Deriving optical metrics of coastal phytoplankton biomass from ocean colour

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A B S T R A C T

An approach to develop accurate local models for the estimation of chlorophyll a concentration (Chl a) and spectral phytoplankton absorption (aph(λ)) from hyperspectral in situ measurements of remote sensing reflectance (Rrs(λ)) in an optically complex water body is presented. The models are based on empirical orthogonal function (EOF) analysis of integral-normalised Rrs(λ) spectra, and spectral normalisation was found to be key to the models’ success. Accurate model estimates of both Chl a and aph(λ) were obtained, with R² values in log₁₀ space (N = 42) of 0.839 found for Chl a, and for aph(λ), R² values ranging from 0.771 (547 nm) to 0.910 (655 nm). A statistical resampling exercise to create training and test data sets showed that stable models could be built with ~15 training spectra and corresponding measurements of Chl a and aph(λ), providing important guidance for the implementation of this approach at other locations. The applicability of the models to a reduced-wavelength resolution (8 wavebands) dataset was tested, and showed that reduction in wavelength resolution had little impact on the models’ skill, with R² values obtained within ~1% of the hyperspectral (101 wavebands) R² values for both Chl a and aph(λ). That the reduced-wavelength resolution models performed as well as the hyperspectral models points to their potential utility for satellite sensors.

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1. Introduction

The coastal ocean comprises only 7% of the surface area of the world ocean, yet in biogeochemical terms, it is one of the world’s most active areas (Borges, 2005). It is estimated to account for 14–30% of total marine organic matter production (Gattuso et al., 1998), and recent studies highlight the large degree of uncertainty surrounding the role of coastal seas in carbon dioxide (CO₂) sequestration (Chen & Borges, 2009; Shadwick et al., 2010). In addition to their role in the global carbon cycle, coastal seas support a diverse and vital range of ecosystem services, including fisheries (up to 90% of the world fish catch is obtained from coastal seas (Pauly & Christensen, 1995)) and the recreation and tourism industries. A 1997 study (Cohen et al., 1997) estimated that 37% of the world’s population lived within 100 km of coastlines, making them especially vulnerable to the effects of anthropogenic influence (Diaz & Rosenberg, 2008; Gilbert et al., 2010; Rabalais et al., 2010; Walsh et al., 2009; Zhang et al., 2010).

Given their importance both in terms of the food resources and habitat they provide and their role in biogeochemical cycling, managers worldwide are now mandated to protect, monitor and study coastal seas. A powerful tool to monitor coastal waters lies in measurement of ocean colour, either in situ or from space, which can reveal synoptic patterns in biological and physical phenomena at various temporal and spatial scales. The colour of the ocean is directly influenced by its constituents and, since the launch of the Coastal Zone Color Scanner (CZCS, Hovis et al. (1980)) in 1978, many approaches have been developed to derive water constituents from measurements of ocean colour. These fall broadly into two classes of algorithms—empirical band-ratio algorithms, which are derived from the statistical relationship between the ratio of two or more wavebands (blue and green) of remote sensing reflectance, Rrs(λ) (sr⁻¹; see Table 1 for a list of symbols and units) and in situ measurements of chlorophyll a concentration, Chl a (mg m⁻³), and semi-analytical algorithms that are based on a combination of radiative transfer theory and empirically derived parameters, and that permit the retrieval of inherent optical properties (IOPs) such as spectral particulate backscattering, bbp(λ) (m⁻¹), and phytoplankton absorption, aph(λ) (m⁻¹), coefficients that can be related to the water constituents of interest.

Band ratio algorithms to retrieve Chl a have been applied successfully in waters where ocean colour is primarily a function of Chl a, i.e. case 1 waters (Morel & Prieur, 1977), for measurements made with...
Table 1
List of symbols, definitions and units.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>a_{ap}(\lambda)</td>
<td>Detrital absorption coefficient</td>
<td>m^{-1}</td>
</tr>
<tr>
<td>a_{fl}(\lambda)</td>
<td>CDOM absorption coefficient</td>
<td>m^{-1}</td>
</tr>
<tr>
<td>a_{ap}(\lambda)</td>
<td>Particulate absorption coefficient</td>
<td>m^{-1}</td>
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<tr>
<td>a_{fl}(\lambda)</td>
<td>Phytoplankton absorption coefficient</td>
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<td>a_{gfl}(\lambda)</td>
<td>Phytoplankton absorption coefficient</td>
<td>m^{-1}</td>
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<tr>
<td>R_{MERIS}^\text{MERIS}(\lambda)</td>
<td>Derived from synthetic MERIS AOP-EOF model</td>
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<td>R_{MERIS}^\text{MERIS}(\lambda)</td>
<td>Derived from synthetic MERIS AOP-EOF model</td>
<td>m^{-1}</td>
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</table>

In addition to CDOM and detrital absorption and particulate backscattering models, some of CDOM absorption and particulate backscattering models also retrieve IOPs (Carder et al., 1999; Franz & Werdell, 2010; Lee et al., 2002; Maritorena et al., 2002; Smyth et al., 2006). These models may perform well in coastal waters (e.g. Lee and Carder (2004)), but model parameters such as the spectral slopes of CDOM + detrital absorption and particulate backscattering may need to be regionally tuned as their local values can vary widely (Craig et al., 2006; Darecki & Stramski, 2004; Hu et al., 2003).

The most commonly used metric of phytoplankton biomass is Chl a (e.g. Boyce et al. (2010); Schwarz and Schodlok (2009); Ulitz et al. (2006)), although it has long been recognised as an imperfect proxy (Cullen, 1982). Chl a has been used as the biomass term in many models of primary productivity (Behrenfeld & Falkowski, 1997; Morel, 1991; Platt, 1986). However, the significance of \( a_{fl}(\lambda) \) as an important parameter to describe the light available for photosynthesis in primary productivity models has been discussed in many studies (Bidigare et al., 1987; Fujii et al., 2007; Kiefer & Mitchell, 1983; Lee et al., 1996a; Lee et al., 1996b; Marra et al., 2007; Mow & Yoder, 2005). Additionally, studies have shown that \( a_{fl}(\lambda) \) is strongly related to phytoplankton size (Bricaud et al., 2004; Bricaud & Stramski, 1990; Ciotti et al., 2002; Hirata et al., 2008), which in turn, can be related to trophic state or phytoplankton functional type (Chisholm, 1992; Cullen et al., 2002; Margalef, 1978).

Clearly, in coastal regions, derivation of Chl a, or arguably more appropriately, \( a_{fl}(\lambda) \) can permit insight into fundamental ecological processes and their response to forcing factors such as anthropogenic perturbation of water and carbon cycles or climate change. However, reliable and robust estimates of Chl a and \( a_{fl}(\lambda) \) remain a challenging endeavour in coastal seas. Here, we describe the development of a simple statistical model to allow the derivation of Chl a or \( a_{fl}(\lambda) \) from measurements of apparent optical properties (AOPs) made in an optically complex estuarine body of water on Canada’s east coast.

We endeavoured to develop an approach that did not rely on any a priori assumptions regarding the relationships between water constituents and AOPs, but rather used purely statistical techniques to reveal the dominant modes of AOP variation and how these could be related to important water constituent properties. The approach is straightforward and site-specific models may be derived in any situation for which concurrent measurements of AOPs and Chl a or \( a_{fl}(\lambda) \) are available, making it ideally suited for implementation in coastal monitoring and management scenarios.

### 2. Methods

All measurements were taken as part of a multidisciplinary integrated programme of research based in Bedford Basin near Halifax, Nova Scotia in Canada (see http://bbomb.ceoi.ca/index.php and http://www.bio.gc.ca/monitoring-monitorage/bbomp-pobb/index-eng.html for programme details). Bedford Basin is an estuary that receives freshwater from the Sackville River and saline input from the Atlantic over a shallow sill, with a flushing time of approximately 11 days (Li & Harrison, 2008). The Compass Buoy station in Bedford Basin (44° 41.62’N, 63° 38.42’W), situated in 70 m of water, has been the site of weekly multi-parameter observations since 1992, and these have formed the basis for many important studies of ecological phenomena (Li & Dickie, 2001; Li et al., 2006; Li & Harrison, 2008).

#### 2.1. In situ measurements

**2.1.1. Water sample acquisition and analyses**

The Compass Buoy station was visited approximately weekly during February 2009–March 2010 using a small Department of Fisheries and Oceans (DFO) Canada launch. Water samples were collected by Niskin bottle at a depth of 1 m for the determination of various water column parameters, that included spectral particulate absorption coefficient, \( a_{fl}(\lambda) \) (m^{-1}), CDOM absorption coefficient, \( a_{fl}(\lambda) \) (m^{-1}) and Chl a. Wherever possible, NASA ocean optics protocols (Pegau et al., 2003) were followed for all sample acquisition, handling, storage and analysis. Briefly, \( a_{fl}(\lambda) \) and \( a_{fl}(\lambda) \) spectra were determined from water samples that were filtered under low pressure through a 25 mm GF/F (Whatman) filter. \( a_{fl}(\lambda) \) in the range 350–800 nm was determined in a Cary 4000
UV–vis spectrophotometer with the filter pad mounted on a quartz glass slide and placed at the entrance to an integrating sphere in a modification (Craig, 1999) of the Shibata (1959) opal glass technique. Samples were de-pigmented by soaking the filters in a 0.1% active chlorine solution of NaClO (Kishino et al., 1985; Tassan & Ferrari, 1995). The absorption spectra of the de-pigmented particles, $a_{0\mu}(\lambda)$ (m$^{-1}$), were then measured as described above and $q_{0\mu}(\lambda)$ calculated from $a_{0\mu}(\lambda) - a_{0\mu}(\lambda)$. $q_{0\mu}(\lambda)$ was determined from water samples passed through a 0.2 µm Nuclepore® polycarbonate filter. This filtrate was decanted into a 0.1 m pathlength quartz cuvette and its absorbance measured, with purified water (Nanopure™) in the reference cell, in the range 320–800 nm in a Cary 4000 UV–vis spectrophotometer. Chl $a$ was determined using the Welschmeyer technique (1994) by extracting particulate matter retained on GF/F (Whatman) filters in 90% acetone at $-20$ °C for 24 h and measuring the extract in a Turner Designs fluorometer.

2.2.1. Calculation of remote sensing reflectance, $R_{rs}(\lambda)$

On each sampling day, depth, $z$ (m), profiles of hyperspectral downwelling irradiance, $E_d(\lambda, z)$ (µW cm$^{-2}$ nm$^{-1}$) and upwelling radiance, $L_u(\lambda, z)$ (µW cm$^{-2}$ nm$^{-1}$ sr$^{-1}$) were made with a Hyperprof (Satlantic Inc.) profiling radiometer. Multiple (usually three) casts were made in quick succession and ~100 m away from the boat to avoid the influence of ship shadow (Mueller et al., 2003). A deck unit mounted to the superstructure of the boat also provided contemporaneous measurements of above-water surface incident irradiance, $E_i(\lambda)$ (µW cm$^{-2}$ nm$^{-1}$) during profile acquisition.

2.2.2. Radiometric data analysis

2.2.1. Calculation of remote sensing reflectance, $R_{rs}(\lambda)$

Raw $E_d(\lambda, z)$, $L_u(\lambda, z)$ and $E_i(\lambda)$ data were processed using custom software (C.T.J.) that applied instrument calibration constants and immersion factors as appropriate. $E_i(\lambda, t)$, where $t$ is the time corresponding to profiler’s depth $z$, was measured on board using a vertically mounted sensor attached to the boat’s superstructure. A dimensionless scaling factor, $s(\lambda, t)$, was created by calculating the ratio of $E_i(\lambda, t(0^{-}))$ to $E_i(\lambda, t(0^+))$ where $t(0^-)$ is the time corresponding to the profiler just beneath the surface, and $t(0^+)$ the time corresponding to the profiler at depth $z$ (Mueller et al., 2003). $s(\lambda, t)$ was subjected to a low pass temporal filter in order to remove high frequency fluctuations due to ship movement, but retain lower frequency fluctuations due to real changes in ambient irradiance. $L_u(\lambda, z)$ and $E_i(\lambda, z)$ profiles were then normalised to $s(\lambda, t)$ spectra to account for variations in ambient irradiance throughout the duration of the cast. These scaled spectra, denoted $L_u^*(\lambda, z)$ and $E_i^*(\lambda, z)$, were then pooled together to give a greater number of data points and so reduce measurement uncertainties and noise in subsequent calculations. Poor quality spectra, most often found very near to the surface and caused by surface wave focussing and the geometry of the HyperPro, were identified using a simple quality control (QC). This consisted of calculating an envelope of ± 2 standard deviations for each integral-normalised spectrum (see Section 3.3 for details of this calculation), and any normalised spectrum with points outside of this envelope were flagged as suspect and excluded from further analysis.

Once near-surface noisy data had been excluded using the QC procedure described above, the minimum depth of the data remaining after QC, $z_{min}$ (m), was ~1 m or greater for all wavelengths. Therefore, in order to calculate $R_{rs}(\lambda)$, it was necessary to first propagate $L_u^*(\lambda, z_{min})$ to just below the surface, i.e. $L_u^*(\lambda, 0^-)$ (µW cm$^{-2}$ nm$^{-1}$ sr$^{-1}$). This was achieved by performing a robust log-linear regression, at each wavelength, of $\ln[L_u^*(\lambda)]$ versus depth, over a depth range spanning $z_{min}$ to 1.5 optical depths. The robust regression procedure ensured that outliers, usually the result of surface wave focussing, did not influence the results and was performed using the MATLAB™ (Mathworks) function robustfit with the ‘Huber’ weighting function and default tuning constant selected. No further statistical analyses were performed to assess whether the robustfit options selected were optimal. The gradient of the regression line yielded the diffuse attenuation coefficient for $L_u^*(\lambda)$, $K_L(\lambda)$ (m$^{-1}$), and the intercept, $L_u^*(\lambda, 0^-)$. Although the HyperPro measured AOPs in the range 350–760 nm, it was decided to limit the log-linear regression to a 400–700 nm range, as very few regression points could be obtained in the $z_{min}$ to 1.5 optical depth range at the highly attenuated far blue (350–400 nm) and red (700–760 nm) wavelengths. The paucity of regression points in these wavebands led to questionable estimates of $L_u^*(\lambda, 0^-)$ and, if included, would have meant discarding spectra that were otherwise of high quality in the 400–700 nm range. Remote sensing reflectance, $R_{rs}(\lambda)$, was then calculated from (Austin, 1974)

$$R_{rs}(\lambda) = \frac{L_u^*(\lambda)}{E_i^*(\lambda, 0^-) - E_i^*(\lambda, 0^+)}$$

where $L_u^*(\lambda)$ is water leaving radiance (µW cm$^{-2}$ nm$^{-1}$ sr$^{-1}$), $\rho$ = 0.025 the Fresnel reflectance of the air sea interface, $n = 1.34$ is the refractive index of seawater, and $E_i^*(\lambda, 0^-)$ is the $E_i^*$ spectrum measured at the beginning of the descent of the profiler.

3. Results and discussion

3.1. Water sample measurements

During the 13-month study period, spanning February 2009–March 2010, a total of 42 data points, spaced approximately weekly, and consisting of AOP spectra and corresponding water constituent measurements were obtained. The $q_{0\mu}(\lambda)$ spectra shown in Fig. 1 exhibited substantial variability both in spectral magnitude and shape, with $q_{0\mu}(443)$ varying over one order of magnitude (0.044–0.545 m$^{-1}$; Table 2), indicating the response of the phytoplankton community to a wide range of environmental conditions. Descriptive statistics for key parameters (Table 2) showed that Chl $a$ was highly variable and spanned two orders of magnitude during our study period. $q_{0\mu}(443)$, $q_{0\mu}(443)$ and $q_{0\mu}(676)$ exhibited less variability and spanned only one order of magnitude, while $q_{0\mu}(443)$ varied by a factor of 6. A time series plot of $q_{0\mu}(443)$, $q_{0\mu}(443)$, $q_{0\mu}(443)$, Chl $a$ and $q_{0\mu}(676)$ is shown in Fig. 2 and illustrates the variability of both Chl $a$ and $q_{0\mu}(\lambda)$ throughout the study period. Chl $a$, $q_{0\mu}(676)$ and $q_{0\mu}(443)$ track each other closely and higher values are observed around the spring bloom in March–April of 2009 and 2010, an

![Fig. 1. $q_{0\mu}(\lambda)$ measurements obtained during the period February 2009–March 2010 at the Compass Buoy station.](image-url)
autumnal bloom in September–October 2009, and an elevated biomass event in June 2009 most likely associated with favourable nutrient and irradiance conditions.

The relationships between these three parameters and $a_{\text{det}}(443)$ and $a_{\text{aph}}(443)$ are more complex, and show weak relationships during certain periods and none in others, as is typical in case 2 waters. A correlation matrix (Table 3) quantifies the relationships amongst all of these parameters for the 42 data points, and shows the effect of wavelength between Chl $a$ and $a_{\text{aph}}(\lambda)$, with a slightly stronger correlation, $R$, observed between Chl $a$ and $a_{\text{aph}}(676)$ ($R=0.939$) than with $a_{\text{aph}}(443)$ ($R=0.846$). $a_{\text{det}}(443)$ is weakly correlated with Chl $a$, $a_{\text{aph}}(443)$ and $a_{\text{aph}}(676)$ ($R=0.409, 0.432, 0.414$ respectively) — also borne out during certain periods in Fig. 2 in which $a_{\text{det}}(443)$ follows the trend of the phytoplankton parameters. Importantly, we can also see that there is an extremely weak or almost no correlation between $a_{\text{det}}(443)$ and Chl $a$ ($R=-0.012$), $a_{\text{aph}}(443)$ ($R=-0.021$), $a_{\text{det}}(443)$ ($R=0.166$), or $a_{\text{aph}}(676)$ ($R=-0.030$).

3.2. AOP measurements

Fig. 3 shows remote sensing reflectance spectra, $R_{\text{rs}}(\lambda)$, derived from HyperPro measurements collected approximately weekly over a time period spanning February 2009–March 2010 and encompassing two spring bloom events. Throughout this period, $R_{\text{rs}}(\lambda)$ showed considerable variability in both spectral shape and magnitude, indicating the wide range of water constituents encountered at our study site.

3.3. Empirical orthogonal function (EOF) analysis of $R_{\text{rs}}(\lambda)$

Mueller (1976) demonstrated that principal components analysis (aka empirical orthogonal function analysis) showed promise for parameterising coastal ocean reflectance spectra and for deriving water constituent information. Empirical orthogonal function (EOF) analysis can be a useful tool for reducing the dimensionality of a data-set. The largest portion of total variance of the data is captured by the first mode, or EOF, and subsequent modes capture progressively less variance. The result is a set of orthogonal (i.e. geometrically independent) modes of oscillation that account for all the variability in the data. By selecting only the first few EOFs, the dimensionality of the data—in this case the number of wavelengths—can be reduced without appreciable loss of information (Mueller, 1976). The selected EOFs can then be represented graphically as independent modes of oscillation in the data—in this case oscillations in spectral shape. Based on Mueller’s (1976) early findings, we hypothesised that EOF analysis of $R_{\text{rs}}(\lambda)$ spectra would reveal information on the factors that drive $R_{\text{rs}}(\lambda)$ variability. Analyses of this type have been used extensively in physical (Rayner et al., 2003; Smith et al., 1996) and optical (Fichot et al., 2008; Garver et al., 1994; Mueller, 1976; Otero & Siegel, 2004; Toole & Siegel, 2001) oceanographic studies to reveal temporal and spatial patterns, and here we propose the use of EOF analysis to explore the relationship between ocean colour and metrics of phytoplankton biomass in an optically complex water body. Our approach is comparable to using a subset of ocean colour data—i.e. reflectance at a small number of wavelength bands—to develop an empirical algorithm to estimate Chl $a$ or another property of the water. As suggested by Mueller (1976), we hope that the EOFs will be superior predictors.

We implemented an EOF analysis using the MATLAB™ function princomp. The input for this function consisted of an $(N \times m)$ array of $R_{\text{rs}}(\lambda)$ spectra, where $N$ was the number of observations, or vectors, and $m$ the number of wavelengths = 101. As our input consisted of vectors of spectra expressed in the same units at each wavelength, normalisation of the data, i.e. division by the standard deviation, was not required as would be if the units were different. The output of the analysis consisted of EOFs, each expressed as a vector of

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl $a$</td>
<td>0.584</td>
<td>18.020</td>
<td>5.163</td>
</tr>
<tr>
<td>$a_{\text{aph}}(443)$</td>
<td>0.044</td>
<td>0.545</td>
<td>0.180</td>
</tr>
<tr>
<td>$a_{\text{aph}}(676)$</td>
<td>0.016</td>
<td>0.240</td>
<td>0.085</td>
</tr>
<tr>
<td>$a_{\text{det}}(443)$</td>
<td>0.024</td>
<td>0.231</td>
<td>0.098</td>
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<tr>
<td>$a_{\text{det}}(676)$</td>
<td>0.151</td>
<td>0.604</td>
<td>0.246</td>
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</tbody>
</table>

Units: Chl $a$ (mg m$^{-3}$); $a_{\text{aph}}(\lambda)$ (m$^{-1}$).

### Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$a_{\text{aph}}(443)$</th>
<th>$a_{\text{aph}}(676)$</th>
<th>$a_{\text{det}}(443)$</th>
<th>$a_{\text{det}}(676)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl $a$</td>
<td>1</td>
<td>0.846</td>
<td>1</td>
<td>0.939</td>
</tr>
<tr>
<td>$a_{\text{aph}}(443)$</td>
<td>0.939</td>
<td>0.964</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$a_{\text{aph}}(676)$</td>
<td>0.409</td>
<td>0.432</td>
<td>0.414</td>
<td>1</td>
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<tr>
<td>$a_{\text{det}}(443)$</td>
<td>-0.012</td>
<td>-0.021</td>
<td>-0.030</td>
<td>0.166</td>
</tr>
</tbody>
</table>

Fig. 2. Time series plot of key water column parameters measured at the Compass Buoy site during February 2009–Mar. 2010.
loadings with one loading for each wavelength. Additionally, a vector of scores associated with each EOF was obtained, which represented the amplitude of the EOF for each observed \( R_{rs}(\lambda) \) spectrum.

The EOF analysis of \( R_{rs}(\lambda) \) spectra showed that the first mode contained 92.4% of the variance (Fig. 4, top panel), and its shape closely resembled the mean shape of \( R_{rs}(\lambda) \) (Fig. 3) indicating that the variance captured was due to variability in spectral amplitude. The second mode (Fig. 4, second panel), however, exhibited a shape not related to spectral amplitude, but rather to an out of phase (i.e. negatively correlated) behaviour between the blue and red regions of the spectrum, suggesting a process (or processes) that affects the short and long wavelength regions of the spectra differently.

In order to focus on changes in spectral shape that are expected from to result from variability in phytoplankton optical properties, it was decided to normalise \( R_{rs}(\lambda) \) to minimise the amplitude component of spectral variability and permit a more informative analysis of the factors that drive variability in shape. \( R_{rs}(\lambda) \) spectra were normalised by their integral according to:

\[
\langle R_{rs}(\lambda) \rangle = \frac{\int_{400}^{700} R_{rs}(\lambda) \, d\lambda}{\int_{400}^{700} \langle R_{rs}(\lambda) \rangle \, d\lambda}
\]

where \( \langle R_{rs}(\lambda) \rangle \) is integral-normalised \( R_{rs}(\lambda) \) (dimensionless). As can be seen in Fig. 5, the normalisation procedure substantially reduced the variability in spectral amplitude from, for example, a factor of 8 to 1.3 at 550 nm. The variability in spectral shape is thus much easier to discern in Fig. 5 than it is in Fig. 3.

The EOF analysis was then repeated on the normalised spectra and the first mode (Fig. 6, top panel), which described changes in spectral shape, was found to be almost identical to the second mode of the un-normalised spectra (Fig. 4, second panel). Normalisation of the spectra meant that variability associated with changes in spectral shape accounted for a much greater proportion of the variance—72.4% for normalised spectra (Fig. 6, top panel) as compared with 5.1% for un-normalised spectra (Fig. 4, second panel)—and thereby provided a more sensitive means to detect variability in AOP spectral shapes brought about by changes in water constituents. It is important to note that normalising the spectra made little change to the cumulative proportion of variance that the first four modes represented—99.6% for un-normalised spectra (Fig. 4) and 98.3% for normalised spectra (Fig. 6).

The modes of oscillation in Fig. 6 are interpretable as signatures of changes in the optical properties of the constituents of the water column. Mode 1 represents variation in the water’s colour, and is likely the signature of bulk oscillations in biomass concentration. Mode 2 superficially resembles the oscillation in the amplitude of \( R_{rs}(\lambda) \), but it does not exhibit the chlorophyll \( a \) fluorescence emission peak at ~683 nm captured by mode 1, suggesting that it is not associated with Chl \( a \). Furthermore, it exhibits an almost exponential shape from 400 to ~555 nm that resembles what might result from light absorbed by CDOM. This mode may therefore be the signature of changes in the
concentration of CDOM that occur independently of changes in Chl \( a \). Mode 3 exhibits a near-linear decrease with wavelength from 400 to 500 nm, the slope of which is correlated (i.e. they have the same sign) with peaks at ~580 and 683 nm. This may be the signature of concomitant changes in \( a_{	ext{det}} \) and Chl \( a \); indeed Table 3 and Fig. 2 showed that \( a_{	ext{det}} \) is sometimes weakly correlated with Chl \( a \). The small spectral inflections in mode 4 may be attributable to variability in phytoplankton pigment complements and chlorophyll \( a \) fluorescence quantum yield. Although mode 4 captured only a very small proportion of the total variability in spectral shape (1.7%), it is not noisy as might be expected from such a minor mode of oscillation, but coherent, and exhibits a spectral feature that corresponds to phytoplankton fluorescence emission at ~683 nm. These speculative interpretations suggested the potential of an EOF analysis of \( R_{545}(\lambda) \) spectra to resolve water constituents.

Motivated by these results, we decided to follow Mueller (1976) and investigate the utility of EOF analysis of reflectance spectra to derive estimates of water constituents in our study area. Although it would have been possible to use and, perhaps, regionally tune one of the several semi-analytical models currently available—indeed, some have been shown to perform well in coastal waters (e.g. Lee and Carder (2004); Smyth et al. (2006))—we chose to pursue the EOF-based approach because of its simplicity of implementation and its amenability to interpretation as described above.

### 3.4. AOP-EOF model for Chl \( a \) and \( a_{	ext{ph}}(\lambda) \)

It should be noted that, from this point forward, all references to EOF analysis pertain to results from the normalised \( R_{545}(\lambda) \) spectra.

When the proportion of the variance represented by each of the EOF modes was examined, it was revealed that 98.3% of the variance was represented by considering only the first four modes (Fig. 6), comparable to the results of similar EOF analyses of un-normalised reflectance spectra performed by Fichot et al. (2008), Mueller (1976), and Sathyendranath et al. (1994). This suggested that the first four modes contained the large majority of information that may be useful in developing EOF-based models of Chl \( a \) and \( a_{	ext{ph}}(\lambda) \).

On this evidence, we derived Chl \( a \) and \( a_{	ext{ph}}(\lambda) \) models by performing multiple linear regressions that used the scores from the first four EOF modes as independent variables (c.f. Mueller (1976)). When the 95% confidence intervals for both the Chl \( a \) and \( a_{	ext{ph}}(\lambda) \) model regression coefficients were examined, it was found that modes 2 and 4 contained zero, i.e. that they were not statistically different than zero. Therefore, we tested the effect on model skill, as determined by \( R^2 \) values in log\(_{10}\) space (Friedrichs et al. (2009); O’Reilly et al. (1998)), of excluding modes 2 and 4, and found that \( R^2 \) was reduced by a statistically negligible amount for Chl \( a \). For the \( a_{	ext{ph}}(\lambda) \) model, the effect on \( R^2 \) was more complex, with the model that used modes 1–4 outperforming the model that used only modes 1 and 3 by ~1% in most spectral regions, but increasing to ~4% in the 550 nm region. To maintain consistency between the Chl \( a \) and \( a_{	ext{ph}}(\lambda) \) models, we chose to retain all 4 modes, recognising that modes 2 and 4 make negligible difference to the Chl \( a \) model but appear to make meaningful contributions to the \( a_{	ext{ph}}(\lambda) \) model, particularly at green wavelengths, and indicating that interpretability of the EOFs extends past their statistical significance in the model. We also appreciate that developing and applying the model in other water types may produce different results in terms of the significance of the modes.

Due to the approximately lognormal distribution of Chl \( a \) and \( a_{	ext{ph}}(\lambda) \) (c.f. Campbell (1995)), the dependent variables used were log\(_{10}\)[Chl \( a \)] and log\(_{10}\)[log\(_{10}\)\(a_{	ext{ph}}(\lambda)\)] in the Chl \( a \) (Eq. 3) and \( a_{	ext{ph}}(\lambda) \) (Eq. 4) models respectively.

\[
\log_{10}[\text{Chl } a_{\lambda}] = \beta_0 + \beta_1 S_1 + \beta_2 S_2 + \beta_3 S_3 + \beta_4 S_4 \quad (3)
\]

\[
\log_{10}[\log_{10}[a_{\text{ph}}(\lambda)]] = \beta_0 + \beta_1 S_1 + \beta_2 S_2 + \beta_3 S_3 + \beta_4 S_4 \quad (4)
\]

In Eq. (3), Chl \( a_{\lambda} \) (mg m\(^{-3}\)) is modelled Chl \( a \), \( \beta_0 \)–4 are the regression coefficients, and \( S_1 \)–4 are the scores of the first four EOFs. In Eq. (4), \( a_{	ext{ph}}^\beta(\lambda) \) (m\(^{-1}\)) is modelled \( a_{	ext{ph}}(\lambda) \), and all other symbols are as for Eq. (3), but, in this case, the regression was performed at each wavelength (400–700 nm) to obtain fully spectral \( a_{\lambda} \) estimates.

At this stage, it is important to clearly state that it was not our intent to develop a model that could be globally applied to coastal measurements of ocean colour, as the coefficients derived for our AOP-EOF models are entirely dependent on the data set used to develop them (Mueller, 1976). Rather, we present a straightforward approach to derive local models for the estimation of Chl \( a \) and \( a_{	ext{ph}}(\lambda) \). Using this approach, models may be derived in any instance where measurements of AOPs and a validation data set are available, making it especially amenable to ocean observation and monitoring activities that are increasingly found as operational components of many research and ecological management programmes.

Since our models were developed in log\(_{10}\) space, all statistics reported are based on log\(_{10}\)-transformed data (c.f. Friedrichs et al. (2009); O’Reilly et al. (1998)). These statistics are \( R^2 \), bias (log\(_{10}\)[mg m\(^{-3}\)] and log\(_{10}\)[m\(^{-1}\)]) and root mean square error, RMSE (log\(_{10}\)[mg m\(^{-3}\)] and log\(_{10}\)[m\(^{-1}\)])], where bias and RMSE were calculated from:

\[
\text{bias} = \frac{1}{N} \sum_{i=1}^{N} (\log_{10}[y_i] - \log_{10}[y_i])
\]

\[
\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\log_{10}[y_i] - \log_{10}[y_i])^2}
\]
and where $y_i$ is the $i$th observation and $\hat{y}_i$ the $i$th modelled value. The units of both these quantities are in decades of $\log_{10}$ space and not easily translated into absolute terms. Therefore, following Campbell et al. (2002) and Friedrichs et al. (2009) we calculated a dimensionless inverse transformed value for bias from:

$$F_{\text{med}} = 10^{\text{bias}}$$

where $F_{\text{med}}$ is the median value of the ratio $\frac{y}{\hat{y}}$. So, for example, if $F_{\text{med}}$ is 1, there is no model bias; if $F_{\text{med}}$ is 2, the model overestimates by a factor of 2; if $F_{\text{med}}$ is 0.5, the model underestimates by a factor of 2.

Fig. 7 shows a plot of measured Chl $a$ versus Chl $a^{\text{Rrs}}$. An $R^2$ value of 0.839 ($N = 42$) and RMSE = 0.172 was obtained, and the data showed a strong linear relationship with a bias of almost zero ($-2.908 \times 10^{-16}$; Fig. 7, Table 4).

Comparisons of measured $\alpha_{\text{ph}}(\lambda)$ with modelled $\alpha_{\text{ph}}^{\text{Rrs}}(\lambda)$ derived from Eq. (4) at selected wavelengths showed that $\alpha_{\text{ph}}^{\text{Rrs}}(\lambda)$ was tightly clustered around the 1:1 line, with the exception of a small number of data points where $\alpha_{\text{ph}}^{\text{Rrs}}(\lambda)$ was obviously overestimated (Fig. 8).

To assess the model’s success over all wavelengths, we calculated spectrally resolved $R^2$ and RMSE (Fig. 9, Table 5). Much of the variability was explained: $R^2(\lambda)$ ($N = 42$; Fig. 9(a)) was found to vary between 0.771 at 547 nm to 0.910 at 655 nm. Interestingly, the peaks exhibited in the $R^2(\lambda)$ spectrum at ~420 nm and 655 nm did not correspond exactly to the positions of peak phytoplankton absorption, which were centred at approximately 440 nm and 675 nm (Fig. 1). A small trough was observed at ~683 nm, perhaps due to the fact that chlorophyll fluorescence emission peaks in this region and adds, rather than removes, photons to the system with variable fluorescence efficiencies (Huot et al., 2007). It is possible that some of this fluorescence yield variability may not have been captured by the first four EOFs.

RMSE (Fig. 9(b)) was an approximate mirror image of $R^2(\lambda)$, and ranged from 0.083 at 418 nm to 0.130 at 520 nm. At ~683 nm a local maximum was observed that corresponded to the minimum observed in the $R^2(\lambda)$ spectra at the same wavelength and thought to be associated with chlorophyll $a$ fluorescence.

The fact that the models accurately estimated both Chl $a$ and $\alpha_{\text{ph}}(\lambda)$ in optically complex waters is very encouraging and indicates that in our dataset, spectral shape, rather than magnitude, contains much of the necessary information required to build accurate models. This ability to capture variability in $R_{\text{ph}}(\lambda)$ spectral shape brought about by changes in phytoplankton absorption is a feature that could ultimately be exploited for tracking changes in phytoplankton community composition (c.f. Ciotti and Bricaud (2006), Hirata et al. (2008)).

An interesting additional result of our analysis was that using integral-normalised $L_u(\lambda)$ spectra ($\langle L_u(\lambda) \rangle$; dimensionless) in place of $\langle R_{\text{ph}}(\lambda) \rangle$ spectra produced results very similar to those reported above. For example, modelling Chl $a$ and $\alpha_{\text{ph}}(443)$ using $\langle L_u(\lambda) \rangle$ resulted in $R^2$ values of 0.848 and 0.899 respectively. The idea behind normalisation by $E_i(\lambda)$ when calculating $R_{\text{ph}}(\lambda)$ is to account for changes in ambient irradiance. Normalising $L_u(\lambda)$ spectra as in Eq. (2) apparently satisfies this purpose, and, significantly, negates the need for an expensive $E_i(\lambda)$ sensor. This result emphasized the key idea of our AOP-EOF model—that it is the colour of the water quantified by spectral shape, and not spectral amplitude, that carries most of the information about Chl $a$ and $\alpha_{\text{ph}}(\lambda)$.

### Table 4

Statistics for the hyperspectral and synthetic MERIS AOP-EOF Chl $a$ models.

<table>
<thead>
<tr>
<th></th>
<th>$R^2$</th>
<th>Bias</th>
<th>$F_{\text{med}}$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl $a^{\text{Rrs}}$</td>
<td>0.839</td>
<td>$-2.908 \times 10^{-16}$</td>
<td>1.000</td>
<td>0.172</td>
</tr>
<tr>
<td>Chl $a^{\text{geom}}$</td>
<td>0.831</td>
<td>$-2.260 \times 10^{-16}$</td>
<td>1.000</td>
<td>0.176</td>
</tr>
</tbody>
</table>

$N = 42$ for both models. Units are log$_{10}$(mg m$^{-3}$). $F_{\text{med}}$ is dimensionless.

Fig. 7. Measured versus modelled Chl $a$ from AOP-EOF model.

Fig. 8. Measured versus modelled phytoplankton absorption, $\alpha_{\text{ph}}^{\text{Rrs}}(\lambda)$, at selected wavelengths.

Fig. 9. Spectrally resolved statistics for $\alpha_{\text{ph}}^{\text{Rrs}}(\lambda)$. (a) $R^2(\lambda)$, (b) RMSE($\lambda$), ($N = 42$).
Table 5

Statistics for hyperspectral and synthetic MERIS AOP-EOF $\alpha_{ph}(\lambda)$ models.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$R^2$</th>
<th>Bias ($\times 10^{-16}$)</th>
<th>RMSE</th>
<th>$\sigma_{\text{med}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>412</td>
<td>0.896</td>
<td>1.071</td>
<td>1.000</td>
<td>0.085</td>
</tr>
<tr>
<td>443</td>
<td>0.890</td>
<td>2.088</td>
<td>1.000</td>
<td>0.087</td>
</tr>
<tr>
<td>490</td>
<td>0.883</td>
<td>3.952</td>
<td>1.000</td>
<td>0.096</td>
</tr>
<tr>
<td>510</td>
<td>0.815</td>
<td>3.674</td>
<td>1.000</td>
<td>0.123</td>
</tr>
<tr>
<td>560</td>
<td>0.786</td>
<td>3.835</td>
<td>1.000</td>
<td>0.129</td>
</tr>
<tr>
<td>620</td>
<td>0.780</td>
<td>3.304</td>
<td>1.000</td>
<td>0.120</td>
</tr>
<tr>
<td>665</td>
<td>0.771</td>
<td>4.177</td>
<td>1.000</td>
<td>0.086</td>
</tr>
<tr>
<td>681</td>
<td>0.896</td>
<td>2.062</td>
<td>1.000</td>
<td>0.107</td>
</tr>
<tr>
<td>493</td>
<td>0.895</td>
<td>2.650</td>
<td>1.000</td>
<td>0.113</td>
</tr>
</tbody>
</table>

$N = 42$ for both models. Units are log10[m$^{-1}$]. $\sigma_{\text{med}}$ is dimensionless.

3.5. Effect of CDOM absorption on EOF model

During our analyses, we observed that absorption due to CDOM, $\alpha_{ph}$, was often very high (Fig. 2, Table 2), and we considered the possibility that the AOP-EOF models were simply detecting changes in spectral shape due to strong CDOM absorption correlated with $\alpha_{ph}$—i.e. that there may be a confounding influence of $\alpha_{ph}$ on $\alpha_{ph}$. We performed two independent tests to ensure that our retrievals of $\alpha_{ph}$ were not confounded by absorption due to CDOM. In the first test, we checked for correlation between $\alpha_{ph}$ and $\alpha_{ph}$ by performing a regression of $\alpha_{ph}(490)$ versus $\alpha_{ph}(490)$ and observed a weak relationship ($R^2 = 0.250$ (Fig. 10(a))) and a strong linear relationship was observed ($R^2 = 0.791$, $N = 42$) indicating that phytoplankton biomass was strongly correlated with the region of maximum variability in normalised AOP spectral shapes. Conversely, a regression of the anomaly against $\log_{10}[\alpha_{ph}(493)]$ (Fig. 10(b), showed an extremely weak relationship ($R^2 = 0.072$, $N = 42$), thus confirming that phytoplankton absorption, and not CDOM concentration, was the factor responsible for spectral variability in normalised AOP spectral shapes. Further evidence for this assertion was provided by considering the shape of the first EOF between 400 and 500 nm (Fig. 6, top panel). CDOM absorption has a characteristic shape described by an exponential decay from short to long wavelengths. If CDOM were responsible for the first mode of oscillation, the loadings of the first EOF would continue to decrease monotonically with decreasing wavelength instead of increasing, as observed in Fig. 6, in a manner that is suggestive of phytoplankton absorption.

3.6. Estimation of AOP-EOF model error using delete-d jackknifing

The AOP-EOF models are essentially calibrations of an ocean colour time series with coincident in situ measurements of optically active water constituents. The acquisition and analysis of high quality in situ validation data is notoriously expensive, both in terms of financial cost and the highly skilled labour required. Therefore, we performed a statistical resampling exercise in order to determine the number of observations required to achieve adequate calibration of the AOP-EOF models for the 13-month time series from Bedford Basin. This exercise took the form of a delete-d, or variable jackknife, procedure (Wu, 1986), in which we systematically recomputed various statistics leaving out d observations at a time. To accomplish this, we constructed a subset of test data by randomly choosing d observations from the full data set ($N = 42$) of Chl $a$ and $\alpha_{ph}$ measurements at 443, 490, 560 and 681 nm using the MATLAB™ function $\text{randsample}$, and varied d from 10 to 35. A second subset of observations to be used for training, and with dimension $(N-d)$, was then created using those not selected by the random sampling process. It should be noted that $\text{randsample}$ selects each data point with equal probability, and it is therefore expected that the test data typically included points spread uniformly in time. This makes it unlikely that the training data set consisted entirely of points from one season. To repeat this process for all possible combinations of d would have resulted in an extremely computationally expensive exercise (e.g. for $d = 10$, $N = 42$, all possible combinations of d gives $1.47 \times 10^{15}$). Therefore, it was decided to limit our computations and randomly select test and training data sets only 1000 times.
For each value of \(d\) (i.e. number of test data points), we performed the following steps 1000 times: EOF scores were computed for the full set \((N = 42)\) of AOP spectra, then multiple linear regressions were performed as described in Section 3.4, in which the EOF scores corresponding to the training data were the independent variables and the dependent variables were the corresponding training data for \(\log_{10}[\text{Chl } a]\) or \(\log_{10}[\text{aph}(\lambda)]\) (Eqs. 3 and 4). To produce jackknife estimates of statistics for this exercise, the 1000 trials procedure described above was repeated 100 times. Mean values of \(R^2\), \(bias\), \(F_{med}\) and \(RMSE\) for each \((N - d)\) (i.e. number of training points) value were then calculated from the resulting jackknife data (Table 6). Percentiles were also calculated for \(R^2\) and \(RMSE\) to produce an upper and lower bound between which 95% of the 100 estimates fell. The regions shaded in grey in Fig. 11 represent the resulting envelope, and the width of each envelope provides an indication of the variability of the jackknife estimates. Note that the width of each envelope is partially a function of the number of trials, with more trials producing narrower envelopes. It is apparent that 1000 trials were more than sufficient to provide precise estimates of the parameters shown in Fig. 11.

In Fig. 11, jackknife \(R^2\) and jackknife \(RMSE\) are shown scaled to \(R^2\) and \(RMSE\) values from the models that used all data points \((N = 42)\) to allow a comparison. For estimates of \(\text{Chl } a\) \(a_{\text{rs}}\) (Fig. 11(a)), it was observed that \(R^2\) increased rapidly from ~0.42 at 7 training points to ~0.75 at 15 training points. For training points greater than 15, the rate of increase of \(R^2\) decreased substantially, but still showed a small upward trend as the number of training points increased. Similarly, \(RMSE\) for \(\text{Chl } a\) \(a_{\text{rs}}\) (Fig. 11(b)) decreased rapidly from 0.43 for 7 training points to ~0.23 at 15 training points. These findings have important implications for researchers and managers planning and implementing field campaigns, and demonstrate that the additional cost of obtaining >15 validation data points may yield only small improvements in \(\text{Chl } a\) model performance.

A similar pattern of behaviour for \(R^2\) and \(RMSE\) was observed for model estimates of \(\text{aph}(490)\) (Fig. 11(c) and (d)). \(R^2\) was observed to increase rapidly from ~0.38 at 7 training points to ~0.75 at 15 training points. For training points greater than 15, the value stabilised, and increased by only a small amount with increasing number of training points.

Table 6:

<table>
<thead>
<tr>
<th>No. of training points</th>
<th>(\lambda) (nm)</th>
<th>(7)</th>
<th>(15)</th>
<th>(32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R^2) Chl (a_{\text{rs}})</td>
<td>(443)</td>
<td>(0.418)</td>
<td>(0.715)</td>
<td>(0.765)</td>
</tr>
<tr>
<td></td>
<td>(490)</td>
<td>(0.523)</td>
<td>(0.812)</td>
<td>(0.850)</td>
</tr>
<tr>
<td></td>
<td>(560)</td>
<td>(0.364)</td>
<td>(0.696)</td>
<td>(0.753)</td>
</tr>
<tr>
<td></td>
<td>(681)</td>
<td>(0.292)</td>
<td>(0.639)</td>
<td>(0.704)</td>
</tr>
<tr>
<td>Bias ((\times 10^{-3})) Chl (a_{\text{rs}})</td>
<td>(443)</td>
<td>(−1.857)</td>
<td>(3.386)</td>
<td>(2.924)</td>
</tr>
<tr>
<td></td>
<td>(490)</td>
<td>(−3.609)</td>
<td>(−0.355)</td>
<td>(0.487)</td>
</tr>
<tr>
<td></td>
<td>(560)</td>
<td>(−4.240)</td>
<td>(0.546)</td>
<td>(0.650)</td>
</tr>
<tr>
<td></td>
<td>(681)</td>
<td>(−8.374)</td>
<td>(−1.045)</td>
<td>(0.060)</td>
</tr>
<tr>
<td>(F_{med}) Chl (a_{\text{rs}})</td>
<td>(443)</td>
<td>(0.996)</td>
<td>(1.008)</td>
<td>(1.007)</td>
</tr>
<tr>
<td></td>
<td>(490)</td>
<td>(0.992)</td>
<td>(1.000)</td>
<td>(1.001)</td>
</tr>
<tr>
<td></td>
<td>(560)</td>
<td>(0.990)</td>
<td>(1.001)</td>
<td>(1.001)</td>
</tr>
<tr>
<td></td>
<td>(681)</td>
<td>(1.003)</td>
<td>(1.007)</td>
<td>(1.006)</td>
</tr>
<tr>
<td>(RMSE) Chl (a_{\text{rs}})</td>
<td>(443)</td>
<td>(0.428)</td>
<td>(0.234)</td>
<td>(0.209)</td>
</tr>
<tr>
<td></td>
<td>(490)</td>
<td>(0.239)</td>
<td>(0.123)</td>
<td>(0.108)</td>
</tr>
<tr>
<td></td>
<td>(560)</td>
<td>(0.319)</td>
<td>(0.163)</td>
<td>(0.143)</td>
</tr>
<tr>
<td></td>
<td>(681)</td>
<td>(0.315)</td>
<td>(0.158)</td>
<td>(0.140)</td>
</tr>
</tbody>
</table>

Units are \(\log_{10}[\text{mg m}^{-3}]\) for \(\text{Chl } a\) and \(\log_{10}[\text{m}^{-1}]\) for \(\text{aph}(\lambda)\). \(F_{med}\) is dimensionless.
RMSE values decreased rapidly between 7 and 15 training points from −0.33 to −0.15 (Fig. 11(d)), and beyond 15 training points, only a small decrease in RMSE with increasing number of training points was observed. In a manner similar to the Chl a models, the jackknifing exercise suggested that the $a_{ph}$ models stabilised at −15 training points, and that model skill increased modestly with increasing number of training points beyond this. A summary of the results from the delete-d jackknifing exercise for the Chl a $a_{ph}$ and $a_{ph}^{\text{SMERIS}}$ models at additional wavelengths is summarised in Table 6, and showed that $R^2$ and RMSE exhibited patterns similar to those in Fig. 11, and that maximum $R^2$ and minimum RMSE were obtained at 443 nm for the wavelengths tested. These findings indicate that, for our study site, −15 training points are sufficient to build stable predictive models for both Chl a and $a_{ph}$, making our approach very suitable for applications in which validation data are logistically or financially expensive to obtain. The results also demonstrated that the models would continue to gradually improve their skill by small amounts as the number of training points increased. This feature of the models to evolve as the number of training points beyond this. A summary of the results from the delete-d jackknifing exercise for the Chl a $a_{ph}$ and $a_{ph}^{\text{SMERIS}}$ models at additional wavelengths is summarised in Table 6, and showed that $R^2$ and RMSE exhibited patterns similar to those in Fig. 11, and that maximum $R^2$ and minimum RMSE were obtained at 443 nm for the wavelengths tested. These findings indicate that, for our study site, −15 training points are sufficient to build stable predictive models for both Chl a and $a_{ph}$, making our approach very suitable for applications in which validation data are logistically or financially expensive to obtain. The results also demonstrated that the models would continue to gradually improve their skill by small amounts as the number of training points increased. This feature of the models to evolve as the number of training points beyond this.

Our data were acquired over a period of approximately one year and can be considered representative of the annual excursions in optical and water column properties associated with the spring bloom and significant meteorological events at our study site. However, extreme events not encompassed by our model development data set may cause the models to predict poorly, and adding data from such events might serve to further improve the models’ predictive skill.

### 3.7 Effect of time series period-specific training points

The jackknifing procedure described above provided insights into how many points were required to adequately train the model, but it was also of interest to study the effect of the models of choosing training points from certain periods of the time series. To accomplish this, we objectively split our Chl a data into two clusters using k-means clustering, where one cluster represented ‘high’ Chl a values (−8–18 mg m$^{-3}$), and the other ‘low’ (−0.6–7 mg m$^{-3}$). The sizes of the clusters were unevenly sized with the ‘high’ cluster containing 16 points and the ‘low’ 26. However, on the basis of our jackknifing exercise, 16 is close to the number of points that should provide adequate model training (Fig. 11). These two clusters were then used to train ‘high’ and test ‘low’, and vice versa. For the model trained with ‘high’ Chl a and tested on ‘low’, an $R^2$ value of 0.492 was obtained. In the reverse scenario when the model was trained ‘low’ and tested ‘high’, a very small $R^2$ value of 0.119 was obtained. These results suggested that, at our study site, training points that include the whole dynamic range likely to be encountered must be included for a well-trained model, but that there was a signal present in the ‘high’ data that allowed reasonable estimation of ‘low’ values.

### 3.8 Application of AOP-EOF models to a synthetic satellite data set

The measurements performed at our study site were part of a large, multidisciplinary research programme, a component of which is the investigation into the use of satellite data to study and monitor coastal ecological trends and patterns. Therefore, in a logical extension of the approach presented above, we created a synthetic MERIS data set from the in situ measurements of hyperspectral $R_{ph}$ to explore the feasibility of using multispectral data to estimate Chl a and $a_{ph}$ from the AOP-EOF models. The synthetic $R_{ph}$ MERIS data, $R_{ph}^{\text{SMERIS}}$ (sr$^{-1}$), were created from hyperspectral HyperPro data by selecting $R_{ph}$ at the waveband centres used on the MERIS sensor between 400 and 700 nm (412, 443, 490, 510, 560, 620, 665, 681 nm). A Gaussian curve was defined with a full width half maximum (FWHM) of 10 nm, chosen to emulate MERIS bandwidths, and this was used to weight $R_{ph}$ values on either side of the band centre. These weighted $R_{ph}$ values were then averaged to give $R_{ph}^{\text{SMERIS}}$.

EOF analysis was performed on integral-normalised $R_{rs}^{\text{SMERIS}}(\lambda)$ spectra, $R_{rs}^{\text{SMERIS}}(\lambda)$ (dimensionless), with dimensions ($N \times m_{\text{SMERIS}}$) where $N$ was the number of synthetic observations (=42) and $m_{\text{SMERIS}}$ the number of wavebands (=8). Multiple linear regressions were performed as described in Section 3.4, in which the EOF scores were the independent variables and the dependent variable either log10[Chl a] or log10[$a_{ph}^{\text{SMERIS}}(\lambda)$]. Model estimates of Chl a and $a_{ph}^{\text{SMERIS}}(\lambda)$ from $R_{rs}^{\text{SMERIS}}(\lambda)$, Chl a $a_{ph}^{\text{SMERIS}}$ (mg m$^{-3}$) and $a_{ph}^{\text{SMERIS}}(\lambda)$ (m$^{-1}$) respectively, were then obtained by using the $\beta$ coefficients from these regressions and the first four EOF scores from the $R_{rs}^{\text{SMERIS}}(\lambda)$ data in Eqs. (3) and (4). For Chl a $a_{ph}^{\text{SMERIS}}$ (Fig. 12(a)), reduction of wavelength resolution from 101 to 8 wavelengths produced $R^2$ and RMSE values of 0.831 ($N=42$) and 0.176 respectively compared with the almost identical values of 0.839 and 0.172 found for the hyperspectral model (Fig. 7, Table 4). Like the hyperspectral model, bias was found to be essentially zero, with a very similar value of $−2.260 \times 10^{−18}$ compared with $−2.908 \times 10^{−16}$ (Table 4).

Estimates of $a_{ph}^{\text{SMERIS}}(\lambda)$ (Fig. 12(b)) were also found to very similar to the values obtained from the hyperspectral model in terms of $R^2$, RMSE and bias (Table 5) with values typically smaller than their hyperspectral counterparts by less than 1%. This showed that reduction in wavelength information from hyperspectral resolution (101 wavebands) to eight wavelengths made a very small

![Fig. 12](image-url)
wavebands) to the multiband resolution of a satellite sensor (8 wavebands) had little impact on the model's ability to estimate $q_a(\lambda)$, and is in keeping with the results of several other studies that have suggested that the number of spectral bands required to derive important water column properties ranges between 4 and 5 (Mueller, 1976; Sathyendranath et al., 1994) to 15 (Lee et al., 2007).

In the context of the shape of the first EOF mode (Fig. 6), this result is, perhaps, unsurprising, as the variance was grouped into a set of correlated wavelengths shorter than 550 nm that moved together with a negative sign, and a group of correlated wavelengths longer than 550 nm that moved together with a positive sign. We speculate that, as long as wavelengths from each of these two groupings are represented in a reduced-wavelength data set, accurate estimation of $q_a(\lambda)$ is still possible. This is a significant finding, and suggests that reduced-wavelength resolution from multisensor platforms, such as those found on satellite platforms, may not negatively impact the performance of the AOP-EOF models described here.

4. Conclusions

An approach to develop accurate local models of Chl $a$ and $q_{ph}(\lambda)$ in an optically complex estuarine water body has been presented. The models are based on EOF analysis of the spectral shape of $R_s(\lambda)$ rather than magnitude—an important feature that was key to their success. Statistical analyses suggested that the models can be derived when ~15 data points of coincident AOP and in situ measurements of Chl $a$ and/or $q_a(\lambda)$ over a seasonal cycle are available. However, this must be validated for other locations. When applied to a reduced-wavelength resolution synthetic data set intended to mimic eight MERIS wavebands, the models exhibited negligible loss of skill and were able to predict Chl $a$ and $q_a(\lambda)$ with an accuracy almost identical to that of the hyperspectral models. This finding was particularly encouraging and suggested that, as long as adequate atmospheric correction can be achieved in coastal waters, multiband $R_s(\lambda)$ measured from satellite platforms may provide estimates of Chl $a$ and $q_{ph}(\lambda)$ from AOP-EOF models. Future work will address the applicability and universality of our approach to in situ AOP measurements made in different coastal and optically complex water bodies and ultimately, to satellite measurements.

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