

Article

Bio-Optical Response of Phytoplankton and Coloured Detrital Matter (CDM) to Coastal Upwelling in the Northwest South China Sea

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Abstract: To examine the bio-optical response to coastal upwelling, we measured inherent optical properties (IOPs) and biogeochemical parameters simultaneously off Hainan Island in the northwest part of the South China Sea (SCS) during late summer 2013. Bio-optical relationships between IOPs and phytoplankton were used for calculating vertical profiles of the total chlorophyll a concentration (Chl-a) and the absorption by coloured detrital matter (CDM). These bio-optical properties, which showed distinct horizontal and vertical distributions across the continental shelf, were strongly influenced by upwelling processes, as well as the shelf topography. Phytoplankton biomass and CDM absorption in surface waters showed much higher values along the coast, with their spatial distributions related to topographic variability. Vertical distributions of phytoplankton were characterised by a subsurface chlorophyll maximum (SCM) layer. The strongest SCM (Chl-a = 4.22 mg m⁻³) was observed at 24 m depth in coastal waters near the northeast cape of Hainan Island. The depth of the SCM varied between 16 and 60 m at different stations, appearing to coincide with the isotherm of 22 °C. The SCM depth was inversely correlated with the magnitude of the SCM. Different shapes of Chl-a profiles were observed, which suggested that the vertical distributions of phytoplankton biomass were driven by different environmental factors. Elevated concentrations of CDM were mainly observed near the bottom, which suggest that the benthic nepheloid layer may be an important source of detrital material. The relationship between the absorption coefficient of CDM at 443 nm, $a_{\text{CDM}}(443)$, and Chl-a exhibited distinct differences between waters in upper ocean and in bottom layers, with the threshold depth being modulated by shelf topography. Our results highlight the utility of bio-optical observations with high resolution for better understanding the coupling between physical forcing and biogeochemical variability.

Keywords: upwelling; bio-optical properties; phytoplankton; coloured detrital matter

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1. Introduction

Coastal regions in general, and coastal upwelling systems in particular, are highly dynamic, with strong variations in biological properties at various temporal and spatial scales. The vertical structure of phytoplankton biomass, detrital material, as well as phytoplankton community structure in upwelling areas could be regulated by other physical processes, such as currents and vertical mixing, and their interplay with the local topography [1,2]

Studying coastal upwelling systems at all relevant scales requires appropriate measurement techniques. Recent advances in optical oceanography have led to rapid, continuous in situ techniques to study biogeochemical properties of the ocean at high spatial and vertical resolutions [3–7].

Bio-optical properties, including chlorophyll fluorescence, particulate and phytoplankton absorption, beam attenuation coefficient, and particle scattering coefficients, yield information on various living and non-living materials in the ocean [3,4,8–10]. Changes in optical properties can indicate variations in biogeochemistry at various time scales caused by physical processes [11–13]. Optical measurements have been used to study spatial and vertical variability in upwelling systems [1,2,14,15]. Bio-optical properties can be exploited to investigate differences in algal physiology between upwelling and non-upwelling conditions [13,15,16], as well as between intense upwelling and relaxation periods [2].

The upwelling system off the coast of Hainan Island in the northwestern South China Sea (SCS) is well known for its significant impact on nearshore environment [17–21]. The upwelling occurs mainly during the period from April to September every year and becomes strongest in June and July. The upwelling centre is generally located to the east and northeast of Hainan Island. Recent studies have focused mainly on the general characteristics of this upwelling and on its dominant dynamic features [17,19,22,23]. Based on high-resolution satellite data and intensive field surveys, the spatiotemporal variability and potential mechanisms associated with the upwelling and upwelling-induced fronts have been examined [17]. Complex interactions between the topography and the coastal upwelling were found to modulate the vertical distribution of water constituents, resulting in large variability in phytoplankton distributions and in biogeochemical cycles [18,23–26]. Coastal upwelling also plays a key role in regulating the phytoplankton community structure [27–29], as well as the species richness and abundance of zooplankton in this region [30]. With advances in ocean colour remote sensing, research on the environmental consequences of the coastal upwelling off Hainan Island has attracted widespread attention [17,22,26]. However, vertical distribution of phytoplankton and coloured detrital matter has not been well studied due to in situ under sampling and due to the intrinsic limits of ocean colour remote sensing, which is constrained to studies of surface properties.

In this study, we investigate bio-optical properties of the upwelling system off Hainan Island in northwestern SCS using in situ optical measurements with high vertical resolution. A simple empirical model was developed for discriminating the absorption contribution by coloured detrital matter from that of phytoplankton. Variability of bio-optical properties on both horizontal and vertical dimensions during the upwelling event were examined, and the roles of phytoplankton and coloured detrital material in modifying the optical properties were investigated. This study could contribute to the understanding of the depth-resolved ecological impact of coastal upwelling.

2. Materials and Methods

2.1. Field Measurements

Field observations were conducted in the east and northeast of Hainan Island from 30 August to 2 September during a cruise in 2013 in the northwestern SCS, supported by the National Science Foundation Council. Hydrographic measurements for temperature, conductivity, and depth were conducted at 86 stations with a SeaBird Electronics SBE-911 CTD (Bellevue, Washington, DC, USA). WET Labs ac-s spectral absorption and attenuation sensors were deployed at 40 stations to acquire the hyperspectral absorption and attenuation data with high vertical resolution of one meter. The locations of the field sites are shown in Figure 1. Seawater samples were collected with Niskin bottles at discrete depths

(0, 10, 25, the bottom layer at coastal stations and 0, 25, 50, 75, 100 m in open ocean) for analysing phytoplankton biomass (Chl-a) and the spectral particulate absorption coefficient.

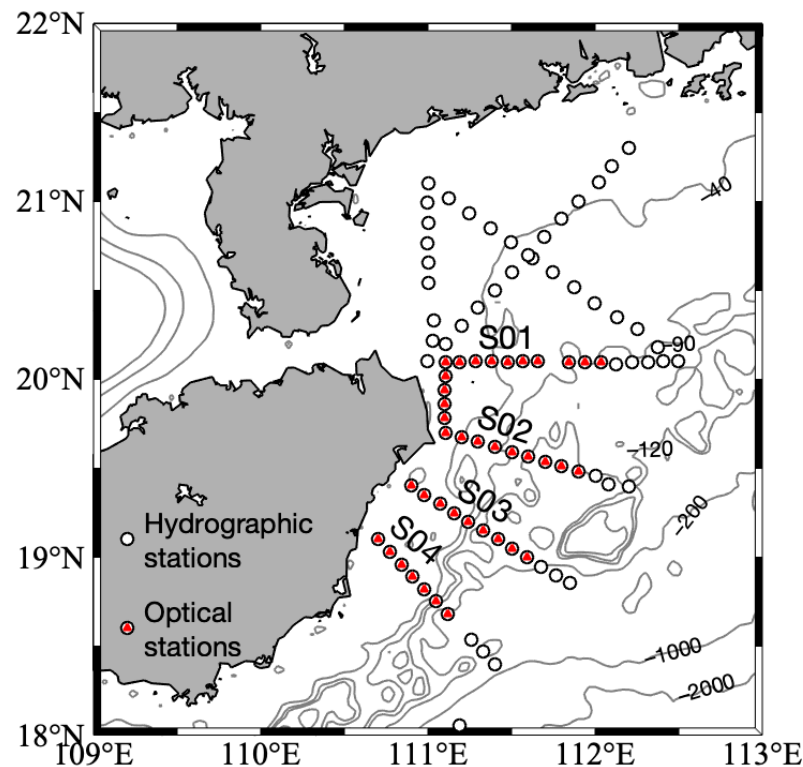


Figure 1. Sampling stations off the east coast of Hainan Island in the northwestern South China Sea from August 30th to September 2nd in summer 2013. Hydrographic measurement stations (blank circle) and optical measurement stations (red triangle) are shown with different symbols. Bathymetric contours are in meters.

2.1.1. Phytoplankton Biomass (Chl-a)

Discrete seawater samples for determination of Chl-a were filtered through a 25 mm diameter GF/F glass-fiber filter, and the filters were flash-frozen and stored initially in liquid nitrogen and then at -80°C in a freezer until analysis in the laboratory. Water samples collected at standard depths over the euphotic zone were filtered for measuring the Chl-a. Filtered volumes (0.5 to 1 L) varied based on the anticipated amount of particulate matter. Following the filtration, Chl-a was extracted with acetone at -20°C for about 24 h in the dark and then analysed with a Turner Designs 10 fluorometer [31].

2.1.2. Spectral Absorption of Particles and Phytoplankton

Spectral absorption of phytoplankton was measured using the quantitative filter technique (QFT) [32,33]. Surface water samples for measuring the particulate absorption were filtered onto Whatman GF/F filters. The filtration volume varied between 1 and 3 L depending on the stations. The optical density spectrum was measured over the 240–800 nm spectral ranges in 5 nm increments with the UV-2550 (SHIMADZU Inc., Kyoto, Japan) dual beam spectrophotometer equipped with an integrating sphere. Transmission method was used. The pigmented material on the sample filter was extracted with methanol to decompose the non-algal particulate absorption contribution from the total one [34]. The final optical density values for the samples were corrected by zeroing the absorption in the near-infrared spectral region [35]. The path length amplification effect caused by the filter was corrected using the constant value (2.0) as proposed by [36].

2.1.3. Spectral Absorption and Attenuation Coefficients of Seawater

In situ optical property measurements were conducted by deploying an optical profiling system equipped with absorption and attenuation meters (acs-s, WETLabs). In total, 40 vertical profiles measurements were performed in stations located in coastal waters (until the bottom) and offshore (up to 100 m). These stations spanned 4 cross-shelf sections off the east coast of Hainan Island (Figure 1). The total absorption and attenuation coefficients, excluding pure water contributions, were measured using a spectral absorption-attenuation meter, specifically the WETLabs ac-s instrument with 82 wavelengths ranging from 401.6 to 744.1 nm and a 25 cm path length. The ac-s instrument was calibrated prior to the field campaigns using optically pure water obtained from a Milli-Q system to determine any instrumental offsets in pure water. To account for temperature and salinity effects on the optical properties of water, corrections were applied following the method described by [37]. Furthermore, to correct for the incomplete recovery of scattered light in the absorption tube of the ac-s, the signal at a longer wavelength (around 716 nm) was subtracted from the values at all other wavelengths, as described by [38]. The data from the CTD and ac-s were merged and binned to 1 m intervals.

2.2. Satellite Remote Sensing Data

Surface cooling in the coastal upwelling region in the northwestern SCS were identified with the sea surface temperature (SST) images with a resolution of 6×6 km. These SST data, obtained from January 2006 to September 2013, were generated by the UK Meteorological Office and combined with in situ measurements, as well as microwave and infrared satellite-derived SST data provided by the Group for High-Resolution Sea Surface Temperature (GHRST) project (<http://data.nodc.noaa.gov/ghrsst/L4/GLOB/UKMO/> (accessed on 10 December 2024)). Daily wind data used in this study were obtained from the National Climatic Data Center of National Oceanic and Atmospheric Administration (NOAA), with a spatial resolution of 0.25° (<https://www.ncei.noaa.gov/products/wind> (accessed on 10 December 2024)). Ekman pumping (W_E) was estimated using the following formula:

$$W_E = \frac{1}{f\rho_w} \left(\frac{\partial \tau_y}{\partial x} - \frac{\partial \tau_x}{\partial y} \right) \quad (1)$$

where

$$f = 2\omega \sin\theta \quad (2)$$

and where τ_x and τ_y are the east and north components of wind stress, respectively; θ is the latitude in degrees; ρ_w is the seawater density (1024 kg m^{-3}); and ω is the angular speed of the earth's rotation ($7.292 \times 10^{-5} \text{ s}^{-1}$).

2.3. Statistical Analysis of Bio-Optical Relationships

2.3.1. Bulk Variability of Inherent Optical Properties

Variations of inherent optical properties were related to the Chl-a, which also showed different patterns for samples collected at different depths (Figure 2 and Table 1). Based on the vertical variability of IOPs, the whole water column was separated into two layers (the upper ocean and the bottom waters). The threshold depth was defined as the depth at which the attenuation coefficient at 443, $c(443)$, tended to increase rapidly to the bottom. Figure 2 shows that for samples collected in the upper portion of the water column, phytoplankton make a large contribution to the variations in $a(443)$, the absorption coefficient at 443 nm, and $c(443)$, the attenuation coefficient at 443 nm, with the r^2 of the power law relationships being 0.81 and 0.68, respectively (Table 1). Samples from the bottom waters exhibit higher absorption and attenuation values for the same Chl-a compared with those from the upper

ocean, which can be attributed to the relatively large contributions of detrital materials, including the non-algal particles and the coloured dissolved organic matter (CDOM). Even though there is higher scatter, $a(443)$ and $c(443)$ in bottom waters also exhibit good correlations with the in situ measured Chl-a, the r^2 being 0.70 and 0.43 respectively, for the fitted power law function. Phytoplankton degradation could be a major source of the detrital matter. For samples collected in bottom layers, particle scattering (b_p) was found to have a large contribution to light attenuation, with the averaged $b_p(443)/c(443)$ being as high as 0.83, which is higher than that in the upper ocean (average of about 0.56).

The absorption line height at 676 nm, $a_{LH}(676)$, was calculated from the absorption differences at long wavelengths as shown by the following equation [39], which reduced the effect of coloured detrital matter.

$$a_{LH}(676) = a(676) - \left[\frac{a(715) - a(650)}{715 - 650} * (676 - 650) + a(650) \right] \quad (3)$$

Observations of $a_{LH}(676)$ from the upper ocean and the bottom waters exhibit similar variability with Chl-a, as shown in Figure 2c and Table 1, with the r^2 for the power law function being 0.55 and 0.77, respectively. The $a_{LH}(676)$ from measured hyperspectral absorption data has been widely used as a measure of chlorophyll concentration [39–41], and non-linear and linear models have been proposed for the relationship between Chl-a and $a_{LH}(676)$, with coefficients varying for different regions and seasons [42]. For our 148 samples collected in situ over discrete depths, a power law function could be used for describing the relationships between $a_{LH}(676)$ and Chl-a, with the r^2 being 0.54 and the log-transformed root mean square error (RMSE_log) being 0.18.

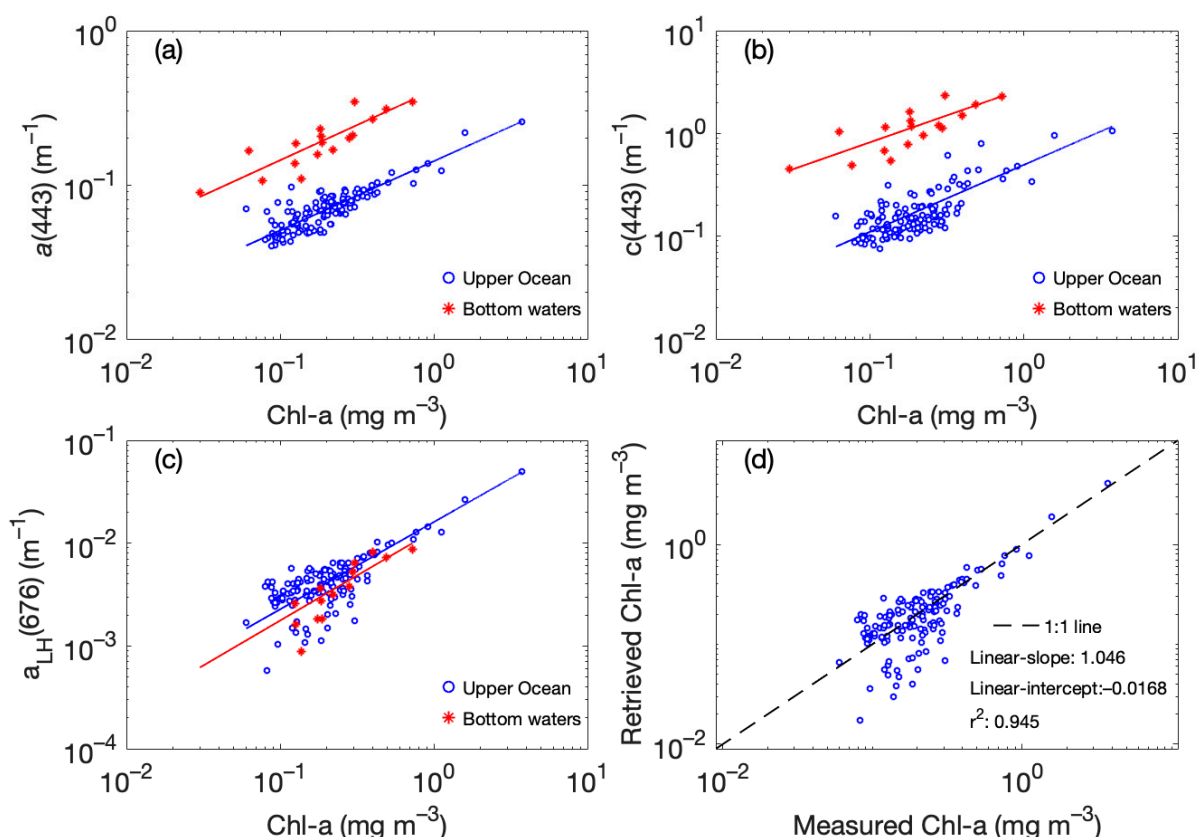


Figure 2. Regression relationships of inherent optical properties of non-water absorption at 443 nm, $a(443)$ (a) non-water attenuation coefficient at 443 nm, $c(443)$ (b) absorption line height at 676 nm, $a_{LH}(676)$ (c) with in situ measured Chl-a. (d) Comparison of Chl-a estimated from $a_{LH}(676)$ using the model of reference [40] with in situ Chl-a data.

Table 1. Statistics of power law regression between inherent optical parameters (m^{-1}) and Chl-a (mg m^{-3}). $y = A * x^B$.

		A	B	r^2	N
Upper ocean	a(443)	0.1357	0.4236	0.73	134
	c(443)	0.4373	0.6167	0.59	134
	$b_p(443)$	0.2834	0.7202	0.456	134
	$a_{LH}(676)$	0.0126	0.6955	0.55	134
Bottom waters	a(443)	0.3933	0.4369	0.74	17
	c(443)	2.5833	0.5125	0.63	17
	$b_p(443)$	2.1928	0.5291	0.615	17
	$a_{LH}(676)$	0.0159	1.1034	0.82	14

2.3.2. Estimation of Vertical Chlorophyll a Profiles

The power law model proposed by [40] based on a large dataset collected during the Tara Ocean Expedition gave results comparable with our local function (Figure 2d), with the RMSE on log-transformed Chl-a being 0.22 mg m^{-3} , slightly higher than that obtained for the local model. In this study, the model proposed by [40] was used for calculating the Chl-a profiles from hyperspectral absorption data measured by ac-s as shown by Equation (4).

$$[\text{Chl-a}] = 157a_{LH}(676)^{1.22} (\text{mg m}^{-3}) \quad (4)$$

Due to the measurement limits of ac-s, there remains considerable scatter, especially for bottom water samples with low signals ($a_{LH}(676) < 0.001 \text{ m}^{-1}$). To extract reliable Chl-a profiles, we processed the data as follows: (1) $a_{LH}(676)$ data lower than 0.001 were discarded; and (2) Chl-a profiles were interpolated and smoothed within valid depths.

The Chl-a profiles over our studied area could be classified into five main types on the basis of visual analysis, and these types could be referred to as SCM, modified SCM, two-peaks SCM, homogeneous, and complex [5,43–45]. The SCM shape was tested first. If the mixed layer depth (MLD) is above the depth of a single SCM layer (Z_{SCM}) and if the magnitude of SCM ($\text{Chl}_{\max}$) is twice as large as the surface Chl-a, the profile is classed in the standard SCM category. If not, and there is still an obvious maximum layer of Chl-a, it is classed as modified SCM. Two-peaks SCM refers to those that showed another small peak as well as the major SCM [46]. The homogeneous shape has been commonly used to describe Chl-a vertical profiles with less variability in the top layer and then decreasing with depth. Other Chl-a profiles are classed in the complex category, which may exhibit many peaks.

2.3.3. Decomposition of Total Non-Water Absorption into Contributions of Phytoplankton and CDM

In situ hyperspectral non-water absorption coefficients by ac-s include contributions by phytoplankton and coloured detrital matter (CDM): CDM is defined as the sum of CDOM and non-algal particles, with both of them showing similar spectral features.

$$a(\lambda) = a_{ph}(\lambda) + a_{CDM}(\lambda) \quad (5)$$

Empirical or non-linear optimisation models have been used for decomposing the absorption contributions into that by phytoplankton, non-algal particles, and CDOM [47–50]. Here, we have followed a different approach. It is known that there is a good relationship between Chl-a and phytoplankton absorption at 443 nm ($a_{ph}(443)$). Based on a dataset ($N = 315$) collected in the northern SCS during summer cruises [48], a power function could

be used for describing the non-linear relationships between $a_{ph}(443)$ and Chl-a, with the r^2 being 0.91.

$$a_{ph}(443) = 0.0602[\text{Chl-a}]^{0.605} \quad (6)$$

These data were collected at different depths within the euphotic zone, and the power law relationship showed no dependence on water depth, as shown in Figure S1. This power function (Equation (6)) was also validated with in situ data collected in surface waters ($N = 33$), with Chl-a calculated using the model of [3]. The estimated $a_{ph}(443)$ shows a good linear relationship with that measured in situ, the linear regression slope being around 0.89, and the normalised RMSE being only 26%. The absorption by CDM at 443 nm ($a_{CDM}(443)$) could then be obtained by subtraction of $a_{ph}(443)$ from the total non-water absorption (Equation (3)), which was then used for studying the variability of coloured detrital material, relative to that of phytoplankton. For the vertical structures of $a_{CDM}(443)$, a threshold depth (Z_{CDM}) was used for separating the water column into two parts (upper ocean and bottom layers). Z_{CDM} was defined as the depth at which the $a_{CDM}(443)$ tends to increase rapidly to the water bottom, while the Chl-a tends to decrease or shows less variability.

3. Results

3.1. Hydrological Properties of the Upwelling Event

Based on in situ observation, the spatial distribution of water temperature at about 5 m is shown in Figure 3a, in which the upwelling centre is observed in the northeast sea area of Hainan Island, with the temperature difference being around 2 °C. A band of cold water is observed along the coast off Hainan Island, extending from the western to northeastern regions (Figure 3a). The upwelling region is primarily located off the east coast and northeast cape of Hainan Island (NE cape), exhibiting SST that are generally 1–2 °C lower than the adjacent open ocean waters of the outer shelf. This phenomenon was also found in the satellite image of SST corresponding to the time of the field observations (Figure 3b). The strongest upwelling signals occurred in the subsurface waters, about 30–50 m deep waters, with the temperature difference being up to 7 °C and the salinity difference being up to 0.7 psu (as shown by Figure 5 of reference [51]).

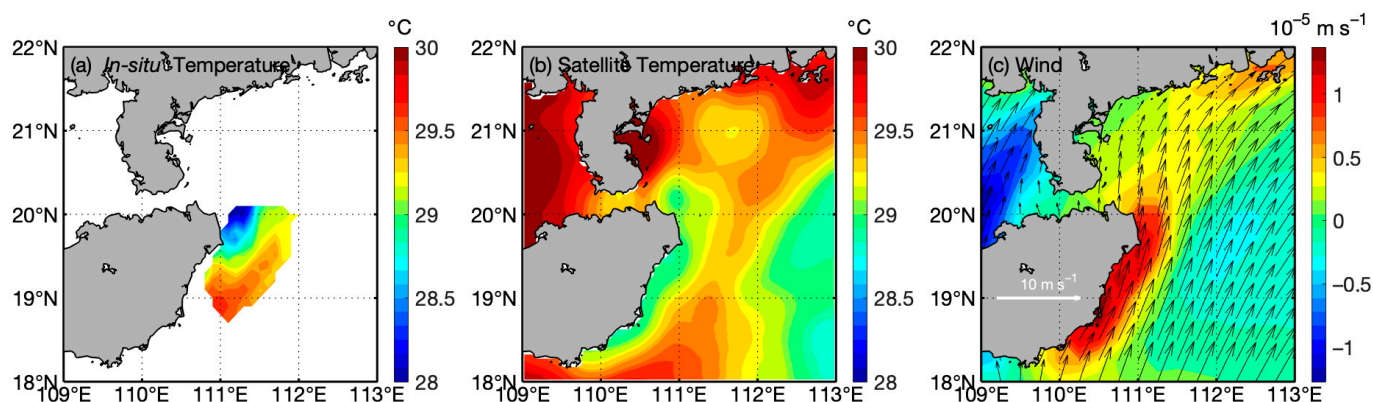


Figure 3. (a) Spatial distributions of in situ measured temperature (contours in °C) at 5 m; (b) remote sensing sea surface temperature (SST, °C); (c) wind vectors (vectors in m s^{-1}) and Ekman pumping velocity (W_E , m s^{-1}) during our observation from 30 August to 2 September.

Figure 3c shows the distribution of averaged wind vector (black vectors in m s^{-1}) and Ekman pumping (W_E , in m s^{-1}) between 30 August and 2 September in the area of eastern Hainan Island. During the cruise, the prevailing winds along the eastern coast were southwesterly monsoon winds, and the wind-driven Ekman pumping was found to

account for the coastal upwelling. Meanwhile, as the reference [51] showed, the upwelling structure in the upper ocean might have been destroyed by tropical cyclones passing immediately before the observations. The upwelling event experienced a subduction period (30–31 August) and rebuilding period (1–3 September). To show the variability of upwelling water, the vertical distributions of temperature and salinity for the four cross-shelf sections are presented in Figure 4. Throughout the observation period, there is a persistent presence of pronounced upward-tilted isotherms that intersect the shelf isobaths, notably on the northeastern shelf of Hainan Island (as seen at coastal stations on the S01 and S02 sections). A sharp dipping of the isotherms and wave-like features were observed over the S01 and S02 (Figure 4a–d), which could likely result from the interactions between the intense tidal flow and the bottom topography [17]. In contrast, the wave-like features are not prominently observed in the eastern sections (S03 and S04), as shown in Figure 4e–h, similar to the results observed by [17] during a summer cruise.

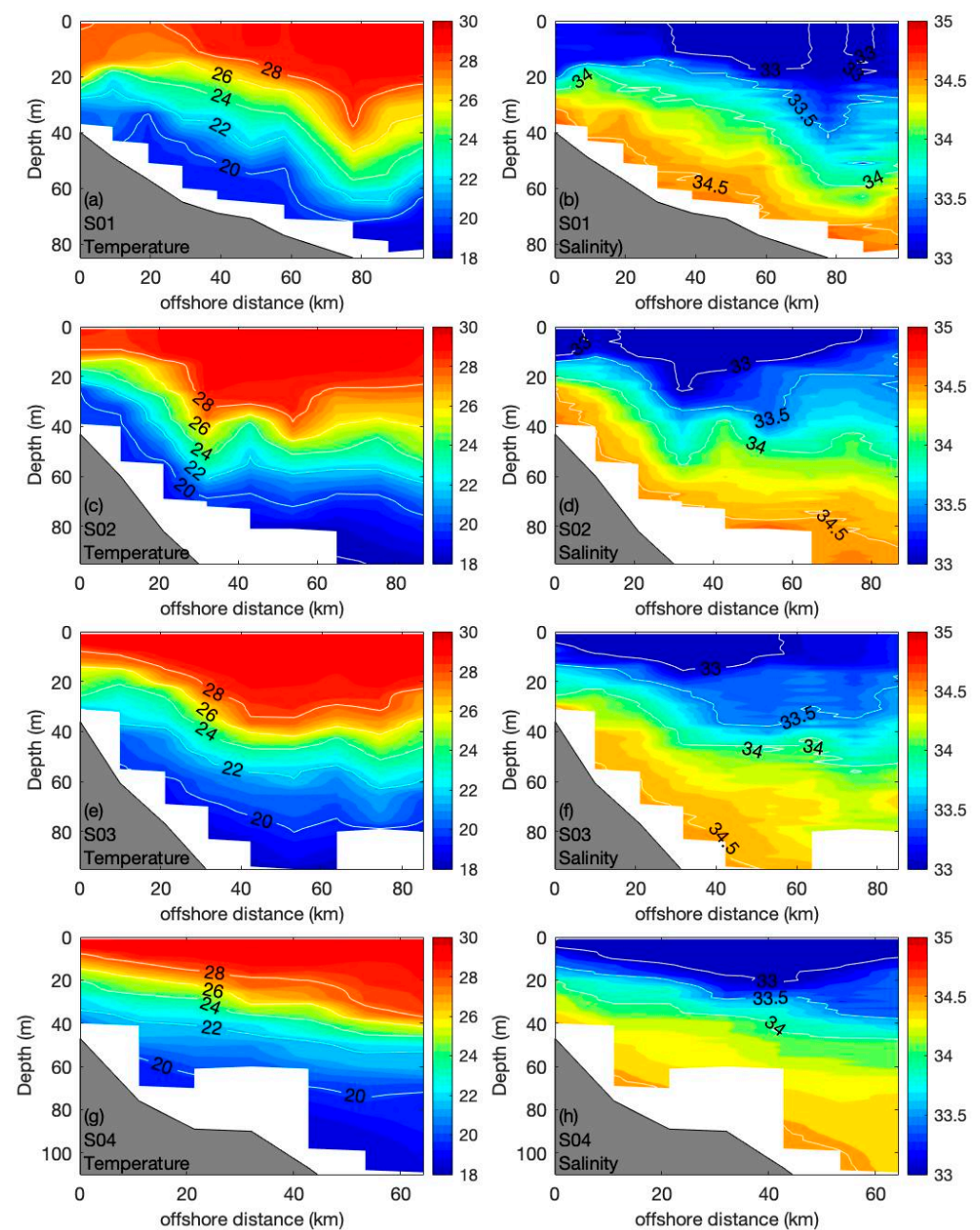


Figure 4. Cross-shelf vertical distributions of the observed temperature (°C) and salinity (psu) in the S01–S04 sections, respectively.

3.2. Bio-Optical Variability in Surface Waters

In response to the upwelling event, the total non-water absorption coefficient at 443 nm ($a(443)$) measured with ac-s in surface waters showed high values along the coast off Hainan Island (Figure 5a), and they dropped significantly with offshore distance. Our estimated Chl-a, as well as the absorption coefficient for CDM at 443 nm ($a_{\text{CDM}}(443)$), exhibit similar spatial distributions (Figure 5b,c). A tongue-like segment of high IOPs (Chl-a values from 0.3 to 0.77 mg m^{-3} , and $a(443)$ from 0.08 to 0.12 m^{-1}) off the NE cape was observed, matching the location and shape of low surface temperature (Figures 3 and 5).

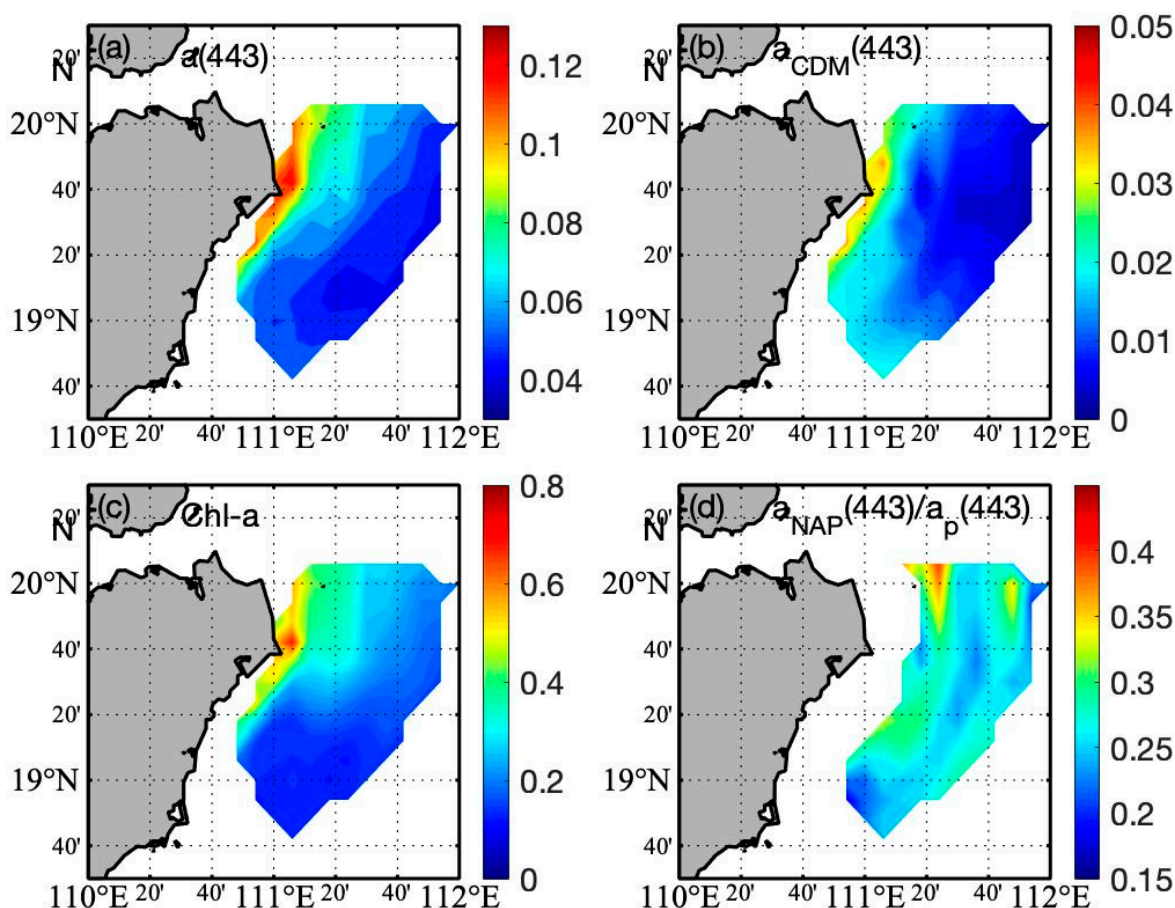


Figure 5. Spatial distributions of bio-optical parameters in the surface waters. (a) $a(443)$ (m^{-1}), (b) $a_{\text{CDM}}(443)$ (m^{-1}), (c) Chl-a (mg m^{-3}), (d) $a_{\text{NAP}}(443)/a_p(443)$.

Surface water samples were collected for measuring the spectral absorption coefficients of suspended particles. Total particulate absorptions, including absorptions by phytoplankton ($a_{\text{ph}}(443)$) and non-algal particles ($a_{\text{NAP}}(443)$), were found to be closely related with Chl-a. In shallow coastal waters, non-algal particles had a relatively higher contribution to total particulate absorption than in offshore waters (Figure 5d). The absorption spectra of non-algal particles ($a_{\text{NAP}}(\lambda)$) could be well represented by an exponential function, the r^2 being around 0.92. The spectral slope of $a_{\text{NAP}}(\lambda)$ ranged from 0.009 to 0.018 nm^{-1} and showed a relatively stable and lower value at coastal stations. The chlorophyll a-specific absorption of phytoplankton exhibited an inverse trend with that of Chl-a, the value at 443 nm ranging from 0.065 to 0.20 $\text{mg}^{-1} \text{m}^2$.

3.3. Vertical Variations in Phytoplankton Biomass

Subsurface phytoplankton blooms off the northeastern and eastern coast of Hainan Island were captured by in situ observations. The strongest subsurface maximum was

observed at the coastal station in the S01 section, the maximum layer depth being around 24 m and the magnitude being up to 4.2 mg m^{-3} . The thickness of this bloom layer was about 10 m. As shown in Figure 6, subsurface chlorophyll maximum (SCM) lays primarily between the isotherms of 22 and 24 °C. At S02, the SCM layer at the coastal station was shallower (about 15 m) than that in S01, with the magnitude of Chl-a at the peak being around 1.6 mg m^{-3} . As this station was quite close to the mainland (Figure 1), the layers with high Chl-a may have been tilted upwards, resulting in a high value of phytoplankton biomass in surface waters. Similar vertical profiles were also observed in coastal areas of S03 and S04, the depth of SCM being around 25 m and 35 m, with magnitudes of 1.8 and 0.70 mg m^{-3} , respectively for the Chl-a peak. With increasing offshore distance, the SCM became deeper (at 40–60 m) and the magnitude of the Chl-a peak lower (average about 0.30 mg m^{-3}). In certain areas, the vertical Chl-a distribution showed complex variability without a distinct maximum layer.

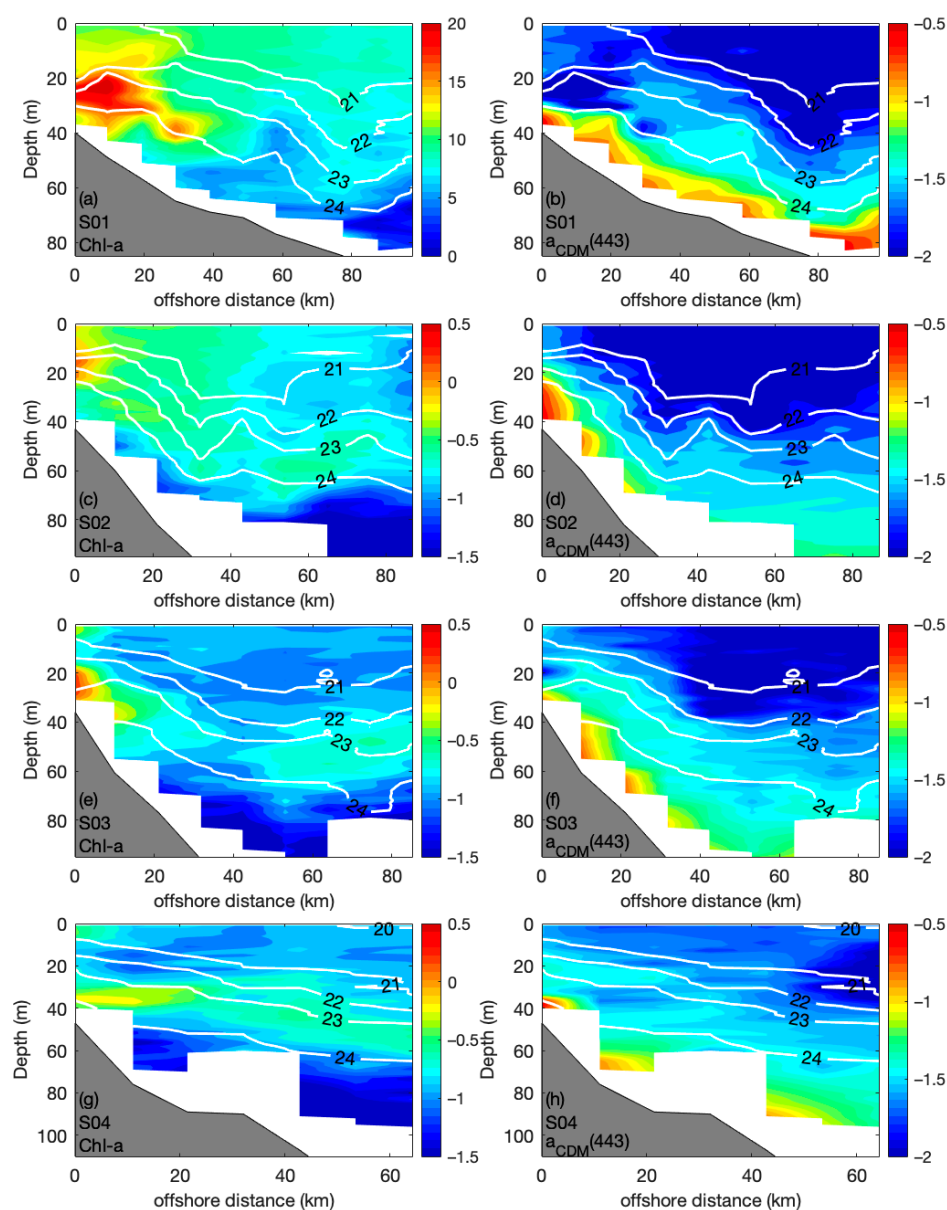


Figure 6. Cross-shelf vertical distributions of the estimated Chl-a (mg m^{-3}) and $a_{\text{CDM}}(443)$ (m^{-1}) in the S01–S04 transects. The white contour lines shown in each frame denote the isopycnal surfaces.

Chl-a profiles showed variable shapes in our study area and could be separated into five main types, as shown in Figures 7 and 8. Each of these types is described below:

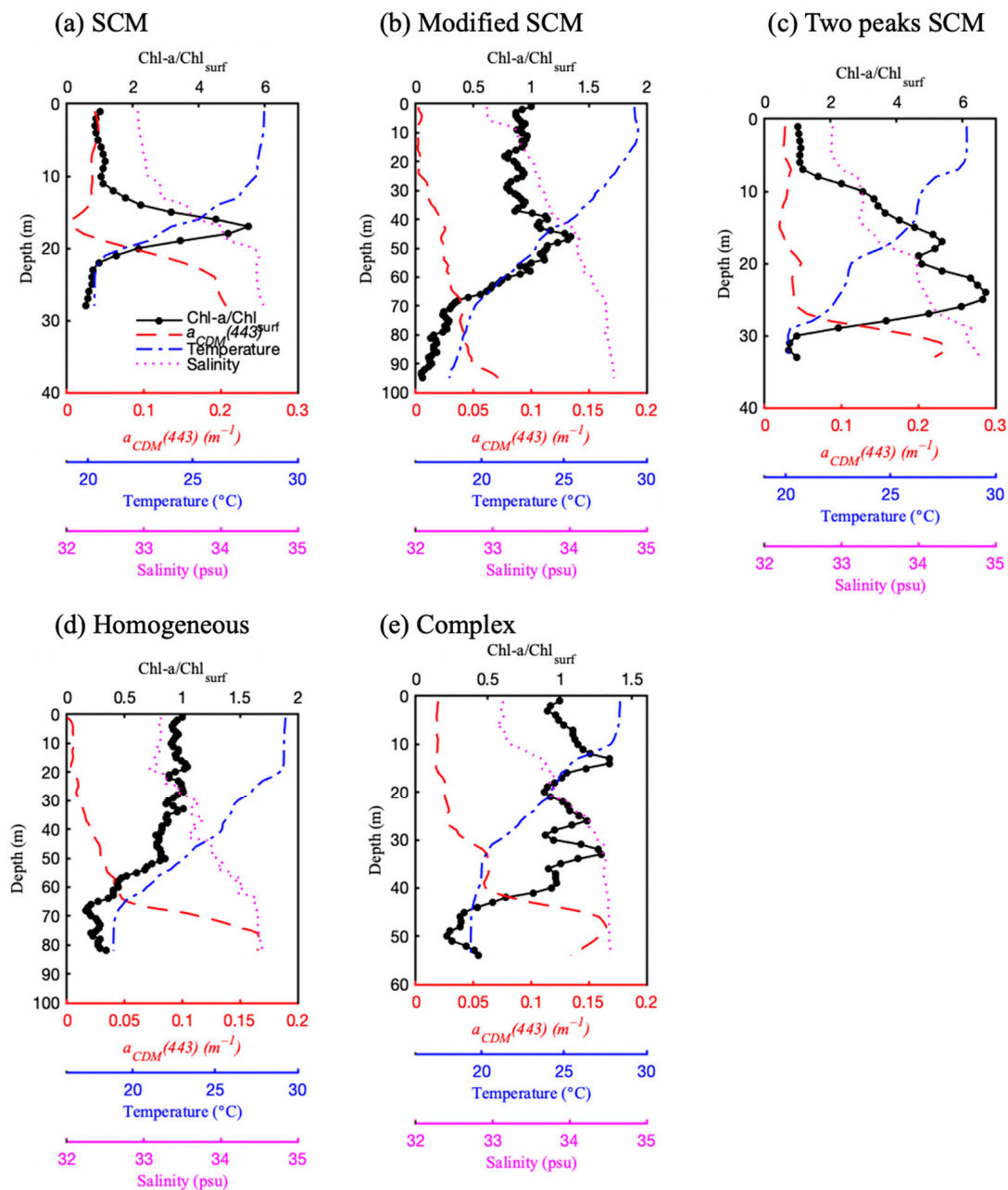


Figure 7. Five typical shapes of the Chl-a profile as compared with the vertical variability of temperature and salinity.

Type 1: The standard SCM shape of this type is characterised by a bell-shaped subsurface maximum in Chl-a (Figure 7a), following the general Gaussian distribution [52]. These profiles were observed at coastal and offshore stations. SCM with high phytoplankton biomass were mainly observed at stations northeast of Hainan Island (Figure 8), with the depth being between 17 and 24 m, and the thickness of the SCM varied from 5 to 16 m. For stratified waters in offshore stations, SCM occurred deeper (at 32 to 57 m), with much lower magnitudes.

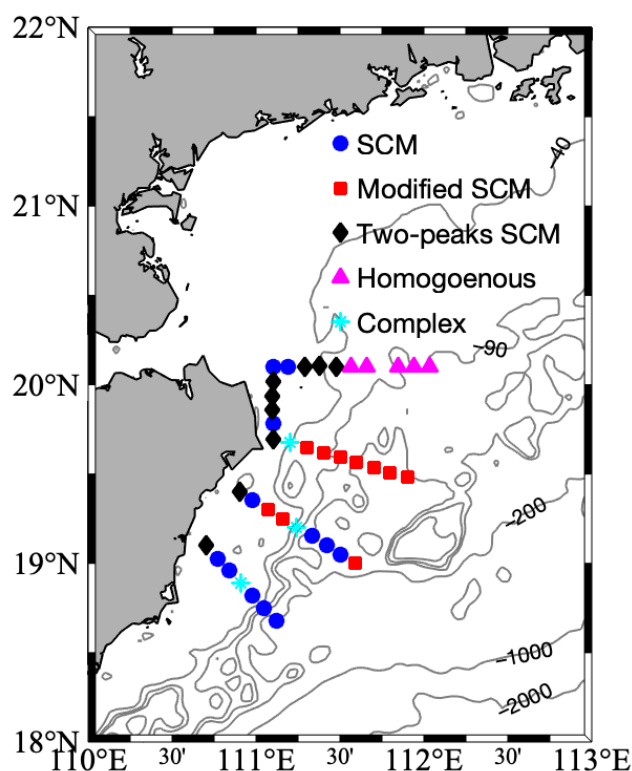


Figure 8. Spatial distribution of five Chl-a profile shapes.

Type 2: Modified SCM type displays chlorophyll-a (Chl-a) profiles characterised by relatively high Chl-a values within the mixed layer, with a Chl-a peak occurring just below it (Figure 7b). This profile shape represented an intermediate condition between the SCM and homogeneous situations. In offshore waters, the modified SCM profiles were consistent with those shown in reference [43] in the Mediterranean Sea, with the depth ranging between 32 and 60 m.

Type 3: Two-peak SCM type showed a secondary peak in addition to the main Chl-a peak (Figure 7c). Typically, the secondary peaks lay above the main peak and occasionally occur at the surface of the water.

Type 4: Homogeneous type represents homogeneous vertical profiles mainly observed in offshore stations of section S01 (about 80 km away from the coast) (Figures 7d and 8). In this type, the Chl-a is quite uniform within an upper layer (with concentrations spanning from 0.20 to 0.27 mg m⁻³) but then decreased with further increase in depth. No obvious peaks were found below the mixed layer in this class.

Type 5: This type represents complex Chl-a profiles observed at some offshore stations off the east of Hainan Island (Figures 7e and 8), which showed several peaks. MLD at these stations varied from 11 to 20 m, and the surface Chl-a varied from 0.11 to 0.33 mg m⁻³.

Considering the main feature of Chl-a profiles, the depth of SCM layer (Z_{SCM}) ranged from 16 to 60 m, which was well correlated with the potential density $\sigma_\theta = 23 \text{ Kg m}^{-3}$ and the depth of 22 °C isotherm, with r^2 for the linear regression being up to 0.84 and 0.89, respectively (Figure 9a). Correlation was also found between Z_{SCM} and the bottom depth in these stations, with the r^2 being about 0.71. The magnitude of SCM (Chl_{max}), as well as the surface Chl-a, showed inverse variations with Z_{SCM} . Linear correlations between the log-transformed Chl-a at SCM depth and at the surface with Z_{SCM} were observed, with the r^2 being 0.73 and 0.48, respectively (Figure 9b).

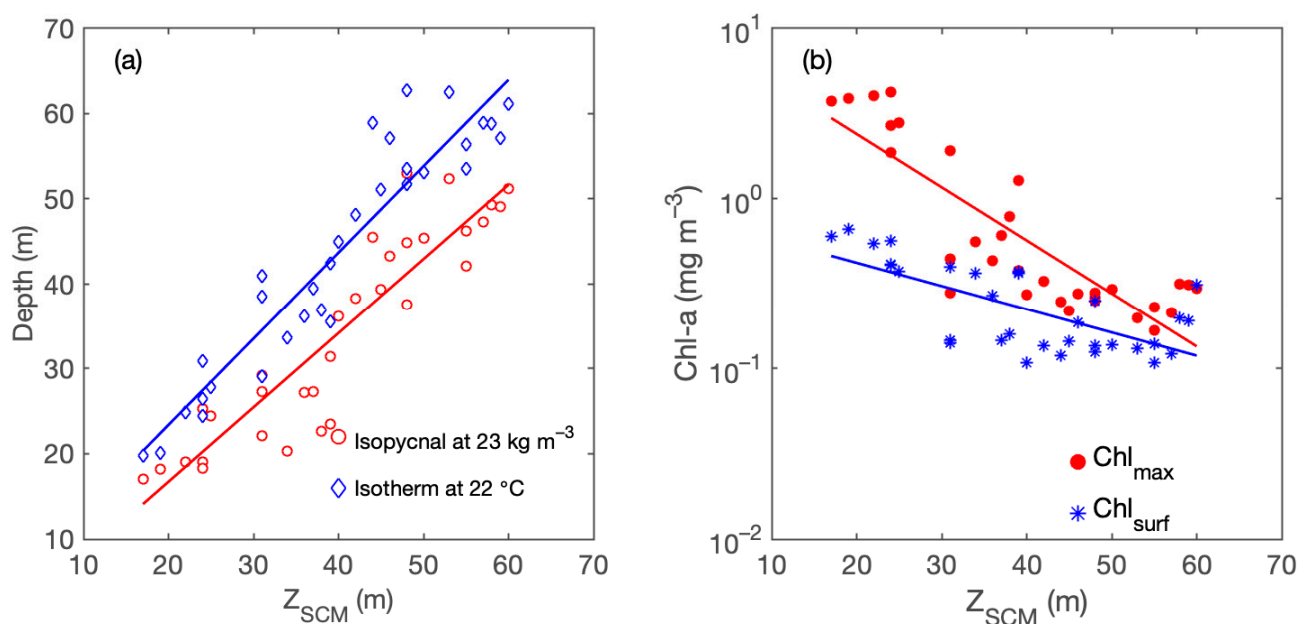


Figure 9. Relationships between the depth of SCM (Z_{SCM}) with variations of thermocline and phytoplankton biomass ($N = 33$). (a) Z_{SCM} with the depth of isopycnal at 23 Kg m^{-3} ($y = 0.87x - 0.75$, $r^2 = 0.84$) and the depth of isotherm at 22 °C ($y = 1.02x + 3.1$, $r^2 = 0.89$); (b) Z_{SCM} with log-transformed Chl-a at subsurface maximum depth ($y = -0.03x + 1$, $r^2 = 0.73$) and at the surface ($y = -0.01x - 0.1$, $r^2 = 0.48$).

3.4. Vertical Variations in CDM Absorption

Vertical distributions of the CDM absorption showed a different pattern from those of Chl-a (Figures 6 and 7). For shallow-water stations (water depth less than 50 m) along the coastline, $a_{CDM}(443)$ exhibited relatively high values in surface waters compared with offshore stations, which also tended to increase rapidly with depth. For middle and outer shelf waters (water depth between 50 and 120 m), a typical characteristic of the CDM profile was that the maximum values were usually found in bottom layers across the shelf, which also showed a small peak concurrently with the SCM layer. In offshore waters, $a_{CDM}(443)$ showed consistent variability with Chl-a, with the subsurface maximum of CDM absorption being observed at a similar depth as the SCM layer. The maximum $a_{CDM}(443)$ value is about 0.35 m^{-1} , which was observed at 35 m in the nearest station of Section 01. However, for the same depth for offshore waters, the $a_{CDM}(443)$ was only around 0.05 m^{-1} . With coastal upwelling, there were pronounced upward-tilted layers of high $a_{CDM}(443)$ values across the shelf over the four transects. This phenomenon was much more obvious for S01, with a thick layer of high CDM beneath the phytoplankton bloom layer, extending from the outer shelf to the inner shelf. Elevated CDM absorption was observed near the bottom, with the threshold depth (Z_{CDM}) ranging from 22 to 90 m. As shown in Figure 10a, Z_{CDM} showed consistent variability with the shelf topography ($r^2 = 0.84$, $N = 29$), as well as with the isopycnal depth at 23 Kg m^{-3} (r^2 being 0.79, $N = 29$). All available $a_{CDM}(443)$ data points observed over the whole water column were separated into two parts according to Z_{CDM} . The relationship between $a_{CDM}(443)$ and Chl-a was analysed to reveal the different sources of CDM in upper ocean and bottom waters. As shown in Figure 10b, for water samples in the upper ocean, $a_{CDM}(443)$ is well related to Chl-a, especially for waters around the SCM layer. However, for bottom waters with low Chl-a, high CDM absorption was observed.

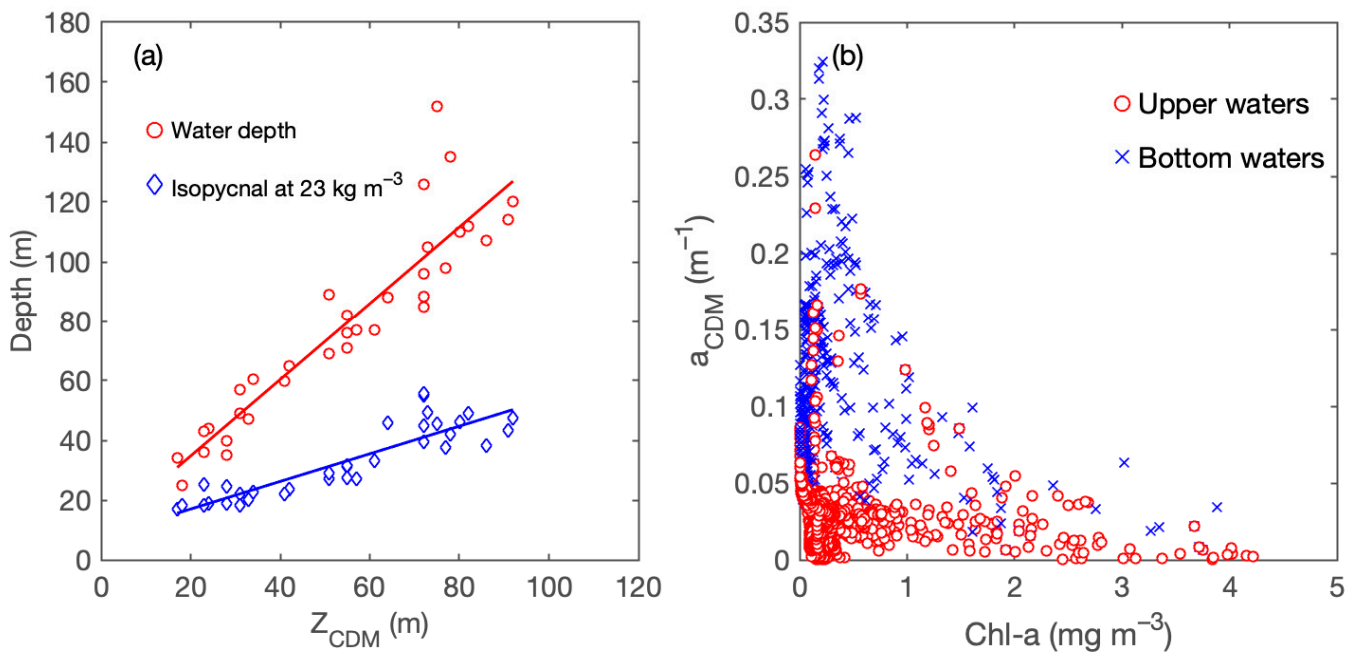


Figure 10. Vertical variations in the CDM absorption. (a) Relationships between the threshold depth of CDM absorption (Z_{CDM}) with shelf topography ($y = 1.28x + 9.17$, $r^2 = 0.84$, $N = 29$) and the thermocline depth represented by isopycnal at 23 Kg m⁻³ ($y = 0.46x + 7.76$, $r^2 = 0.79$, $N = 29$). (b) Scatterplots of CDM absorption at 443 nm ($a_{CDM}(443)$, m⁻¹) with Chl-a in upper ocean (red circles) and in bottom layers (blue dots).

4. Discussion

During the upwelling season, the upwelling system off the coast of Hainan Island in the northwestern SCS has significant production and accumulation of particulate and dissolved organic matter. Phytoplankton were found to play an important role in determining the optical properties of seawater in the upper ocean. However, large scatters were observed for relationships between the optical properties (e.g., $a(443)$, $c(443)$) and the chlorophyll a concentration for bottom waters, suggesting the contributions from non-algal materials in the benthic boundary layer. Relatively higher concentrations of Chl-a and $a_{CDM}(443)$ in surface waters along the coastline are most likely attributed to Ekman transport during the upwelling period. Subsurface chlorophyll maxima and elevated concentrations of CDM in the bottom layer are two distinct bio-optical characteristics of the vertical variability in this upwelling system.

The findings of this study emphasise three significant characteristics related to the spatial and vertical distributions of bio-optical properties during the upwelling process along the coast off Hainan Island: (1) the SCM layer and its fluctuation with thermocline; (2) the presence of relatively elevated concentrations of CDM in the benthic boundary layer; and (3) the effect of shelf topography in determining the spatial variability and vertical structures of bio-optical properties.

4.1. SCM Layers in Response to Upwelling

Subsurface maximum layers of phytoplankton were generally observed in our study area in response to the upwelling event. This feature is different from the three-layer pattern in the vertical distribution of chlorophyll in the coastal upwelling off Oregon [1], which could be attributed to the upwelling intensity. The subsurface Chl-a maximum layer is generally thought to result from the balance of nutrients, light, and mixing, which are in turn affected by complex environmental factors [9]. During our observations, upwelling was in decline with the main signal occurring at about 30–50 m [51]. Along the east and

northeast of Hainan Island, the main contributor to the formation of SCM layers could be the nutrients transported by the coastal upwelling into the subsurface layers where sunlight was present, resulting in the rapid growth of phytoplankton populations. The strongest bloom was at a depth of 24 m at the coastal station of section S01, close to the cold upwelling center, and about 20 km away from the coastline. The exact location was thought to be related to the velocity of the upwelling and integral biological response times [53].

Chlorophyll profiles observed at 40 stations showed large variety in their shapes, suggesting that factors affecting the vertical distributions of phytoplankton biomass are complex and highly variable (Figure 7). SCM was the major characteristic when surface stratification of the water column was observed, with the profile shapes appearing to be modified by other environmental factors. In coastal shallow waters, the SCM shape was modified by the presence of another peak of Chl-a above the main SCM layer (Figure 7c). This shape has been found in other regions, including California Current, the Gulf of Mexico, and the Benguela system [46,54]. However, there are few explanations for this phenomenon. In our region, based on simultaneous observations of hydrological and bio-optical properties, we found that this two-peaks feature was more likely attributed to upwelled subsurface waters with high nutrient and/or high phytoplankton biomass, being coupled with a shallower MLD (6–14 m). As indicated by the temperature profile between 15 and 20 m (Figure 7c), there is an obvious gradient of temperature resulting in a relatively strong stratification. The restratification in MLD could prevent the upward transport of nutrient/phytoplankton, and this event might be related to the sub-meso-scale physical processes [55]. In offshore waters, modified SCM is thought to be an intermediate condition between SCM and homogeneous types [43], the depth of SCM being deeper (32–60 m, averaging about 49m) than that of standard SCM stations (16–57 m, average about 38 m). Homogeneous vertical profiles with stable values within the mixed layer were mainly observed in offshore stations of S01 transect (about 80 km away from the coast). As shown by the vertical distribution of temperature (Figure 4), these stations were found to have well-mixed warm water in the upper ocean. Average surface Chl-a was about 0.23 mg m^{-3} , and nutrients in these stations were found to be relatively lower than that in nearshore stations. During 25–28 August, a tropical cyclone passed through the study area. According to the hydrological studies by [51], this thermal structure was related to the tropical cyclone, which acted to strengthen the mixing in the upper layer and brought subsurface Chl-a to the upper layer. Complex Chl-a profiles with several peaks were found in some stations off the east of Hainan Island, whose structure might be related to the complicated hydrological variability.

Physical forcing could be thought of as the main contributor to the SCM as shown by the close relationships between Z_{SCM} and the depth of isopycnal $\sigma_\theta = 23 \text{ Kg m}^{-3}$ and the depth of isotherm at 22°C (Figure 9). The isopycnal ($\sigma_\theta = 23 \text{ Kg m}^{-3}$) depth, as well as the isotherm (22°C) depth have been used previously for describing the thermocline variability in the coastal upwelling waters off Hainan Island [17,22] and in the South China Sea [7]. These results are quite similar with that observed in the northern SCS [56], although slight differences are evident compared to the results of [57], possibly due to the latter study's specific focus on the open sea. Nutrient-rich waters may be uplifted to shallower depths, with the strength of upwelling determining the depths to which the nutricline is lifted [28,58]. The magnitude of SCM (Chl_{max}) showed inverse variations with Z_{SCM} , which demonstrated that the phytoplankton growth in the upwelling region was mainly determined by nutrient supply from depths and light availability. As shown by the correlations between Z_{SCM} and $\log(\text{Chl}_{\text{surf}})$ (r^2 of 0.48), vertical displacement of SCM across the shelf might be inferred from the surface phytoplankton distributions. However, for

offshore waters with low phytoplankton biomass, the relationship showed large deviations, implying its regulation by different physical processes.

4.2. High CDM Absorption Along the Benthic Boundary Layer

Absorption of CDM could be used as an index of water transport along the surface and bottom layers, including the contributions of CDOM, as well as the non-algal particles. CDM contribution to total non-water absorption in surface waters of coastal stations is high (Figure 5), resulting from the offshore movement of surface waters, and the replenishment with waters from below that are rich in CDM [6].

Vertical variability of $a_{\text{CDM}}(443)$ is very different from that of phytoplankton, showing obviously high values in the bottom boundary layer across the continental shelf. Dynamics of coloured detrital matter in our study area were influenced by many factors. Phytoplankton degradation, as well as the upwelling-linked transport, was found to play an important role. Subsurface phytoplankton blooms probably led to the accumulation of coloured detrital matter below the SCM layer, especially in shallow coastal waters (Figure 10). As is commonly observed in upwelling regions, the sinking and subsequent decomposition of organic matter generated in the euphotic zone can result in remarkably high concentrations of detrital matter [2]. As shown in Figure 10, for water samples in the upper ocean, $a_{\text{CDM}}(443)$ is well related to Chl-a, especially for waters around the SCM layer, which indicated the dominance of a biogenic source of local origin. For bottom waters with low Chl-a, high CDM absorption was found, indicating that the CDM in that layer originated from material transported to that location from elsewhere, or from sinking material that had accumulated there previously. These results are consistent with the variability of particle scattering and backscattering coefficients reported by [29]. Previous observation in areas east of Hainan Island has shown that the bottom type is fine sand [59]. As it is also indicated by the relatively high refractive index (>1.0) [29], mineral particles were found to contribute to the resuspension in the nepheloid layer due to the upwelling event. Based on our observations with high vertical resolution, we detected the transition from optical properties dominated by phytoplankton in the upper ocean to those dominated by coloured detrital materials in the bottom water. Variations in the threshold depth (Z_{CDM}), at which the $a_{\text{CDM}}(443)$ starts to increase rapidly toward the bottom, also exhibited the effect of along-shelf topographic variation on the vertical distributions of water constituents (Figure 10), consistent with recent studies on the role of topography in determining the dynamics of upwelling off northeastern Hainan [23,24]. As we did not make vertical profiles for CDOM, the absorption contributions from CDOM and detrital particles could not be fully separated. However, the resuspension effect of sediment particles could be responsible for the linear relationship between particle scattering at 532 nm ($b_p(532)$) and $a_{\text{CDM}}(443)$ ($b_p(532) = 6.2902 * a_{\text{CDM}}(443) - 0.1965$ $r^2 = 0.89$, $N = 2682$), with both of them showing high values in bottom waters.

4.3. Effect of Shelf Topography on Cross-Shelf Distributions

Striking differences in cross-shelf distributions of phytoplankton, as well as the CDM, were observed over the four transects (Figures 4 and 5). High phytoplankton biomass and CDM absorption were mainly confined in inner shelf waters to the east and northeast coasts of Hainan Island, dropping rapidly toward the outer shelf. Spatial differences of bio-optical properties were found to be sensitive to the shelf topography. The shelf along the eastern coast of Hainan Island is characterised by its steepness and significant widening towards the northeast, particularly from the shelf off the NE cape. Our results showed that the depths of pycnocline and deep chlorophyll maximum, as well as threshold depth at which the CDM absorption tending to increase rapidly to the bottom, are all closely related

with the bottom depth. This topographical feature potentially facilitates the intrusion of nutrient-rich deep water to the surface, thereby enhancing phytoplankton growth in the euphotic zone depth and strengthening the resuspension effect of sediment materials in the nepheloid layer. These topography effects on the upwelling dynamics, which have been investigated based on in situ and model data, play important roles in controlling the location and intensity of coastal upwelling, as well as the cross-shore transport [23,25,26,60].

5. Conclusions

Results from this study clearly showed that bio-optical characteristics of seawater in the northwestern SCS were strongly affected by coastal upwelling during summer. In order to assess the responses of phytoplankton and coloured detrital materials to the upwelling process, empirical models were developed for processing the optical profiles data with high resolution.

Variations in the bio-optical properties of seawater were mainly attributable to the phytoplankton and its accompanying materials, with their spatial distribution being well correlated with topography. Shallow coastal waters showed much higher phytoplankton biomass, with their particle composition being different from those of offshore waters. Vertical distributions of phytoplankton and CDM showed different patterns. Subsurface phytoplankton blooms and high CDM absorption in the bottom layer are two distinguishing characteristics. Five different shapes of Chl-a profile were observed, exhibiting the complex effect of physical–biological interactions. The depth of the major SCM ranged from 16 to 60 m, which showed consistent variability with the thermocline depth and the bottom depth. CDM profiles showed spatial differences, with an increasing trend with depth in shallow coastal waters and consistent shapes with phytoplankton in the upper column of offshore waters. High values of $a_{\text{CDM}}(443)$ were generally observed in benthic boundary layers along the shelf, with the threshold depth being consistent with the topography. Degradation of phytoplankton in the bloom in the upper ocean, as well as the upwelling-linked transport of detrital matter from the bottom, appeared to play important roles in regulating the spatial distributions of coloured detrital matter.

Our results exhibited that in situ observations of inherent optical properties (IOPs) profiles could provide us a useful way to describe the vertical variability of phytoplankton and the coloured detrital materials with high vertical resolution. These subsurface structures of phytoplankton and CDM, as well as their potential relationships with physical processes and topography, enriched our understanding about the biogeochemical impact of the upwelling process off the Hainan Island in the western South China Sea.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/rs17010044/s1>, Figure S1. Phytoplankton absorption coefficient at 443 nm as a function of in situ measured Chl-a concentration for data collected in NSCS at different depths (N = 315). Least-squares fit to log-transformed data is shown.

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