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Characterizing CDOM Spectral Variability Across Diverse Regions and Spectral Ranges

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Key points

- CDOM spectral slope spatial variability is dependent on spectral range used
- CDOM spectral slope variability is not necessarily reflected in CDOM absorption values in ocean regions with little terrestrial influence
- Gaussian peaks fitting lignin absorption show a distinct blue shift from inland to ocean waters
Abstract

Satellite remote sensing of colored dissolved organic matter (CDOM) has focused on CDOM absorption ($a_{\text{CDOM}}$) at a reference wavelength, as its magnitude provides insight into the underwater light field and large-scale biogeochemical processes. CDOM spectral slope, $S_{\text{CDOM}}$, has been treated as a constant or semi-constant parameter in satellite retrievals of $a_{\text{CDOM}}$ despite significant regional and temporal variability. $S_{\text{CDOM}}$ and other optical metrics provide insights into CDOM composition, processing, food web dynamics, and carbon cycling. To date, much of this work relies on fluorescence techniques or $a_{\text{CDOM}}$ in spectral ranges unavailable to current and planned satellite sensors (e.g. <300 nm). In preparation for anticipated future hyperspectral satellite missions, we take the first step here of exploring global variability in $S_{\text{CDOM}}$ and fit deviations in the $a_{\text{CDOM}}$ spectra using the recently proposed Gaussian decomposition method. From this, we investigate if global variability in retrieved $S_{\text{CDOM}}$ and Gaussian components is significant and regionally distinct. We iteratively decreased the spectral range considered and analyzed the number, location and magnitude of fitted Gaussian components to understand if a reduced spectral range impacts information obtained within a common spectral window. We compared the fitted slope from the Gaussian decomposition method to absorption-based indices that indicate CDOM composition to determine the ability of satellite-derived slope to inform the analysis and modeling of large-scale biogeochemical processes. Finally, we present implications of the observed variability for remote sensing of CDOM characteristics via $S_{\text{CDOM}}$. 
1. Introduction

Dissolved organic matter (DOM) is the largest pool of reduced carbon in the ocean [Hansell et al., 2009]. Slight alterations in DOM remineralization can result in significant increases or decreases in the release of CO$_2$ [Mannino et al., 2014] with remineralization rates highly dependent on DOM composition. DOM constituents vary from labile, readily metabolized compounds (e.g. phytoplankton exudates) important to short-term climate dynamics and food web processes to refractive compounds (e.g. microbial by-products) de-coupled from modern climate dynamics and largely precluded from food web dynamics [Hansell, 2013]. DOM contains optically active components in colored and fluorescent dissolved organic matter (CDOM and FDOM, respectively), with CDOM a small, variable portion of the total DOM pool and FDOM a small, variable portion of the CDOM pool [Stedmon and Nelson, 2015]. CDOM impacts the spectral quality and intensity of the underwater light field, surface ocean heating and plays direct and indirect roles in biogeochemical cycling [Andrew et al., 2013; Hickman et al., 2010; Kim et al., 2016].

Advances in optical characterization through absorption and fluorescence techniques have illuminated mechanistic relationships between CDOM molecular composition and optical properties such as the shape of the CDOM absorption spectra indicated by the spectral slope of CDOM ($S_{CDOM}$), where $S_{CDOM}$ is derived from fitting the CDOM absorption spectra to an exponential curve (see Eq. 1) [Helms et al., 2008; Stedmon and Markager, 2005; Walker et al., 2013]. Changes to CDOM optical characteristics have been related to general classifications of the composition of CDOM including molecular weight and origin [Spencer et al., 2008]. The strongest absorption-
based indicators of these properties rely on $S_{CDOM}$ from 275-295 nm and 350-400 nm ($S_{275:295}$ and $S_{350:400}$, respectively) since the largest divergence in spectral properties across compositionally unique CDOM samples are found in these spectral regions [Helms et al., 2008]. Low values of $S_{275:295}$ (~0.01 nm$^{-1}$) generally represent high molecular weight material (e.g. lignin and lignin derivatives) that decreases in molecular size primarily from photodegradation and secondarily from microbial degradation [Del Vecchio and Blough, 2002]. $S_{275:295}$ increases with photodegradation, with terrestrial material often showing markedly different $S_{275:295}$ values due to the presence of lignin. Conversely, $S_{350:400}$ generally decreases with photodegradation, potentially due to the presence of photorefractory chromophores that absorb in this portion of the spectrum [Helms et al., 2013].

Linking $a_{CDOM}$ optical proxies with future hyperspectral satellite data presents a potentially powerful tool to assess spatially and temporally distinct biogeochemical processes associated with $a_{CDOM}$ variability. To date, this connection is complicated by a lack of consistency in the spectral range used to calculate $S_{CDOM}$ and a general focus on a spectral range that best represents the entire $a_{CDOM}$ spectra over the utility of that spectral range [Schwarz et al., 2002; Twardowski et al., 2004]. Broad range $S_{CDOM}$ (e.g. $S_{240:700}$) that best characterize the entire $a_{CDOM}$ spectra have not been considered extensively for mechanistic relationships with CDOM composition. Most studies track $S_{CDOM}$ across salinity gradients [Kowalczyk et al., 2006; Stedmon and Markager, 2003; Stedmon et al., 2011] or distinct in-water processes [Nelson et al., 1998; Organelli et al., 2014], producing correlations between $S_{CDOM}$ and CDOM source or diagenetic state across geographically or temporally unique environments [Organelli et al., 2014; Stedmon and
Some work has suggested that $S_{300:600}$ is a useful indicator of CDOM molecular weight [Stedmon and Nelson 2015], while the general understanding is that broad range $S_{CDOM}$ increases with photodegradation as chromophores are bleached, particularly in the UV region [Del Vecchio and Blough, 2002; Reche et al., 2000]. Optical properties of source material have been considered [Hansen et al., 2016; Visser, 1983] and two major components of CDOM, humic acid and fulvic acid, display slopes of approximately 0.011 nm$^{-1}$ and 0.019 nm$^{-1}$ [Carder et al., 1989]. However, observed slope values across broad spectral ranges can vary above and below these benchmarks and the optical properties of source material are rapidly altered through poorly understood processes [Sharpless et al., 2014], suggesting that the complexity of material and its spectral signal is still poorly constrained.

Based on this, optically estimating CDOM composition from hyperspectral ocean color data requires validation of significant temporal and regional variability in $S_{CDOM}$ and a potential link between observable spectral features and spectral indices capable of estimating CDOM composition. Maximizing CDOM compositional information that can be retrieved by optical methods will enhance our ability to track changes in the CDOM pool through autonomous and remote sensing platforms, providing a way to observe large scale changes in ocean biogeochemical processes and circulation [Nelson et al., 2010]. However, this first requires determination of what information regarding CDOM composition is garnered from a specific spectral range and fully utilizing the information contained within $a_{CDOM}$ spectra to optically estimate CDOM composition. Here, we utilize $a_{CDOM}$ spectra available from public data repositories to address knowledge gaps that have evolved from an inconsistency in spectral range used. We utilize the Gaussian
decomposition approach of Massicotte and Markager [2016] to better estimate $S_{\text{CDOM}}$ and further characterize the CDOM pool and report differences between this approach and the standard exponential model traditionally used for fitting $a_{\text{CDOM}}$ spectra. We describe global variability in $S_{\text{CDOM}}$ within the context of biogeochemical provinces and relate several broad range $S_{\text{CDOM}}$ to $S_{275:295}$, $S_{350:400}$, and $a_{\text{CDOM}}$ at 350 nm ($a_{\text{CDOM}}(350)$) to define the efficacy of each of these parameters to optically estimate CDOM composition based on observations in the literature. Finally, we offer insight into what can be determined about CDOM composition from $S_{350:400}$ and $S_{350:550}$ to step toward defining a methodology that can be applied to hyperspectral, satellite remotely-sensed retrievals of $a_{\text{CDOM}}$.

2. Methods

2.1 CDOM Absorption Spectra

CDOM absorption spectra were obtained from NASA SeaWiFS Bio-optical Archive and Storage System (SeaBASS, https://seabass.gsfc.nasa.gov/) on April 13, 2016 [Werdell et al., 2003]. Only data measured on a bench top spectrophotometer were utilized. The CDOM absorption spectrum is typically modeled using an exponential decay function:

$$a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0) e^{-S_E (\lambda - \lambda_0)} + K$$

(1)

where $\lambda_0$ represents a reference wavelength for initializing the spectrum (nm), $S_E$ is the spectral slope coefficient for an exponential CDOM model (nm$^{-1}$), and $K$ is a constant addressing background noise and potential instrument bias (m$^{-1}$), calculated as the average $a_{\text{CDOM}}$ from 690-700 nm (Fig. 1). Spectra were quality controlled by selecting
spectra representing a broad quasi-exponential function: if the fit with Equation 1 displayed an $r^2 > 0.9$ (suggesting no contamination or instrumentation issues), spectra were kept for further analysis [Massicotte and Frenette, 2011].

Deviations from the decaying expression in Eq. 1 can result from absorption by specific chromophores (e.g. lignin), and can vary in degree and location [Massicotte and Markager, 2016]. To detect regions where such deviations exist, spectra were fit with the standard exponential in Eq. 1 and then trimmed by removing data with residuals greater than the mean absolute residual multiplied by the weighting factor, $C$. $C$ is dependent on the quality of the data (signal to noise ratio), the environment and spectral range considered and governs the number of residuals considered for Gaussian fitting by defining the threshold for excluding these points from the baseline exponential fit; we utilized a $C$ of 1 to maintain consistency across spectra. With the remaining points, spectra were again fit with Eq. 1 with the result defined as the baseline exponential. Massicotte and Markager [2016] utilized a spectral range from 240-700 nm with Gaussian fitting performed on residuals from 250-500 nm. $S_{CDOM}$ is sensitive to the spectral range used for calculation when using the exponential model [e.g. Twardowski et al. 2004]. To determine the influence of spectral range on $S_{CDOM}$ using the Gaussian decomposition model, we considered spectral ranges of 240-700 nm, 300-700 nm and 350-550 nm, with Gaussian fitting performed on residuals below 500 nm to avoid concerns with a low signal-to-noise (SNR) ratio at longer wavelengths [Massicotte and Markager, 2016]. For spectral ranges below 300 nm, we found including wavelengths down to 240 nm, rather than a 250 nm cutoff, better accounted for absorption deviations likely due to lignin or lignin-derivatives. This and altering the spectral range considered
were the only deviations from the methodology as described by Massicotte and Markager [2016]. The optimal number of Gaussian components modeled for each spectrum was chosen based on minimizing the Bayesian information criterion (BIC) score, with the final equation represented as:

\[
a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0)e^{-S G (\lambda - \lambda_0)} + K + \sum_{i=0}^{n} \varphi_i e^{-\frac{(x-\mu_i)^2}{2\sigma_i^2}} + \varepsilon
\]  

(2)

where \(S_G\) (nm\(^{-1}\)) is the spectral slope coefficient for a Gaussian decomposition CDOM model, \(\varphi\) (m\(^{-1}\)) is the height of the Gaussian peak, \(\mu\) (nm) is the position of the center of the peak, \(\sigma\) (nm) is the width of the peak and \(\varepsilon\) are the residuals after fitting of the full model. An example spectra fitted with and without the Gaussian decomposition approach is shown (Fig. 1), illustrating the change in slope. For this approach, fitted \(K\) as described for Eq. 1 is also used as a threshold for the minimum height of fitted Gaussian components to add certainty that the Gaussian components are fitting chromophores and not instrument noise. We also acknowledged that many different instruments with varying accuracy were used to obtain this large data set. Considering this, we calculated the mean \(K\) value across all measured spectra (0.0004) and applied this as a threshold value for fitting Gaussian components: if the spectra-specific \(K\) value was smaller than the mean \(K\), the mean \(K\) was used for fitting Gaussian components; the spectra-specific \(K\) value was used for all other spectra.

The inclusion of \(K\) in equations 1 and 2 is often debated, with many researchers considering it an unknown variable that has no physical basis. Others have pointed out its ability to account for instrument noise in regions of the spectrum that should have no, or very little, signal from CDOM absorption. We have included it in this analysis for several reasons: 1) many of the spectra that we considered had some noise at longer wavelengths.
 (> 600 nm) within an otherwise good absorption spectra, suggesting some instrument noise in measuring a very low signal; 2) our analysis focuses primarily on the shape of the spectra, which is not altered by including a K term; 3) our aCDOM analyses are focused on shorter wavelengths (e.g. 350 nm) where the percent contribution of the K term to the overall signal analyzed is generally quite small (mean of 0.6%); and 4) K was used as the threshold for fitting Gaussian components, leading to stricter fitting.

Spectral slope was retrieved for the following wavelength ranges: 275-295 nm, 350-400 nm, 240-700 nm, 300-700 nm and 350-550 nm. We also considered spectral slope from 300-600 nm, 350-600 nm, and 350-700 nm; however, slope values and Gaussian statistics for these spectral range were not significantly different from 300-700 nm and thus were not considered further. Throughout the manuscript, slope coefficient subscripts indicate fitting procedure (E for exponential decay with Eq. 1 and G for Gaussian with Eq. 2) along with the spectral range of data utilized for the fit. For example, $S_{G300:700}$ would indicate results from a fit with Eq. 2 from 300 to 700 nm.

2.2 Data Distribution

We focused on aggregating aCDOM spectra into biogeochemical provinces following Longhurst [2006] biogeochemical province designations (provided by VLIZ [2009]). We considered all 54 Longhurst biogeochemical provinces and aggregated all inland water samples into an ‘INLAND’ biogeochemical province, resulting in 55 potential regions. Of these, 35 were represented within the SeaBASS dataset: 34 Longhurst provinces and the INLAND province. Grouping samples for the INLAND province was justified by two considerations: 1) sampling locations were all in the eastern half of the United States or the Laurentian Great Lakes, and 2) retrieved spectral
slope was tightly grouped, ranging from 0.01-0.025 m$^{-1}$ (see the discussion below regarding Figure 5). To be considered for analysis, we required each province to contain 5% of the maximum number of samples found within the most sampled province. While sample size is typically treated through consideration of group variance, we found undersampled provinces displayed little variability typically due to all samples coming from a single oceanographic cruise. In effect, our threshold considered provinces with at least 100 spectra for spectral ranges <300 nm (less frequently sampled spectral range) and provinces with at least 200 spectra for spectral ranges ≥300 nm (more frequently sampled spectral range).

Absorption spectra were also considered within three depth classes defined as the first and second optical depths, calculated as 2.3 and 4.6 divided by $K_d(490)$, respectively, and below the photic zone (BPZ), comprising depths greater than the second optical depth but less than 1500 m [Kirk, 1994]. The majority of spectra below 1500 m were sampled at the Bermuda Atlantic Times Series (BATS) site; hence, we imposed the 1500 m threshold to avoid a potential bias from deep water spectra in this region. The depth classes for each province were identified by the average light extinction coefficient at 490 nm, $K_d(490)$, determined from MODIS-Aqua seasonal climatologies for each province. Seasonal $K_d(490)$ was used to ensure samples from different seasons fell within a similar underwater light field to maintain relatively constant photodegradation rates across samples. Thus, a boreal winter sample near the lower limit of the first optical depth in a province could be a few meters deeper than a boreal summer sample near the upper limit of the second optical depth in the same province. Biogeochemical provinces for each depth class were included in the analysis using the same 5% of maximum
sampling criterion described above for the complete dataset, resulting in similar sample
sizes. For most analyses, only the first optical depth is presented in the figures due to
space constraints. Additional depth data for these analyses can be found in the
Supplemental Material Tables 1-3. Seasonal distribution of data within the provinces did
not allow representation across all four seasons, thus, results focus only on spatial trends
in CDOM metrics.

2.3 Analysis of CDOM Metrics

Spectral slope calculated for the Gaussian decomposition and standard
exponential methodologies were compared using linear regression. $S_{G240:700}$, $S_{G300:700}$ and
$S_{G350:550}$ were compared to $S_{E275:295}$ and $S_{E350:400}$ to determine their potential for
estimating CDOM molecular weight, source, and degradation state using linear
regression. Non-linear least squares fits were used to assess the ability of log-normalized
$a_{CDOM}(\lambda)$ at wavelengths of 350, 412, and 443 nm to estimate $S_{G240:700}$, $S_{G300:700}$, $S_{G350:550}$,
$S_{E350:400}$ and $S_{E275:295}$.

We sought to determine if observed differences in $S_{CDOM}$ between biogeochemical
provinces were significant. We first applied a one-way analysis of variance (ANOVA) to
$S_{CDOM}$ categorized by biogeochemical province to determine if the mean slope values
between biogeochemical provinces were significantly different ($p < 0.01$). The least
significant difference multiple comparison of means (MCM) test was then applied using
the results of the ANOVA to determine if the distribution of spectral slope mean values
between provinces was significantly different ($p < 0.05$) [Rafter et al., 2002]. It is
recognized the least significant difference (LSD) methodology offers looser statistical
thresholds for significance than the Tukey-Kramer methodology [Hayter, 1986].
However, as an exploratory exercise aimed at defining potential differences, the more liberal LSD methodology was deemed more suitable here. Throughout the Results section, multiple comparison of means tests are presented on bioplots as a way to visualize the degree of similarity in $S_{\text{CDOM}}$ between different biogeochemical provinces. A line between boxes on a bioplot indicates mean $S_{\text{CDOM}}$ values between those provinces are statistically similar, while no connection indicates that mean $S_{\text{CDOM}}$ values between considered provinces are statistically unique. These results are further clarified within maps of the regions displaying which provinces are statistically similar and how similar (the number of related provinces) within groups displaying connectivity (statistical similarity). The bioplots illustrate which provinces displayed mean $S_{\text{CDOM}}$ values that are explicitly similar while the maps give a global representation of provinces that are statistically affiliated (all provinces are related to at least one other province within that group).

### 3. Results

#### 3.1 Comparison of CDOM Models

We compared spectral slope retrieved with the standard exponential to the Gaussian decomposition approach (Fig. 3). For all spectral ranges, the majority of points fell at or above the 1:1 line in Fig. 3, demonstrating the Gaussian decomposition fit resulted in identical or larger slope values for a given spectral range. When considering the spectral ranges investigated, differences between $S_{\text{G240:700}}$ and $S_{\text{E240:700}}$ were smallest for inland and coastal provinces and largest for open ocean provinces (Fig. 4a), although this comparison relies on only one open ocean province (NPTG). Absolute differences
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between $S_{G300:700}$ and $S_{E300:700}$ did not show a distinct spatial trend, as both NWCS (coastal) and NASW (open ocean) contained the largest absolute differences between the methodologies (0.025 and 0.0279 nm$^{-1}$, respectively). However, overall mean differences between $S_{G300:700}$ and $S_{E300:700}$ were smallest for inland and coastal regions and increased in open ocean regions, while environments characterized by a greater magnitude of a$_{CDOM}$ (Arctic, inland and coastal waters) more frequently displayed no difference in calculated slope between the two methodologies (Fig. 4b). This is not surprising, as the Gaussian peaks fitted in the 300-700 and 350-550 nm spectral ranges for these environments were relatively small in magnitude. Following this expectation, differences between $S_{G350:550}$ and $S_{E350:550}$ were quite small overall and did not display any regional trends (Fig. 4c).

### 3.2.1 Slope Values: Spectral and Spatial Trends

$S_{E275:295}$ displayed the largest variability in values across all biogeochemical provinces with coastal waters displaying smaller values, typically 0.02-0.03 nm$^{-1}$. Oceanic, Atlantic regions displayed larger values relative to all Pacific regions except NPSW (Fig. 5a,f; Supplementary Material Table 1). $S_{G240:700}$ displayed large differences between provinces influenced by terrestrial CDOM (INLAND, coastal and Arctic waters) and slope values observed in NPTG. $S_{G300:700}$ displayed similar trends, with INLAND, coastal and Arctic waters displaying slope values typically $<0.025$ nm$^{-1}$; however, it should be noted that coastal, sub-Arctic and Arctic provinces displayed more variability in slope values than the INLAND province, particularly with a longer tailed distribution towards higher $S_{G300:700}$ values (Fig. 5d; Supplementary Material Table 1). Open ocean regions tended to display higher slope values but variability and distribution of variables was higher and irregular. In contrast to $S_{G300:700}$, $S_{G350:550}$ tended towards higher values.
in coastal provinces and lower values in open ocean provinces, with some open ocean
provinces displaying higher variability and irregular distributions (Fig. 5e; Supplementary Material Table 1). Overall, $S_{\text{E275:295}}$ displayed the broadest distribution of $S_{\text{CDOM}}$ values while the other spectral ranges clustered more tightly around a group mean in generally a normal distribution when considered across all biogeochemical provinces. Mean slope values for each spectral range were 0.036, 0.018, 0.021, 0.020 and 0.016 nm$^{-1}$ for $S_{\text{E275:295}}$, $S_{\text{E350:400}}$, $S_{\text{G240:700}}$, $S_{\text{G300:700}}$ and $S_{\text{G350:550}}$, respectively, suggesting that $S_{\text{CDOM}}$ values decrease as the spectral range considered shifts to longer wavelengths, an important bias to consider when choosing a spectral range for a given application.

While previous studies have shown a generally decreasing slope value with depth, $S_{\text{E350:400}}$ was the only spectral range that showed a consistent relationship between increasing depth zone and decreasing spectral slope value. $S_{\text{G350:550}}$ decreased with depth zone, $S_{\text{E275:295}}$ decreased below the first optical depth but did not display a trend between the second optical depth and below the photic zone for most provinces, while $S_{\text{G240:700}}$ and $S_{\text{G300:700}}$ displayed relatively consistent slope values across all depth zones for most provinces (Supplementary Material Table 1). Overall, variability in the slope value decreased with depth for all spectral ranges considered.

### 3.2.2 Slope Values: Global Trends

The relationship between $S_{\text{CDOM}}$ values and biogeochemical province was considered for $S_{\text{E275:295}}$, $S_{\text{E350:400}}$, $S_{\text{G300:700}}$ and $S_{\text{G350:550}}$. Provinces with statistically similar $S_{\text{CDOM}}$ mean values are presented as clusters where each province presented displays similar mean $S_{\text{CDOM}}$ values to at least one other province for that spectral range. $S_{\text{E275:295}}$ showed the clearest spatial relationships, with provinces dominated by high $a_{\text{CDOM}}$ and
riverine input displaying lower mean $S_{E275:295}$ values (0.024 nm$^{-1}$; Fig. 6a,b) and open ocean regions, presumably dominated by photobleaching, displaying high mean $S_{E275:295}$ values (0.039 nm$^{-1}$, Fig. 6c,d; 0.044 nm$^{-1}$, Fig. 6e,f; 0.048 nm$^{-1}$, Fig. 6g,h). Lower $S_{E275:295}$ values (0.026 nm$^{-1}$; Fig. 6i,j) are found in provinces with a significant portion of samples taken in upwelling regions or regions where deep ocean waters pass over continental shelves (within the first optical depth). The remaining regions were either independent in their mean $S_{E275:295}$ value or displayed similarity with one other province (SANT and ANTA). INLAND displayed the lowest mean $S_{E275:295}$ value of 0.014 nm$^{-1}$.

Spatial trends for $S_{E350:400}$ were not as clear, with high aCDOM coastal, sub-Arctic and Arctic provinces showing similar spectral slope values as all Atlantic provinces considered ($S_{E350:400}=0.017$ nm$^{-1}$, Fig. 7a,b). Open ocean provinces from the Pacific, Indian and Southern Oceans clustered with slope values either higher ($S_{E350:400}=0.021$ nm$^{-1}$, Fig. 7c,d) or lower ($S_{E350:400}=0.014$ nm$^{-1}$, Fig. 7e,f) than the $S_{E350:400}$ value from higher aCDOM provinces, suggesting differences in the balance between photo- and microbial degradation relative to source signal. $S_{G300:700}$ showed little variation in mean slope value across all provinces while still producing three distinct clusters and INLAND as an independent province ($S_{G300:700}=0.021$ nm$^{-1}$, Fig. 8a,b; $S_{G300:700}=0.023$ nm$^{-1}$, Fig. 8c,d; $S_{G300:700}=0.019$ nm$^{-1}$, Fig. 8e,f; $S_{G300:700}=0.016$ nm$^{-1}$, Fig. 8g). Clustering appears to be a mix of results from $S_{E275:295}$ and $S_{E350:400}$, suggesting that a lack of contribution from wavelengths below 300 nm and a broad spectral range lead to greater similarities between disparate CDOM pools. While also displaying a relatively narrow range of mean slope values, $S_{G350:550}$ showed the most connectivity between proximal provinces and region while also separating into four distinct clusters ($S_{G350:550}=0.016$ nm$^{-1}$, Fig. 9a,b;
3.3 Gaussian Components

The number of Gaussian components fit was highly dependent on the spectral range considered (Fig. 10). $S_{G240:700}$ peak fitting was dominated by the lignin peak with the mean first Gaussian component location occurring at 276 nm for all 6 biogeochemical provinces considered. Fewer Gaussian components were fit in INLAND and coastal provinces due to lignin peak fitting dramatically improving the goodness of fit (Fig. 10a,11a; Supplementary Material Table 2). This is also evidenced by NPTG having the most Gaussian components fit relative to other provinces while peak height was generally small for this province. Arctic and sub-Arctic provinces also saw an increase in fitted components relative to other provinces with relatively high $a_{CDOM}$ (e.g. INLAND). For this spectral range, the location of the first component was strongly influenced by sample source and proximity to terrestrial material, as the first Gaussian component location was always below 300 nm for INLAND, NWCS, CARB and BERS while the first Gaussian component location ranged up to 385 and 381 nm for BPLR and NPTG, respectively. For $S_{G300:700}$, INLAND, sub-Arctic, Arctic and Atlantic provinces were fit with more Gaussian components than Pacific and Southern Ocean provinces (Fig. 10b,11d; Supplementary Material Table 2). This spectral range also observed the most fitted peaks across all provinces. $S_{G350:550}$ observed similar trends relative to ocean province as $S_{G300:700}$, but with fewer fitted peaks on average, likely due to peak height for components located in this fitting range being less prominent features of the absorption spectra (Fig.
Interestingly, BPLR and BERS were fitted with significantly more peaks in this spectral range, potentially due to relatively high productivity and strong riverine influence in these regions leading to a complex CDOM pool. BPLR and BERS were fit with large Gaussian peaks below 350 nm, also suggesting that fitting strictly above 350 nm capture smaller deviations in the absorption spectrum that are effectively masked with the improvement in fitting single, large deviations at shorter wavelengths.

Gaussian peak height, $\varphi$, was found to correlate quite well with $a_{\text{CDOM}}(350)$ ($r^2=0.88$), although the distribution appears bifurcated with a break-point between $a_{\text{CDOM}}(350) \leq 15$ m$^{-1}$ ($r^2=0.76$) and $a_{\text{CDOM}}(350) > 15$ m$^{-1}$ ($r^2=0.90$) (Supplementary Material Figure 1). Both relationships suggest a large dependency between $\varphi$ and the magnitude of $a_{\text{CDOM}}$ in the system. This effect was accounted for by normalizing $\varphi$ with the modeled $a_{\text{CDOM}}$ at the wavelength associated with the Gaussian peak location as described in the Methods section. Normalized $\varphi$ showed that open ocean Gaussian components are more prominent relative to the magnitude of CDOM in the system when compared to terrestrial components, with INLAND mean normalized $\varphi=0.03$ while ocean provinces had a mean normalized $\varphi=0.1$ (data not shown). Overall, provinces with high $a_{\text{CDOM}}$ tended to be fit with Gaussian peaks with larger peak height and width. Gaussian component location did not change significantly with depth for all spectral ranges considered (Fig. 11, Supplementary Material Table 2), while Gaussian component location only displayed unique mean locations for INLAND ($S_{G300:700}$) and NASW ($S_{G300:700},S_{G350:550}$), suggesting that these features originate from a relatively small pool of chromophores that are likely unique to terrestrial and ocean regions. Across all spectral
ranges, chromophores tended to be fit within spectral regions known to contain lignin species, photorefractory chromophores and degradation products produced in situ (see Discussion).

3.4 CDOM Metric Comparisons

3.4.1 Comparison of Broad Range Slopes to $S_{275:295}/S_{350:400}$

The influence of capturing absorption below 300 nm and the likely influence of lignin for relating broad range spectral slopes to absorption from $S_{275:295}$ is clear, as regions dominated by terrestrially-sourced CDOM show tight relationships between $S_{E275:295}$ and $S_{G240:700}$ in the first optical depth ($r^2=0.83-0.95$; Supplementary Material Table 3). Relationships between $S_{E275:295}$ and $S_{G300:700}$ were generally poor while relationships between $S_{E275:295}$ and $S_{G350:550}$ entirely deteriorate for most regions and depths ($r^2 < 0.2$; Supplementary Material Table 4), suggesting a distinct difference in the processes these spectral ranges describe. Notably, APLR $a_{CDOM}$ spectra displayed consistent slope values across diverse spectral ranges.

As expected, $S_{E350:400}$ related inversely to broad slope ranges relative to $S_{E275:295}$. Most $S_{G240:700}$ correlations were relatively poor ($r^2=0-0.34$) with INLAND and CARB displaying relationships of 0.49 and 0.82, respectively, suggesting a broad influence of absorption by lignin or lignin-derivatives in these regions. Overall, $S_{E350:400}$ showed distinct trends from spectral ranges capturing terrestrial features, suggesting a utility for monitoring in situ processes within this spectral range (Supplementary Material Table 3).

3.4.2 Comparison between $a_{CDOM}$ and $S_{CDOM}$

We considered relationships between $a_{CDOM}$ at 350, 412, and 443 nm and the calculated slope values to determine the feasibility of using the magnitude of $a_{CDOM}$ at a
reference wavelength to estimate $S_{CDOM}$. 412 and 443 nm, or nearby wavelengths, have applications to heritage satellite sensors while 350 nm is the shortest wavelength anticipated to be available for NASA’s Plankton, Aerosol, Cloud, ocean Ecosystem (PACE) sensor, providing maximum signal-to-noise for retrieving $a_{CDOM}$ while also avoiding overlap with phytoplankton pigments, including mycosporine-like amino acid absorption peaks around 330 and 360 nm [Pavlov et al., 2014]. Relationships were best fit using a non-linear least squares exponential fit. The goodness of fit did not change significantly between different reference wavelengths; subsequently, we only focus on $a_{CDOM}(350)$ in anticipation of future sensor capabilities. $S_{E275:295}$ had the strongest relationships with $a_{CDOM}(350)$, $S_{G300:700}$ relationships were highly variable, while $S_{E350:400}$ and $S_{G350:550}$ did not correlate with $a_{CDOM}(350)$ for almost all regions and depths considered (Supplementary Material Table 3).

We also assessed the error introduced in satellite-derived estimates of $a_{CDOM}(412)$ by using an assumed $S_{CDOM}$ value. CDOM has traditionally been considered alongside non-algal particulate (NAP) material, as both have absorption spectra that follow an approximately exponentially increasing with decreasing wavelength relationship. These absorption terms, $a_{CDOM}$ and $a_{NAP}$, are combined into a single term, colored detrital matter (CDM) absorption such that $a_{CDM}=a_{CDOM}+a_{NAP}$ and $a_{CDM}$ has an average spectral slope ($S_{CDM}$) representative of the slope and percent contribution of each component. The GSM algorithm and the Quasi-Analytical Algorithm (QAA) assume an $S_{CDM}$ of 0.015 and 0.013-0.017 nm$^{-1}$, respectively [Lee et al., 2002; Maritorena et al., 2002]. Global observations of $a_{NAP}$ suggest it accounts for 10-20% of the $a_{CDOM}$ signal, and a typical spectral slope for $a_{NAP}$ is 0.011 nm$^{-1}$ with a range of values much smaller than $S_{CDOM}$.
[Dong et al., 2013; Hoepffner and Sathyendranath, 1993; Roesler et al., 1989]. Assuming an $S_{CDOM}$ of 0.015 nm$^{-1}$, a contribution of 10% and 20% of $a_{NAP}$ with spectral slope of 0.011 nm$^{-1}$ results in an assumed $S_{CDOM}$ of 0.016 and 0.0154 nm$^{-1}$, respectively. We assessed the percent error between mean $a_{CDOM}(412)$ observed for each province and $a_{CDOM}(412)$ calculated for the province using the mean $a_{CDOM}(443)$ and these assumed $S_{CDOM}$ values. Error rates were similar when assuming 10% and 20% contributions from $a_{NAP}$ to $a_{CDOM}$. When assuming a 20% contribution and an $S_{CDOM}$ of 0.0154 nm$^{-1}$, estimated $a_{CDOM}(412)$ error varied from 4-22% of the observed mean $a_{CDOM}(412)$ (Fig. 12).

4. Discussion

4.1 CDOM Models

Bias introduced in the $S_{CDOM}$ parameter from varying the spectral range has been widely recognized for some time [Twardowski et al., 2004]. Despite this understanding, only a few narrow range spectral slope parameters have been adopted consistently, $S_{275:295}$ and $S_{350:400}$ [Helms et al., 2008], with highly variable broad range slopes reported throughout the literature. Regardless of the CDOM model used, exponential or Gaussian decomposition, the bias due to spectral range considered remains an issue. $S_{CDOM}$ differences between the exponential CDOM and Gaussian decomposition models are relatively minor for most spectra, with $S_{CDOM}$ values generally higher for the Gaussian decomposition model. However, differences between the models suggest that removing deviations from the exponential model and modeling these features with Gaussian curves allows for a better characterization of the underlying exponential signal and a better fit of
the measured CDOM spectra through improved r-squared and RMSE. This, in turn, will allow more consistent comparisons of $S_{\text{CDOM}}$ from the same spectral range and a stronger basis for estimating CDOM composition optically [Del Vecchio and Blough, 2004a]. In particular, we found the Gaussian decomposition method to be crucial for accurately modeling CDOM spectra strongly influenced by terrestrial material.

4.2 $S_{\text{CDOM}}$

Various spectral ranges have been used to characterize $S_{\text{CDOM}}$, with narrow range slopes typically focusing on specific attributes related to CDOM source, diagenetic state and molecular weight [Helms et al., 2008; Spencer et al., 2008]. The basis for linking optical properties to estimates of CDOM composition has strong backing in the literature [Boyle et al., 2009; Coble, 2007; Hernes and Benner, 2003; Kowalczuk et al., 2005; Wünsch et al., 2015]. Here, we assessed how broad spectral range $S_{\text{CDOM}}$ relates to common optical indicators of CDOM composition (e.g. $a_{\text{CDOM}}(\lambda)$, $S_{275:295}$) and varies across spectral ranges, ocean biogeochemical provinces and depth ranges.

CDOM absorption at a reference wavelength is often used as an indicator of CDOM composition as it relates well with $S_{\text{E275:295}}$ and lignin concentration [Fichot et al., 2016; Mannino et al., 2014]. Past studies have shown strong relationships between $a_{\text{CDOM}}$ and $S_{\text{CDOM}}$ along transects from lower salinity coastal waters to higher salinity offshore waters where the range in $a_{\text{CDOM}}(\lambda)$ typically varies by orders of magnitude [Kowalczuk et al., 2006; Pavlov et al., 2016; Stedmon and Markager, 2003], while a study in the Arctic Ocean found that CDOM absorption and $S_{\text{CDOM}}$ do not relate well between marine and terrestrially-derived CDOM pools [Granskog et al., 2012]. For our study, $S_{\text{E275:295}}$ displayed relatively strong relationships with $a_{\text{CDOM}}(350)$ for most
provinces ($r^2 > 0.5$). Notably, APLR displayed a poor relationship between $a_{\text{CDOM}}(350)$ and $S_{\text{CDOM}}$ across all spectral ranges, while most provinces displayed highly variable or poor relationships between $a_{\text{CDOM}}(350)$ and $S_{350:400}$. Relationships between broad range $S_{\text{CDOM}}$ and $a_{\text{CDOM}}$ were highly variable and were generally poor, even within the INLAND province where variability in $a_{\text{CDOM}}(350)$ is high across similar $S_{\text{CDOM}}$ values, an observation also seen by Meler et al. [2016]. We consider these inconsistencies within the literature and our findings as representative of a decoupling between $a_{\text{CDOM}}(\lambda)$ and $S_{\text{CDOM}}$ in systems that display higher variability in one parameter over the other or when data sets are not taken within a single sampling period. Open ocean CDOM has been characterized as a mix of degraded terrestrial material and contributions from in situ production [Andrew et al., 2013], suggesting that spectral shape due to CDOM composition is reflected by varying contributions from these processes within the context of low $a_{\text{CDOM}}(350)$ values. We hypothesize that within oceanic regions with little terrestrial influence, process-specific $S_{\text{CDOM}}$ variability (e.g. photodegradation and alteration by the microbial community) is not necessarily reflected in $a_{\text{CDOM}}(350)$ values at different times. These degradation processes occur regardless of the amount of CDOM; thus, an $a_{\text{CDOM}}(350)$ value of 0.1 m$^{-1}$ could be affiliated with a spectral shape consistent with microbial alteration of the CDOM pool or with a spectral shape consistent with photodegraded terrestrial material depending on the time and/or location sampled. This is a potential bias of ship-based sampling that should be accounted for when attempting to accurately estimate $a_{\text{CDOM}}$ from satellite-based remote sensing.

Spatial trends across all spectral ranges indicate that $S_G$ is quite variable across the global ocean (Fig. 5). Typically, global distributions of CDOM are presented as satellite-
derived climatologies of colored dissolved and detrital matter (CDM) absorption ($a_{CDM}$), where non-algal particulate (NAP) absorption ($a_{NAP}$) and CDOM are retrieved together and $a_{NAP}$ typically accounts for <20% of CDM in the global ocean [Nelson et al., 1998].

These climatologies typically display low $a_{CDM}(\lambda)$ in subtropical ocean gyres and higher $a_{CDM}(\lambda)$ along continental margins, the equator, and high latitudes [Siegel et al., 2005].

$S_G$ did not follow spatial patterns observed in satellite observations of $a_{CDM}$ for any spectral range considered, reinforcing a disconnect between the magnitude of $a_{CDOM}(350)$ and $S_{CDOM}$.

Existing methods that estimate $a_{CDOM}$ from satellite radiometry requires assuming $S_{CDOM}/CDM$ or estimating $a_{CDOM}$ by parameterizing non-algal particulate absorption ($a_{NAP}$) through empirical relationships and treating $a_{CDOM}$ as the residual [Matsuoka et al., 2013]. Attempts to estimate $S_{CDOM}$ directly have relied on removal of the $a_{NAP}$ signal and adjusting an initially-assumed $S_{CDOM}$ using ratios of remotely-sensed reflectance [Dong et al., 2013]. We found that assuming an $S_{CDOM}$ of 0.0154 nm$^{-1}$, equivalent to a 90% contribution of $a_{CDOM}$ to the $a_{CDM}$ signal [Nelson et al., 2010], and using $a_{CDOM}(443)$ results in errors in $a_{CDOM}(412)$ of 4-22% relative to the average $a_{CDOM}(412)$ observed in the provinces, suggesting that the assumed values or starting points used for $S_{CDOM}$ should be regionalized to reduce uncertainty (Fig. 12).

Retrieving $S_{CDOM}$ independently without assumptions would be a first step towards estimating CDOM composition through a direct, rather than parameterized, observation. $S_{E350:400}$ can potentially be retrieved using NASA’s PACE sensor. However, we found clearer separation between regions using $S_{G350:550}$, suggesting that accounting for a broader spectral range and Gaussian components within that range draws sharper
contrasts between distinct CDOM pools in the global ocean. Neither $S_{E350:400}$ or $S_{G350:550}$ related well with $S_{E275:295}$; thus, both will likely be poor proxies for evaluating terrestrial contribution and, potentially, molecular weight [Helms et al., 2008].

Biogeochemical models assume an $S_{CDOM}$ slope [Xiu and Chai, 2014] with some models accounting for microbial and photodegradation of CDOM over appropriate time scales [Dutkiewicz et al., 2015]. While the inclusion of optical parameters in global biogeochemical ocean models is a recent development, further partitioning the spectral properties of CDOM by region would enhance the accuracy when modeling the underwater light field. Past studies have found changes in CDOM spectral characteristics with depth to be significant [Hickman et al., 2010; Pérez et al., 2016]. We found changes in mean CDOM spectral characteristics to change up to 0.034, 0.02, 0.008 and 0.009 nm$^{-1}$ between biogeochemical provinces while changes across depth ranges within a given biogeochemical province varied up to 0.016, 0.003, 0.005 and 0.004 nm$^{-1}$ for $S_{E275:295}$, $S_{G240:700}$, $S_{G300:700}$, and $S_{G350:550}$, respectively. While spatial variability in $S_{CDOM}$ were greater between provinces than variability by depth within provinces, $S_{E350:400}$ displayed ranges up to 0.007 nm$^{-1}$ between provinces and by depth within provinces. From this, we suggest that in situ production pathways for CDOM are more variable by depth than across global ocean provinces. To aid in future modeling and satellite remote sensing efforts, we’ve presented slope values for each spectral range, province and depth range (Supplementary Material Table 3).

We observed differences between slope values measured across the spectral ranges for each province, suggesting that each spectral range does not convey the same information about CDOM composition. To understand what could be determined about
CDOM composition from each spectral range, we considered how $S_{G_{240:700}}$, $S_{G_{300:700}}$ and $S_{E_{350:550}}$ related to $S_{E_{275:295}}$, which is regarded as an indicator of source, molecular weight and photobleaching of CDOM \cite{D'Sa et al., 2014; Helms et al., 2008}, and $S_{E_{350:400}}$, a slope range less entrenched in the literature but indicative of photobleaching, molecular weight and microbial processing and production of CDOM \cite{Helms et al., 2008; Helms et al., 2013; Helms et al., 2015; Matsuoka et al., 2015}. We found that $S_{E_{350:400}}$ likely characterizes \textit{in situ} production and degradation of CDOM with potential links to microbial processes \cite{Matsuoka et al., 2015; Nelson et al., 2004; Seidel et al., 2015} as this parameter varied throughout the global ocean, showed consistency across presumably diverse CDOM pools (e.g. INLAND and ocean provinces; Fig. 7) and consistently increased with depth. $S_{G_{240:700}}$ is strongly correlated with $S_{E_{275:295}}$ in most regions ($r^2=0.48-0.95$, excluding BERS) suggesting that wavelengths below 300 nm strongly influence $S_{CDOM}$ in this spectral range. $S_{G_{300:700}}$ displayed variable relationships with $S_{E_{275:295}}$ ($r^2=0-0.90$) and $S_{E_{350:400}}$ ($r^2=0.01-0.86$). Typically, a region characterized by a poor relationship between $S_{300:700}$ and $S_{E_{275:295}}$ displayed a strong relationship between $S_{300:700}$ and $S_{E_{350:400}}$ (e.g. BPLR). A strong relationship with each parameter would be expected if $S_{300:700}$ represents CDOM composition in a similar manner to $S_{E_{275:295}}$ or $S_{E_{350:400}}$. However, considering that a consistent trend with one over the other was not observed, it is likely that $S_{G_{300:700}}$ blurs characteristics of each into a single parameter that may not be particularly effective at characterizing the CDOM pool except under ideal circumstances such as a single, dominant process contributing to the CDOM pool. Thus, past work that has found potential relationships between molecular weight and $S_{G_{300:600}}$ a
parameter we found to behave quite similarly to $S_{G300:700}$, may be contingent on the environment [e.g. Stedmon and Nelson 2015].

Considering the variability and trends in slope for the different spectral ranges and relationships with $S_{E275:295}$, it is likely that $S_{G350:550}$ will be sensitive to a smaller suite of processes than spectral ranges that extend down to or below 300 nm. While $S_{G350:550}$ could be useful for accurately modeling $a_{CDOM}$ above 350 nm, it appears to be limited for extending $a_{CDOM}$ lower than 350 nm. $S_{G350:550}$ showed greater differentiation between biogeochemical provinces while maintaining a strong relationship with $S_{E350:400}$ in most provinces. Few studies have reported spectral slope from 350-550 nm to our knowledge [Hancke et al., 2014; Kowalczuk et al., 2006], making it difficult to directly assess what $S_{G350:550}$ estimates about CDOM composition. We propose that $S_{E350:400}$ is a better metric for tracking compositional changes in the CDOM pool affiliated with photodegradation and in situ production of CDOM as suggested by Helms et al. [2013, 2015]. However, $S_{G350:550}$ displayed greater uniqueness between provinces while $S_{E350:400}$ displayed more consistent trends with depth across all spectral ranges. If these trends are consistent in future datasets, we propose that $S_{G350:550}$ will be an ideal parameter for directly estimating compositional changes in autochthonous CDOM from hyperspectral ocean color data while changes in $S_{E350:400}$ will be indicative of vertical transport of unique CDOM or distinct in situ production pathways. Based on previous studies, $a_{CDOM}(\lambda)$ will likely remain a useful parameter for estimating terrestrial CDOM contributions from hyperspectral satellite observations [Fichot et al., 2014; Mannino et al., 2014]. These parameters appear to relate well with oceanic, in situ processes with the potential for
tracking vertical movement of the CDOM pool and informing estimates of CDOM composition.

4.3 Gaussian Components

The spectral range used to fit $a_{CDOM}$ strongly impacted the number of Gaussian components fitted. When the first absorption peak was below 300 nm, presumed to be lignin [McKnight and Aiken, 1998], the goodness of fit increased so significantly that smaller peaks at longer wavelengths that were fitted in the 300-700 nm spectral range were no longer fitted. Fitting from 300-700 nm resulted in the most peaks fitted for all provinces, while 350-550 nm fitted fewer peaks than 300-700 nm suggesting that chromophores between 300-350 nm can be fit while still fitting features at wavelengths $>350$ nm. In waters where lignin is a strong or moderate contributor to $a_{CDOM}$ below 300 nm, fitting from 240-500 nm, then fitting from 300-500 nm, may be a better approach, although blending models could become an issue. The majority of waters sampled to 240 nm in the SeaBASS dataset occurred in waters that historically have a strong terrestrial component [Benner et al., 2005; D'Sa et al., 2014; D'Sa and DiMarco, 2009; Del Vecchio and Blough, 2004b], precluding a thorough analysis of the 240-700 nm spectral range across the full range of oceanic conditions observed in the entire SeaBASS dataset. However, $S_{E275:295}$ suggests that the trend in spectral slope values that account for $a_{CDOM}$ below 300 nm prevails in the global oceans. For spectra fitted with a peak below 300 nm, mean peak location was 286 nm, suggesting that $S_{E275:295}$ is strongly influenced by the shape of the Gaussian component, if present, rather than the underlying exponential curve. It is likely that the large, complex molecular structure of lignin and the absorption peak associated with lignin drive the relationship between $S_{E275:295}$ and CDOM molecular
weight [McKnight and Aiken, 1998]. Additionally, we observed a shift in the location of the lignin absorption peak from terrestrial waters to oceanic waters (Fig. 11a) consistent with photodegradation of this component [Del Vecchio and Blough, 2004a].

Absorption peaks at wavelengths less than 300 nm can extend beyond these wavelengths through a complex process of charge-transfer interactions in the CDOM pool [Del Vecchio and Blough, 2004a]. For waters strongly impacted by terrestrial material and displaying a low $S_{275:295}$ spectral signature, the first Gaussian component occurred at a much smaller wavelength in the spectra. Past studies have shown that terrestrial material absorption is dominated by lignin which absorbs below 300 nm [McKnight and Aiken, 1998; Spencer et al., 2008]; however, the deviation from the baseline associated with this peak extends beyond 300 nm [Fichot et al., 2016], resulting in a distortion of $S_{300:700}$ in these waters. Fitting Gaussian peaks provides a method to pick out unique components within the CDOM pool, similar to fitting fluorescence peaks in excitation-emission matrix spectroscopy (EEMs) and accounts for deviations that impact $S_{\text{CDOM}}$ in the spectral range considered. More work is required to determine the significance of these absorption-based features to particular groups of molecules in the CDOM pool, including whether features fitted between 300-325 nm in the 300-700 nm spectral range are unique chromophores or a residual effect from the strong absorption of lignin absorption extending above 300 nm.

Across all regions, spectral ranges that were commonly fitted were associated with spectral locations (~350 nm, 375 nm) of chromophores that are likely photorefactory [Helms et al., 2013] or chromophores that have been found to be produced from photobleaching of autochthonously produced CDOM [Swan et al., 2012]. The latter, a
feature observed between 410-420 nm and noted in previous studies [Bricaud et al., 2010; Swan et al., 2012], was the most commonly fitted peak across all provinces in the 300-700 nm spectral range. This feature was noticeably present across all spectral ranges, typically representing the second peak fitted in the 240-700 nm spectral range when more than one peak was fitted to the spectrum in this spectral range.

Two provinces that stood out regarding the average number of Gaussian peaks fitted per spectra were BPLR and BERS (Fig. 10). BPLR was dominated by measurements in the Chukchi Sea, a region with a greater magnitude of CDOM than the global ocean but less than most Arctic shelf regions due to predominantly authochthonously-produced CDOM [Dainard and Guéguen, 2013]. However, both BPLR and BERS have elevated levels of CDOM, likely a contributing factor to significantly more fitted peaks on average than other provinces. Both provinces were predominantly sampled during or shortly after the intense spring phytoplankton blooms associated with ice melt in these regions [Arrigo et al., 2014; Goes et al., 2013]. Phytoplankton absorption spectra in this region frequently display absorption in UV wavelengths due to the presence of mycosporine-like amino acids, a feature previously observed in the CDOM pool in Arctic habitats [Pavlov et al., 2014]. This, in conjunction with an active microbial community [Matsuoka et al., 2015] are potential explanations for why these regions were dominated by spectra with an average of more than four Gaussian components. The dramatic reduction in number of Gaussian peaks fitted to aCDOM spectra in BERS and BPLR from 300-700 nm to 350-550 nm despite a relatively constant mean location of peaks (when fitted) suggests that further consideration can be given to the weighting factor in environments with a diverse CDOM pool if spectral
range is a limiting factor. In these environments, reducing the weighting factor removes
more residuals, allowing for more, smaller peaks to potentially be fit if the data presents
an appropriate signal-to-noise (SNR) ratio while not distorting the BIC analysis. Locating
and observing changes in these peaks can potentially provide insight into links between
the phytoplankton community and CDOM as well as the degradative state of CDOM.

APLR spectra were typically fitted with few features and stood out as a unique
province in most analyses (Fig. 6-9). This is potentially due to low a_{CDOM} for some
samples, but many samples contained a_{CDOM}(350) greater than 0.1 m^{-1}. This province is
categorized by autochthonously produced CDOM, with a distinct S_{275:295} signal and a
high correlation of a_{CDOM}(325) with chlorophyll concentrations and upwelled waters
transporting subsurface water with elevated levels of CDOM into the photic zone [D'Sa
and Kim, 2017; Ortega-Retuerta et al., 2010; Ortega-Retuerta et al., 2009]. For many of
these spectra, the lack of components is likely due to old, upwelled CDOM that behaves
remarkably consistent across all spectral ranges, evidenced as an approximate one-to-one
line in slope comparisons across different spectral ranges (not shown). This feature was
also seen in CCAL, another province seasonally driven by upwelling and displaying
different CDOM signatures between upwelled waters and waters dominated by
phytoplankton blooms [Day and Falloona, 2009]. Considering that the number of
Gaussian components decreased with depth for most provinces, zones of upwelling will
likely display unique CDOM characteristics that include relatively uniform spectra with
deviations primarily resulting from recent biological contributions.

The utility of Gaussian peak height, \( \varphi \), and width, \( \sigma \), are less certain from our
analysis. When we normalized for peak height by modeled a_{CDOM} at the location of \( \mu \),
oceanic waters presented a broader range of normalized \( \phi \) including larger values, suggesting that these peaks are more prominent features relative to other chromophores contributing to \( a_{CDOM} \) in these regions. This suggests these regions contain chromophores that are consistently produced amid a background of relatively degraded CDOM or are photorefractory in nature, consistent with the spectral locations of the peaks relative to previous studies [Helms et al., 2013; Swan et al., 2012].

We did not find any significant trends in \( \sigma \) for any spectral ranges considered. While \( \mu \) and \( \phi \) are relatively intuitive features, the parameterization of \( \sigma \) carries more uncertainty related to the methodology. While peak location and height can shift due to changes in \( C \) (weighting factor for residual removal) and spectral range used for fitting, they are largely grounded in features of the \( a_{CDOM} \) spectra as evidenced by similarity in location and height across spectral ranges used. Peak width can change dramatically based on \( C \) and, to a lesser extent, spectral range used, suggesting less interpretability.

For our analysis, \( C \) was held constant at one for the entire dataset. Thus, while our results are not impacted by changes in \( C \), it is an important consideration for the community as the method becomes utilized more broadly.

### 4.4 Applications to Remote Sensing

Previous studies have found reliable relationships between \( a_{CDOM} \) at specific wavelengths, including \( a_{CDOM}(412) \) and \( a_{CDOM}(443) \), and spectral slope values, including \( S_{E275:295} \) [e.g. Mannino et al. 2014]. For our analysis, \( S_{E275:295} \) could potentially be retrieved with reasonable accuracy in most biogeochemical provinces assuming an accurate retrieval of \( a_{CDOM}(\lambda) \) and a predetermined relationship between these two parameters. However, the INLAND and BPLR regions displayed particularly poor
relationships, suggesting high variability in CDOM pools and significant differences in CDOM characteristics with similar $a_{CDOM}(\lambda)$ values. Thus, some regions would be precluded from this methodology. Considering that most regions displayed unique trends and distributions of slope, a global relationship is anticipated to poorly predict $S_{E275:295}$.

NASA’s PACE sensor is anticipated for launch in the near future and is expected to have hyperspectral (every 5 nm) capabilities down to 350 nm. Considering this, it is prudent to advance the knowledge of what can be determined regarding CDOM composition using $a_{CDOM}$ in this spectral range. To this end, we applied the methodology of Massicotte and Markager [2016] to identify spectral regions frequented by deviations that can impact satellite-derived estimates of chlorophyll-a and phytoplankton pigments, particularly methods utilizing band ratios as the most common region of deviations occurred from 410-440 nm. Hyperspectral sensors may allow for a baseline exponential absorption spectra, such as $S_{E350:550}$, to be fitted to $a_{CDOM}$ spectra, allowing for these features to be ignored if the SNR of the sensor doesn’t allow for confident fitting of these features or if methodologies cannot separate out diverse inherent optical property (IOP) signals. An accurate $S_{E350:550}$ directly estimated from hyperspectral satellite data may also aid in accounting for deviations in $a_{CDOM}$ that are currently centered on or near multispectral bands. Our approach allows for these spectral regions and their frequency to be assessed to determine if regional accounting for these features can decrease error propagated through the spectrum by an ill-defined $a_{CDOM}(\lambda_0)$.

We also investigated the impact of inaccurate $S_{CDOM}$ values for estimating $a_{CDOM}(412)$ by comparing calculated $a_{CDOM}(412)$ to mean $a_{CDOM}(412)$ for each province. The resultant errors, from 4-22%, suggest that poorly parameterizing $S_{CDOM}$ lends...
significant uncertainty to satellite estimates of IOP’s strictly introduced through $S_{\text{CDOM}}$ or $S_{\text{CDM}}$. For multispectral algorithms, we suggest accounting for differences in $S_{\text{CDOM}}$ between geographical regions, such as the provinces presented here, and continued consideration of the mean ratio of $a_{\text{NAP}}/a_{\text{CDOM}}$ across distinct biogeochemical regions for methods that utilize $S_{\text{CDM}}$.

5. Conclusions

In an attempt to close the knowledge gap and move towards a common methodology, we have presented $S_G$ values for three broad spectral ranges, 240-700 nm, 300-700 nm and 350-550 nm as well as $S_E$ for 275-295 nm and 350-400 nm. We also explored the ability of the Gaussian decomposition method to expand our optical understanding of CDOM composition from a global database. Ideally, $S_{\text{CDOM}}$ can both adequately model the $a_{\text{CDOM}}$ spectra and relate to CDOM characteristics. We presented $S_{\text{CDOM}}$ as a diagnostic tool that can provide insights into CDOM composition with the potential to be applied to hyperspectral ocean color applications for optical estimates of CDOM composition.

Of the slope ranges considered, we found $S_{E275:295}$ and $S_{E350:550}$ display clear, unique spatial trends that can be exploited for optically estimating changes in CDOM across diverse open ocean environments. $S_{E350:400}$ displayed potential for tracking changes to in situ production of CDOM, particularly with depth at a given location. $S_{G300:700}$ is a useful metric for particular regions if the underlying CDOM pool is known; however, this metric displayed good relationships with both $S_{E275:295}$ and $S_{E350:400}$, implying that the
metric itself does not clearly delineate specific compositional traits that impact the optical
signature of CDOM.

Hyperspectral capabilities may allow for direct estimates of $S_{\text{CDOM}}$, providing
insight into CDOM degradative state and in situ production pathways. However, $S_{\text{CDOM}}$
calculated using wavelengths anticipated to be available from NASA’s PACE sensor (> ~350 nm) differs significantly from $S_{\text{E275:295}}$, requiring alternative methods for estimating
terrestrial contribution, lignin content and molecular weight. The divergence in optical
properties of $S_{\text{E350:400}}$ and $S_{\text{E275:295}}$ observed here and documented in the literature suggest
that $S_{\text{E350:400}}$ can provide insight into in situ production pathways; however, further
consideration should be given to this parameter in future studies along with whether a
broader spectral range such as $S_{\text{G350:550}}$ provides more insight into these processes or
clearer regional distinctions.

Beyond tracking changes in CDOM and presenting a way to estimate CDOM
composition, $S_{\text{CDOM}}$ is also important for accurately modeling $a_{\text{CDOM}}$. We considered the
mean $a_{\text{CDOM}}(443)$ for each province and assessed how much error is introduced to the
$a_{\text{CDOM}}$ parameter using an assumed $S_{\text{CDOM}}$ of 0.0154 nm$^{-1}$ and propagating $a_{\text{CDOM}}$ to 412
nm. We found this assumed slope introduced errors in $a_{\text{CDOM}}(412)$ of 4-22% across all
provinces relative to the mean $a_{\text{CDOM}}(412)$ observed (Fig. 12). Thus, poorly
parameterizing $S_{\text{CDOM}}$ with a constant global slope can introduce a similar, if not greater,
level of uncertainty in retrieved $a_{\text{CDOM}}$ to mischaracterizing the percent contribution of
$a_{\text{NAP}}$ to $a_{\text{CDOM}}(412)$.

Ultimately, CDOM will be best considered using a suite of metrics applied to
ocean color imagery. Past work focusing on relationships between $a_{\text{CDOM}}$ at a given
reference wavelength to estimate $S_{E275:295}$ and lignin content can continue to be improved using *in situ* data and are anticipated to provide additional information not directly available from NASA’s anticipated PACE sensor. The emphasis should be on continuing to relate quality, *in situ* measurements with $S_{E350:400}$ and $S_{G350:550}$, two metrics anticipated to be directly available via NASA’s PACE sensor in the near future, to maximize data potential from remotely-sensed imagery. It is our view that, prior to mission launch, the community will be well served with a better understanding of what information is directly retrievable with $S_{CDOM}$ and which spectral range is best suited for discrimination between distinct CDOM pools within the spectral capability of the mission.
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Figure Captions

1. Example of exponential (Equation 1) and Gaussian decomposition fitting (Equation 2) of $a_{CDOM}$ spectra from the Chukchi Sea. The black line is the observed data, the blue dash-dot line is the exponential fit for the spectra from 240-700 nm ($S_{E240:700}=0.0178 \text{ nm}^{-1}$), and the red dashed line is the Gaussian decomposition fit from 240-700 nm ($S_{G240:700}=0.0180 \text{ nm}^{-1}$). Two Gaussian components were fitted to this spectra, with $\varphi$, $\mu$ and $\sigma$ for each component indicated within the figure.

2. Map of $a_{CDOM}$ observation locations for all spectral ranges considered: 350-550 nm (cyan, blue, black, red), 300-700 nm (blue, black, red), 275-295 nm (black, red), and 240-700 nm (red). The majority of INLAND samples are taken from rivers and lakes along the east and southeastern coast of the United States or from the Laurentian Great Lakes. Colored regions indicate Longhurst provinces used for analysis of spatial trends in the data set [Longhurst, 2006]. SATL, KURO, CHIN, NPSW, SSTC, ISSG and ANTA were only used for $S_{350:400}$ and $S_{275:295}$ analyses due to data restrictions described in Section 2.2. Following those restrictions, data points indicated here in uncolored regions are only used for aggregate slope comparisons depicted in Fig. 3a-c and are not used for any other analysis.

3. Probability density functions comparing $S_{E}$ (equation 1) vs. $S_{G}$ (equation 2) for (a) 240-700 nm, (b) 300-700 nm and (c) 350-550 nm spectral ranges. Dashed lines indicate a 1:1 relationship.

4. Mean difference between $S_{G}$ and $S_{E}$ for each province in the (a) 240-700 nm, (b) 300-700 nm and (c) 350-550 nm spectral ranges.
5. Spectral slope distribution for the first optical depth of each province with spectral range for each row as (a,f) $S_{E275:295}$, (b,g) $S_{E350:400}$, (c) $S_{G240:700}$, (d) $S_{G300:700}$ and (e) $S_{G350:550}$. Missing histograms in row (c) indicate provinces that did not have enough spectra measured down to 240 nm to be considered here.

6. Global maps displaying provinces grouped based on results from the multiple comparison of means test. Connecting lines indicate provinces within the group are statistically similar. Province color indicates the number of provinces found to have a statistically similar mean slope based on the multiple comparison of means test. Provinces that appear more than once were found to have a mean and uncertainty in the mean (described in the Methods section) overlapping with provinces in two different groups. Subplots display corresponding maps and biplots as (a,b) Cluster 1 ($S_{E275:295}=0.0244 \text{ nm}^{-1}$), (c,d) Cluster 2 ($S_{E275:295}=0.0440 \text{ nm}^{-1}$), (e,f) Cluster 3 ($S_{E275:295}=0.0399 \text{ nm}^{-1}$), (g,h) Cluster 4 ($S_{E275:295}=0.0485 \text{ nm}^{-1}$), (i,j) Cluster 5 ($S_{E275:295}=0.0267 \text{ nm}^{-1}$), (k, biplot only) SANT and ANTA ($S_{E275:295}=0.0313 \text{ nm}^{-1}$) and (l) indicates provinces with unique mean $S_{275:295}$ values: INLAND ($S_{E275:295}=0.0148 \text{ nm}^{-1}$), KURO ($S_{E275:295}=0.0352 \text{ nm}^{-1}$) and CHIN ($S_{E275:295}=0.0284 \text{ nm}^{-1}$).

7. Global maps displaying provinces grouped based on results from the multiple comparison of means test. Connecting lines indicate provinces within the group are statistically similar. Province color indicates the number of provinces found to have a statistically similar mean slope based on the multiple comparison of means test. Provinces that appear more than once were found to have a mean and uncertainty in the mean (described in the Methods section) overlapping with
provinces in two different groups. Subplots display corresponding maps and bioplots as (a,b) Cluster 1 ($S_{E350:400}=0.0176 \text{ nm}^{-1}$), (c,d) Cluster 2 ($S_{E350:400}=0.0210 \text{ nm}^{-1}$) and (e,f) Cluster 3 ($S_{E350:400}=0.0230 \text{ nm}^{-1}$) to indicate groups with 2 or more statistically similar province means while (g) APLR displayed a unique mean $S_{E350:400}$ value ($0.0230 \text{ nm}^{-1}$).

8. Global maps displaying provinces grouped based on results from the multiple comparison of means test. Connecting lines indicate provinces within the group are statistically similar. Province color indicates the number of provinces found to have a statistically similar mean slope based on the multiple comparison of means test. Provinces that appear more than once were found to have a mean and uncertainty in the mean (described in the Methods section) overlapping with provinces in two different groups. Subplots display corresponding maps and bioplots as (a,b) Cluster 1 ($S_{G300:700}=0.0212 \text{ nm}^{-1}$), (c,d) Cluster 2 ($S_{G300:700}=0.0237 \text{ nm}^{-1}$) and (e,f) Cluster 3 ($S_{G300:700}=0.0191 \text{ nm}^{-1}$) while (g) INLAND displayed a unique mean $S_{G300:700}$ ($0.0166 \text{ nm}^{-1}$).

9. Global maps displaying provinces grouped based on results from the multiple comparison of means test. Connecting lines indicate provinces within the group are statistically similar. Province color indicates the number of provinces found to have a statistically similar mean slope based on the multiple comparison of means test. Provinces that appear more than once were found to have a mean and uncertainty in the mean (described in the Methods section) overlapping with provinces in two different groups. Subplots display corresponding maps and bioplots as (a,b) Cluster 1 ($S_{G350:550}=0.0167 \text{ nm}^{-1}$), (c,d) Cluster 2
(SG350:550=0.0177 nm$^{-1}$), (e,f) Cluster 3 (SG350:550=0.0156 nm$^{-1}$) and (g,h) Cluster 4 (SG350:550=0.0140 nm$^{-1}$) while (i) APLR displayed a unique mean SG350:550 value (0.0232 nm$^{-1}$).

10. Number of Gaussian components indicated by color in the first optical depth for (a) 240-700 nm, (b) 300-700 nm and (c) 350-550 nm.

11. Distribution of Gaussian component spectral location between ocean and inland observations for (a-c) 240-700 nm, (d-f) 300-700 nm and (g-i) 350-550 nm for the first (a,d,g) and second (b,e,h) optical depths and below the photic zone (c,f,i).

12. Percent error between mean observed a$_{\text{CDOM}}$(412) for each province and calculated a$_{\text{CDOM}}$(412) using mean observed a$_{\text{CDOM}}$(443) and an assumed S$_{\text{CDOM}}$ of 0.0154 nm$^{-1}$. 
Figure 1.
Absorption (m$^{-1}$)

- $\varphi_1=0.203$ m$^{-1}$
- $\mu_1=271.1$ nm
- $\sigma_1=12.0$ nm

- $\varphi_2=0.021$ m$^{-1}$
- $\mu_2=426.0$ nm
- $\sigma_2=27.6$ nm

Wavelength (nm)
Figure 2.
Figure 3.
Figure 4.
Figure 8.
Figure 9.