i - x_i)|/x_i$, where y_i represents the satellite-derived value and x_i represents the in situ value.
5. Root-mean-square difference (RMSD in mg/m^3) between the satellite-derived and in situ values, $RMSD = 1/N \sqrt{\sum [(y_i - x_i)]^2}$, where N is the number of matchup data pairs

3. Results

3.1. Formulation of Cl_{POC} and BG Band-Ratio Algorithms

Figure 3 shows the relationship between in situ POC and satellite-derived Cl_{POC} (Figure 3a) and the relationship between in situ POC and satellite-derived BG band ratio of R_{rs} (Figure 3b) for 297 in situ-satellite matchup data pairs for SeaWiFS. The relationship between in situ $\log_{10}(\text{POC})$ and Cl_{POC} appears different between low-POC stations with $Cl_{POC} < -0.0005 \text{ sr}^{-1}$ and high-POC stations with $Cl_{POC} \geq -0.0005 \text{ sr}^{-1}$. Most likely, one of the main factors causing this difference is a change in water optical properties. The low Cl_{POC} values are observed predominantly in the open ocean environments, and the high Cl_{POC} values are expected to occur typically in coastal waters. Thus, separate linear relationships between $\log_{10}(\text{POC})$ and Cl_{POC} and between $\log_{10}(\text{POC})$ and $\log_{10}[R_{rs}(443)/R_{rs}(555)]$ were established for $Cl_{POC} < -0.0005 \text{ sr}^{-1}$ and $Cl_{POC} \geq -0.0005 \text{ sr}^{-1}$. Because a small gap occurred in the data between $Cl_{POC} < -0.0005 \text{ sr}^{-1}$ and $Cl_{POC} \geq -0.0005 \text{ sr}^{-1}$, the best fit regression coefficients were slightly adjusted to ensure convergence of the two separate relationship at $Cl_{POC} = -0.0005 \text{ sr}^{-1}$. The final best fit regression equations for the Cl_{POC} algorithm are shown in Figure 3a. Similarly, the BG algorithm was formulated using the same data set for $Cl_{POC} < -0.0005 \text{ sr}^{-1}$ and $Cl_{POC} \geq -0.0005 \text{ sr}^{-1}$. The final equations for the BG algorithm are shown in Figure 3b. We note that the form of the regression functions in Figure 3b is different from the NASA standard BG algorithm, which is described by the power function of the form $\text{POC} = A (R_{rs}[443]/R_{rs}[555])^B$ where $A = 203.2$ and $B = -1.034$ are the best fit coefficients obtained by linear regression applied to log-transformed data of POC and $R_{rs}(443)/R_{rs}(555)$ (Stramski et al., 2008).

Figure 3. (a) Relationships between in situ $\log_{10}(\text{POC})$ and satellite-derived Cl_{POC} and (b) in situ $\log_{10}(\text{POC})$ and satellite-derived $\log_{10}[R_{rs}(443)/R_{rs}(555)]$. Separate relationships are given for $\text{Cl}_{\text{POC}} < -0.0005 \text{ sr}^{-1}$ and $\text{Cl}_{\text{POC}} \geq -0.0005 \text{ sr}^{-1}$. Both Cl_{POC} and $R_{rs}(443)/R_{rs}(555)$ band ratio were calculated from satellite measurements with Sea-viewing Wide-Field-of-view Sensor (SeaWiFS). The best fit regression equations are given where the variable y is $\log_{10}(\text{POC})$ and the variable x is either Cl_{POC} or $\log_{10}[R_{rs}(443)/R_{rs}(555)]$. The values for the squared correlation coefficient R^2 are also given.

3.2. Evaluation of Algorithm Performance

Both Cl_{POC} and BG algorithms produce reasonable POC retrievals when applied to remote-sensing reflectance derived from SeaWiFS images (Figure 4). Table 1 provides the statistical parameters calculated from comparisons of satellite-derived and in situ values of POC. In the analysis based on SeaWiFS images, overall 455 matchup data pairs (73 for lower values of Cl_{POC} and 382 for higher values of Cl_{POC}) were used; these data included the subset of matchup data used to develop the algorithms. Table 1 shows that for $\text{Cl}_{\text{POC}} < -0.0005 \text{ sr}^{-1}$ (i.e., predominantly open ocean waters) the two algorithms have similar statistical parameters, especially MAPD and RMSD, although the values of Slope and MR are somewhat closer to 1 for the Cl_{POC} compared with the BG algorithm. For $\text{Cl}_{\text{POC}} \geq -0.0005 \text{ sr}^{-1}$ all statistical parameters with the exception of Slope are better for the Cl_{POC} than the BG algorithm. For example, MAPD is 21.5 and 25.8% for the Cl_{POC} and the BG algorithms, respectively. The values of RMSD are 79.8 and 109.2 mg m^{-3} , respectively. This evaluation analysis based on SeaWiFS-in situ matchup data set suggests that the use of Cl_{POC} algorithms can be advantageous, especially in coastal waters with relatively high color index Cl_{POC} .

Similar evaluation analysis of POC algorithms was also carried out with the satellite-in situ matchup data sets based on MODIS/Aqua and MERIS Level-2 R_{rs} data. For MODIS, the Cl_{POC} algorithm for $\text{Cl}_{\text{POC}} < -0.0005 \text{ sr}^{-1}$ was slightly changed to $\text{POC} = 10^{(155.72\text{Cl}_{\text{POC}} + 1.97)}$ to account for small differences in wave band center and

bandwidth between MODIS and SeaWiFS sensors. For MERIS, the same algorithm coefficients were used as for SeaWiFS. Figures 5 and 6 show the comparisons of satellite-derived POC with in situ matchups of POC for the Cl_{POC} and BG algorithms for MODIS and MERIS, respectively. We note that whereas the number of matchup data pairs for MODIS is quite large, i.e., 343 and 556 for $\text{Cl}_{\text{POC}} < -0.0005 \text{ sr}^{-1}$ and $\text{Cl}_{\text{POC}} \geq -0.0005 \text{ sr}^{-1}$, respectively, the number of matchup data for MERIS is small (34 and 38, respectively). Similar to the analysis of SeaWiFS matchups, the statistical parameters characterizing the performance of both algorithms examined with MODIS and MERIS matchups are similar in open ocean waters when $\text{Cl}_{\text{POC}} < -0.0005 \text{ sr}^{-1}$ (Table 1). For $\text{Cl}_{\text{POC}} \geq -0.0005 \text{ sr}^{-1}$ the statistical parameters of the Cl_{POC} algorithm are generally better compared with the BG algorithm; for example, the MAPD and RMSD values are smaller for the Cl_{POC} algorithm (Table 1). These results further support the notion that the use of Cl_{POC} algorithm can yield better POC retrievals in coastal waters with relatively high values of color index.

Figure 4. Comparison between in situ POC and Sea-viewing Wide-Field-of-view Sensor (SeaWiFS)-derived POC using the Cl_{POC} and blue-green (BG) band-ratio algorithms. The inset shows the geographical distribution of in situ POC sampling stations. The performance statistics are listed in Table 1.

Table 1

Summary of Performance of the BG Band-Ratio Algorithm and the Cl_{POC} Algorithm Developed in This Study When Applied to Satellite Data From Three Ocean Color Sensors, SeaWiFS, MODIS/Aqua, and MERIS

Sensor	Algorithm	$Cl_{POC} < -0.0005 \text{ sr}^{-1}$				$Cl_{POC} \geq -0.0005 \text{ sr}^{-1}$				R	N
		Slope	MR	MAPD(%)	RMSD (mg/m^3)	Slope	MR	MAPD(%)	RMSD (mg/m^3)		
SeaWiFS	BG	0.68	1.13	20.23	15.15	1.00	0.94	25.80	109.19	0.67	73 ($CI < -0.0005 \text{ sr}^{-1}$)
	Cl_{POC}	0.74	1.10	19.98	15.32	0.93	1.02	21.45	79.75	0.82	382 ($CI \geq -0.0005 \text{ sr}^{-1}$)
MODIS	BG	0.29	0.82	25.04	46.53	4.39	0.83	37.73	520.87	0.34	343 ($CI < -0.0005 \text{ sr}^{-1}$)
	Cl_{POC}	0.34	0.82	25.07	45.81	0.91	0.98	25.66	118.93	0.70	556 ($CI \geq -0.0005 \text{ sr}^{-1}$)
MERIS	BG	0.76	0.97	14.47	9.81	1.11	1.07	25.39	107.73	0.77	34 ($CI < -0.0005 \text{ sr}^{-1}$)
	Cl_{POC}	0.75	0.97	12.84	10.49	0.99	0.93	19.47	71.92	0.87	38 ($CI \geq -0.0005 \text{ sr}^{-1}$)

Note. The correlation coefficient R was calculated from the entire data set including $CI < -0.0005 \text{ sr}^{-1}$ and $CI \geq -0.0005 \text{ sr}^{-1}$. The statistical parameters Slope, median ratio (MR), median absolute percent difference (MAPD), and root-mean-square difference (RMSD) are explained in text. MERIS, Medium-Resolution Imaging Spectrometer; MODIS, Moderate Resolution Imaging Spectroradiometer; SeaWiFS, Sea-viewing Wide-Field-of-view Sensor. R is the correlation coefficient and N the number of data.

3.3. Algorithm Performance for Satellite Images

The performance of the Cl_{POC} and BG algorithms was further evaluated using example satellite images. In this comparison, many quality control flags were turned on to mask all invalid pixels. These flags include the atmospheric correction failure, land, high sun glint, total radiance greater than a predefined threshold, large satellite zenith angle, stray light, cloud/ice, coccolithophores, large solar zenith angle, low water-leaving radiance, chlorophyll algorithm failure, questionable navigation, maximum iterations reached for NIR iteration, chlorophyll warning, and atmospheric correction warning.

Figure 7 shows an example of the comparison of the two algorithms for SeaWiFS GAC Level 2 images in the coastal waters off the west coast of the United States. The two algorithms exhibit similar performance for seven field sampling locations in this satellite image. Specifically, for the BG algorithm the values of MAPD and RMSD are 23.6% and 35.0 mg/m^3 , respectively. For the Cl_{POC} algorithm these values are 29.3% and 32.2 mg/m^3 , respectively. Similar comparisons but for the satellite MODIS/Aqua Level-2 data in Gulf of Maine and adjacent waters are depicted in Figure 8. In this case the ocean waters are generally more turbid and contain higher concentrations of POC compared with waters presented in the image off the west coast of the United States. In the MODIS image, the two algorithms produced similar pattern of the POC gradient from the coastal to open ocean waters; however, the BG algorithm yielded a higher POC than the Cl_{POC} algorithm in coastal waters. The comparisons of algorithm-derived POC with in situ matchup measurements for the five field stations showed larger differences for the BG algorithm than the Cl_{POC} algorithm. For the BG algorithm the values of MAPD and RMSD are about 119.3% and 197.3 mg/m^3 . For the Cl_{POC} algorithm these statistical parameters are reduced to 70% and 125.5 mg/m^3 , respectively. This comparative analysis of POC algorithms for example satellite images is consistent with the results presented in Table 1, suggesting that the Cl_{POC} algorithm can perform better than the BG algorithm, especially in coastal waters with high color index.

Figure 5. Same as Figure 4 but for the satellite data from Moderate Resolution Imaging Spectroradiometer (MODIS). The inset shows the geographical distribution of in situ POC sampling stations. The performance statistics are listed in Table 1.

Figure 9 illustrates potential improvements associated with the use of the Cl_{POC} algorithm due to its lower sensitivity to artifacts and noise in the generation of satellite ocean color imagery. This figure shows the results obtained with the two POC algorithms when applied to MODIS/Aqua Level-2 data in oligotrophic open ocean waters after turning the quality control flags off. The BG algorithm produces a pattern of possibly suspicious POC values that are lower than those in nearby waters (the area encircled by the red line in Figure 9a). In contrast, the Cl_{POC} algorithm does not show such patterns which can be related to successful correction for image artifacts associated with sun glint and other sources of noise (Figure 9b).

4. Discussion

Several IOPs of seawater have shown some degree of correlation with POC concentration in the upper ocean. Field measurements showed that the

Figure 6. Same as Figure 4 but for the satellite data from Medium-Resolution Imaging Spectrometer (MERIS). The inset shows the geographical distribution of in situ POC sampling stations. The performance statistics are listed in Table 1.

particulate scattering or backscattering coefficients may exhibit strong correlation with POC and can serve as a proxy for POC concentration, especially in the open ocean where organic particles are primary source of optical variability (Loisel & Morel, 1998; Stramski et al., 1999, 2008). However, some studies showed that organic particles may have strong contribution to absorption but less contribution to backscattering coefficient (Hunter et al., 2008; Stramski et al., 2001). Laboratory studies of phytoplankton cultures suggested that the particulate beam attenuation coefficient (c_p , m^{-1}) can be a good proxy for estimating POC concentration associated with phytoplankton (e.g., Stramski & Reynolds, 1993). Gardner et al. (2006) also found relatively strong correlation between POC and c_p using an extensive data set of field measurements of POC and c_p in the Atlantic, Pacific, and Indian Oceans. Whereas these results indicate that c_p can be a good optical proxy for POC estimation, the application of the POC versus c_p relationships to satellite

measurements is difficult because c_p is a sum of particulate absorption (a_p) and total particulate scattering (b_p) that is typically dominated by forward scattering, to which the remote-sensing reflectance is theoretically insensitive.

Recognizing this difficulty associated with the potential for remote-sensing estimation of c_p , most efforts for remote-sensing estimation of POC have been focused on two approaches based on b_{bp} and a_p . A two-step empirical POC algorithm ($R_{rs} \Rightarrow b_{bp}$, $b_{bp} \Rightarrow \text{POC}$) was proposed in several studies based on the relationship between POC and b_{bp} , mostly in open ocean waters (Allison et al., 2010b; Loisel et al., 2002; Stramski et al., 1999; Stramski et al., 2008). However, it has also been recognized that the POC versus b_{bp} relationship is variable due to various factors, such as particle size distribution, particle refractive index, POC distribution within the particulate assemblages, and the presence of other scattering non-POC constituents such as mineral particles and bubbles (Stramski & Tęgowski, 2001; Woźniak et al., 2010). All these factors introduce uncertainties in the POC retrievals from the two-step algorithm as applied to remote-sensing data. The required estimation of b_{bp} from satellite determinations of remote-sensing reflectance also leads to additional uncertainties in the results obtained with the two-step POC algorithms (Evers-King et al., 2017). Figure 10a shows a relatively weak relationship between in situ POC and matchup satellite data of total backscattering coefficient at 547 nm, $b_b(547)$, which were obtained from MODIS/Aqua imagery of remote-sensing reflectance using the QAA algorithm (Lee et al., 2002). This relatively weak relationship confirms earlier findings indicating that the b_{bp} -based two-step algorithm is not the best choice for remote-sensing applications on global ocean scale or large basin scales (Allison et al., 2010b; Evers-King et al., 2017; Stramski et al., 2008).

Figure 7. Distribution of surface POC derived from (a) the blue-green band-ratio algorithm and (b) the Cl_{POC} algorithm using satellite Sea-viewing Wide-Field-of-view Sensor (SeaWiFS) measurements on 21 January 2007 in coastal waters off the west coast of the United States. The comparison of SeaWiFS-derived and in situ POC was carried out for seven field stations indicated by white crosses in panel (a). The geographical coordinates are shown for each map and the color scale bar represents POC concentration in mg/m^3 .

Figure 8. Same as Figure 7 but for the satellite measurements with Moderate Resolution Imaging Spectroradiometer (MODIS)/Aqua on 9 August 2007 in Gulf of Maine and adjacent waters. The comparison of MODIS-derived and in situ POC was carried out for five field stations indicated by white crosses in panel (a).

For global and large-scale remote-sensing applications, an empirical POC algorithm based on the BG band ratio of remote-sensing reflectance has been the preferred option (Allison et al., 2010b; Evers-King et al., 2017; Stramska & Stramski, 2005; Stramski et al., 2008). The changes in the BG band ratio of R_{rs} are driven largely by changes in the total absorption coefficient of seawater, a , at least for most ocean waters which are within the open ocean environments. This suggests that absorption is effectively a useful optical proxy for POC retrieval, possibly better than backscattering. A comprehensive analysis of optical properties of particles in complex coastal environments also showed that variations in POC-specific particulate absorption coefficient are more constrained than variations in POC-specific particulate scattering coefficient (Woźniak et al., 2010). The tighter relationship between in situ POC and satellite-derived total absorption coefficient (Figure 10b) than between in situ POC and satellite-derived backscattering coefficient (Figure 10a) further supports the notion of an important role of absorption as an optical proxy for POC estimation from satellite observations. We note that the absorption coefficient $a(488)$ presented in Figure 10b was estimated using the inverse reflectance algorithm (QAA) as applied to the MODIS-derived R_{rs} data.

Whereas the absorption coefficient of seawater is an important (albeit implicit) variable driving changes in the BG band ratio of remote-sensing reflectance, the performance of the BG approach in remote-sensing applications can be affected by a number of factors. First, because the empirical BG algorithms have been traditionally developed as *in-water* algorithms on the basis of in situ R_{rs} and POC data, their remote-sensing application is affected by uncertainties in satellite-derived R_{rs} . These uncertainties can be caused by various factors, most notably imperfect atmospheric correction, especially in coastal waters (e.g., Wang et al., 2009). Second, as described in Hu et al. (2012), the band-ratio algorithms, especially in clear waters, are subject to satellite sensor noise, which induces residual error in satellite-derived R_{rs} . In addition, as the in situ data sets used to formulate the existing in-water empirical POC algorithms were collected mostly in open ocean waters where the variations in the optical properties are driven primarily by phytoplankton and associated matter, the performance of such algorithms is naturally expected to deteriorate in coastal waters where the optical properties are often largely affected by mineral particles and CDOM.

The color index approach based on band difference can provide an alternative choice to reduce some of these limitations and uncertainties. In this

Figure 9. Comparison of POC distributions derived from (a) the blue-green band-ratio algorithm and (b) the Cl_{POC} algorithm in the South Pacific Subtropical Gyre. The results were obtained with Moderate Resolution Imaging Spectroradiometer (MODIS)/Aqua data acquired on 4 March 2003. The quality control flags were turned off to highlight the tolerance of the Cl_{POC} algorithm to sun glint correction residual errors and other sources of noise (area encircled with red dashed line). The geographical coordinates are shown for each map, and the color scale bar represents POC concentration in $mg\ m^{-3}$.

Figure 10. Relationship between in situ POC and (a) satellite-derived $b_b(547)$ and (b) satellite-derived $a(488)$ in the global ocean (number of data $N = 849$). The $b_b(547)$ and $a(488)$ were estimated from Moderate Resolution Imaging Spectroradiometer (MODIS)-derived R_{rs} using the QAA algorithm.

study, the remote-sensing reflectance at 490, 555, and 670 nm was selected to calculate a color index (Cl_{POC}) for POC retrieval. The relatively good performance of this approach (Figures 4–6 and Table 1) can be attributed to three main reasons. First, although Cl_{POC} is primarily a function of total absorption in oceanic waters, it still retains the effects associated with independent variability of b_{bp} because R_{rs} is, to the first order, proportional to b_b/a (Gordon & Morel, 1983), and the band difference does not cancel the variation in the numerator. Therefore, Cl_{POC} can be used to estimate POC in clear waters where b_b is dominated by water molecules and coastal waters where variations in b_b may be largely decoupled from variations in absorption. Second, we used the 490 nm band for calculating Cl_{POC} , which can reduce the impact of CDOM absorption when $Cl_{POC} \geq -0.0005 \text{ sr}^{-1}$, which corresponds primarily to coastal waters. Although the Cl_{POC} and BG algorithms yielded similar monthly mean POC distribution patterns in the global ocean (Figures 11a and 11b), the BG algorithm provided higher POC than the Cl_{POC} algorithm (Figure 11c), which may be related to the CDOM effects (Siegel et al., 2005). Lastly, the band-difference algorithm is less sensitive to spectrally dependent errors in satellite-derived R_{rs} than the band-ratio algorithms (Hu et al., 2012). These errors often originate from satellite sensor noise and imperfect atmospheric correction (including sun glint and whitecap correction), but they are mostly related to each other spectrally (Hu et al., 2013). Such potential improvements in the image quality are demonstrated in Figure 9.

The analysis presented in this study provides encouraging results with regard to the potential applicability of the color-index approach for estimating POC from satellite observations, especially potential improvements for coastal waters with relatively high values of color index ($\geq -0.0005 \text{ sr}^{-1}$). The Cl_{POC} algorithm formulated in this study is, however, subject to all potential shortcomings of empirical algorithms; for example, any non-POC-related perturbation to the Cl_{POC} versus POC relationship will lead to errors in the POC retrieval. In addition, this algorithm has not been formulated as in-water algorithm because the variable of R_{rs} used in the Cl_{POC} algorithm formulation was estimated from satellite determinations of remote-sensing reflectance. Therefore, the established relationship between Cl_{POC} and POC does not reflect the in-water (in situ) relationship between these variables but is also affected by various factors involved in the determination of satellite-derived R_{rs} . Specifically, the presented Cl_{POC} algorithm parameterization is affected by specific algorithm used for atmospheric correction of satellite measurements and other components of processing the data of raw top-of-the-atmosphere radiance signal to estimate R_{rs} . Whereas this approach to the algorithm development may show reasonable performance because the atmospheric correction errors and other sources of uncertainty in satellite-derived R_{rs} may be accounted for to some degree in the algorithm formulas, the limitation arises from the sensitivity of the algorithm parameterization to the choice of atmospheric correction algorithm and other components of the processing of raw satellite measurements. Another important limitation of this approach is a lack of stronger physical foundation in terms of linking the in situ variables of POC and R_{rs} . This limitation does not exist in the more traditional approach of in-water algorithms.

Figure 11. Moderate Resolution Imaging Spectroradiometer (MODIS)/Aqua monthly mean global distribution of POC in March 2010 derived from (a) the blue-green band ratio algorithm and (b) the Cl_{POC} algorithm. (c) The relative differences between the two algorithms. The relative differences in percent are calculated as $(y - x)/(y + x) \times 200\%$ where y and x represent POC from the blue-green algorithm and Cl_{POC} algorithm, respectively. The geographical coordinates are shown for each map. The color scale bar for panels (a) and (b) represents POC concentration in mg/m^3 . The color scale bar for panel (c) corresponds to difference in percent.

In this study the Cl_{POC} versus POC relationship was formulated with data covering the range of $Cl_{POC} \leq 0.0015 \text{ sr}^{-1}$. For more turbid waters with $Cl_{POC} > 0.0015 \text{ sr}^{-1}$, such as river-discharge dominated regions, strong absorption by CDOM and/or backscattering by mineral particles could significantly influence the Cl_{POC} versus POC relationship. In these cases, other algorithm approaches, such as multiple regression (Le et al., 2017) or neural network, may provide useful alternatives. In addition, the potential internal methodological inconsistencies within the data sets used in the algorithm development may also introduce uncertainties. In this study, in situ POC data were extracted from the NASA SeaBASS repository of data collected by many different groups of researchers in various oceanic regions, so any potential inconsistencies in this data set may affect the established algorithm relationships.

5. Conclusions

This study demonstrates that the color-index (band-difference) approach is applicable to the POC retrieval from remote-sensing reflectance in open ocean and coastal waters. This applicability can be attributed to the three-band design of color-index approach, which is sensitive to the total absorption coefficient of seawater, while also taking into account the effects on reflectance associated with changes in the backscattering coefficient. Therefore, this approach effectively exploits the advantages of absorption- and backscattering-based algorithm designs, which can result in improved performance compared with the band-ratio algorithms, especially in coastal waters. The color-index approach also makes the algorithm less sensitive to errors or noise in the satellite-derived remote-sensing reflectance, which are associated with atmospheric correction and other sources of uncertainty. This can lead to improved image quality. The formulation of color index algorithm in this study has been based on matchup data of satellite-derived reflectance and in situ POC, rather than both variables measured in situ. This has some limitations such as the sensitivity of algorithm parameterization to the processing of raw satellite data including specific atmospheric correction procedure. Further work to examine and evaluate the color index approach for POC estimation and its potential implementation in the processing of satellite ocean color measurements appears to be warranted. In particular, it would be useful to examine this approach with quality controlled field data sets of simultaneous and co-located in situ determinations of POC concentration and spectral remote-sensing reflectance in various oceanic environments.

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