Vertical and Horizontal Variability of Chlorophyll-a and Its Relationship with Environmental Parameters in the Waters of Sangihe and Talaud Islands, North Sulawesi, Indonesia

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Abstract

The chlorophyll-a is an important biological parameter that could act as a proxy to indicate the abundance of phytoplankton and the primary productivity of an aquatic ecosystem. This paper investigates the vertical and horizontal variability of chlorophyll-a in the waters of Sangihe and Talaud Islands, Indonesia, and its correlation with water environmental parameters. In this study, the distribution of chlorophyll-a, temperature, salinity, and nutrients (NO_3 and PO_4) from the surface to a depth of 200 m (photic zone) was measured at 29 research stations. The results showed that the distribution of chlorophyll-a in the waters of the Sangihe-Talaud Islands was varied vertically and horizontally. The waters around the Sangihe Islands generally exhibited a higher chlorophyll-a distribution and shallower Deep Chlorophyll Maxima compared to the water around the Talaud Islands. The concentration of chlorophyll-a varied between 0.0017 and 1.2155 mg.m^{-3}, with most of the water column in Sangihe-Talaud considered oligotrophic, although some stations or depths were mesotrophic or slightly eutrophic. The maximum chlorophyll-a concentration was found in the sub-surface layer at depths between 46 and 101 m. The low N:P ratio (<16) and N:Si ratio (<1) indicate that the water columns of Sangihe-Talaud, up to a depth of 200m, were N-limited. Based on the GAM analysis, chlorophyll-a concentration in Sangihe-Talaud waters was primarily regulated by temperature, salinity, and the N:P ratio, with weak influence from phosphate and the N:Si ratio. The analysis also suggests that primary productivity in Sangihe-Talaud is sensitive to temperature changes, indicating its vulnerability to future warming events.

Keywords: *Celebes sea, deep chlorophyll maxima, generalized additive model, Mollucas sea, nutrients*

Introduction

The waters of the Sangihe and Talaud islands, located north of Makassar Island, are rich in dynamic oceanographic and geologic phenomena (Bock *et al.*, 2003; Widiwijayanti *et al.*, 2004; Gordon *et al.*, 2010; Taufiqurrahman *et al.*, 2019; Pang *et al.*, 2021; Sriwijayanti *et al.*, 2019; Wijayanti *et al.*, 2020; Sani *et al.*, 2021; Santoso *et al.*, 2022). These waters are passed by two primary pathways of the Indonesian Throughflow (ITF), namely the channels of Makassar Strait and the Molucca Sea (Gordon *et al.*, 2010; Sprintall *et al.*, 2019; Pang *et al.*, 2021; Santoso *et al.*, 2022). The ITF is a massive water mass transport system between the Pacific and Indian oceans through Indonesian passages. Between 2004 and 2006, the transport volume of the ITF reached 14–15.7 Sv, of which Makassar Strait accounted for about 80%, namely 11.3–11.8 Sv (1 Sv = 106 $m^3 \cdot s^{-1}$) (Gordon *et al.*, 2010; Santoso *et al.*, 2022). Furthermore, the Sangihe and Talaud waters are geologically complex areas due to a long history of break-out and collision of three major tectonic plates, namely the Philippine Sea Plate, the Eurasian Plate,

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and the Indo-Australian Plate (Bock *et al.*, 2003; Widiwijayanti *et al.*, 2004). These tectonic interactions shape the steep bathymetry in these regions and form the ridges of the Sangihe and Talaud islands. The Sangihe arc shows volcanic activity and is home to two identified submarine volcanoes, namely Kawio and Banua Wuhu (Paris *et al.*, 2014; Triarso and Troa, 2016). These unique oceanographic and geologic phenomena, in turn, will affect many aspects of the water characteristics.

The National Research and Innovation Agency (BRIN) of Indonesia organized a cruise in 2018 called the Expedition of Widya Nusantara (EWIN 2018) to explore the characteristics of the waters around the Sangihe and Talaud islands. The Sangihe waters cover the eastern part of the Makassar Sea, while the Talaud waters cover the northern part of the Molucca Sea. This expedition found that the waters of these two seas had different temperatures, salinities, and densities, although they were adjacent. Some previous studies with various objectives have generally also identified this phenomenon (Radjawane and Hadiputranto, 2010; Triyulianti *et al.*, 2018; Wirasatriya *et al.*, 2019) In addition, Ismail *et al.* (2020) and Wirasatriya *et al.* (2019) discovered that the surface temperature of the eastern Celebes Sea was higher than that of the north of the Molucca Sea; the margin was about 2^{o}C. Ismail *et al.* (2020) also discovered a gradual change in salinity from the eastern part of the Molucca Sea to the western region of the Celebes Sea during the Southeast Monsoon period. Wirasatriya *et al.* (2019) analyzed the cause of distinct variabilities in sea surface temperature (SST) in the Celebes Sea and the northern part of the Molucca Sea. Their analysis of satellite imagery revealed that the difference was probably caused by mountain ranges on the Gorontalo and Sulawesi mainland blocking southeast winds. This phenomenon causes the winds that blow above the Celebes Sea to be weaker than those above the Molucca Sea.

Previous research has successfully highlighted differences in the characteristics of the waters in the Sangihe and Talaud Islands regencies (Radjawane and Hadiputranto, 2010; Triyulianti *et al.*, 2018; Wirasatriya *et al.*, 2019). However, these prior studies primarily focused on the physical and chemical attributes of the water, such as temperature, salinity, density, and pH. Consequently, there remains a gap in our understanding of specific biological information related to this phenomenon. This study aims to address this gap by investigating one of the fundamental biological aspects of these two marine regions: chlorophyll. The distribution of chlorophyll can serve as an indicator of the primary productivity of the aquatic ecosystem, which reflects its capacity to sustain marine life (Tholkapiyan *et al.*, 2020; Bouman *et al.*, 2020; Frey *et al.*, 2020). Although various types of chlorophyll exist, including chlorophyll a, b, c1, c2, d, e, and f, chlorophyll-a is the primary pigment found in phytoplankton. Consequently, it is commonly used as a proxy to estimate phytoplankton distribution and primary productivity (Falkowsky and Raven, 2007; Demidov *et al.*, 2019; Bouman *et al.*, 2020; Bai *et al.*, 2021; Gorbunov and Falkowski, 2021). This study is essential because chlorophyll is a crucial biotic parameter for understanding trophic systems in aquatic ecosystems. Additionally, the timing of this study coincided with the last El Nino event, which occurred during 2018-2019 (Wahyudi *et al.*, 2018). Therefore, this study will also provide valuable insights into the dynamics of biological, chemical, and physical oceanography in the study area during the El Nino event.

Materials and Methods

This study was a part of the Widya Nusantara Expedition conducted in October 2018 by the National Research and Innovation Agency (BRIN) of Indonesia in the waters of the Sangihe and Talaud Islands Regencies. Previously, the name of this area was the Regency of Sangihe-Talaud Islands. However, in 2002, this area was separated into two new regencies based on Law Number 8 of 2002: the Regency of Sangihe Islands and the Regency of Talaud Islands. The waters of the Sangihe Islands Regency are located in the eastern part of the Makassar Sea, while the waters of the Talaud Islands Regency are located in the northern region of the Molucca Sea, adjacent to the western part of the Pacific Ocean. This study area is a part of the Global Ocean Conveyor Belt system since it is traversed by the massive water mass transport from the Pacific Ocean to the Indian Ocean called the Indonesian Throughflow (Gordon, 2010; Sprintall *et al.*, 2019; Auer *et al.*, 2019; Forget and Ferreira, 2019; Lee *et al.*, 2019; Yuan *et al.*, 2022; Guo, 2023). Samples were collected from 29 locations using the Baruna Jaya VIII Research Vessel. See Table 1.

Chlorophyll-a data

The distribution of chlorophyll-a in the study area was measured per meter at the photic zone (up to 200 m depth). Measurement of chlorophyll-a was carried out using Wet Labs ECO-AFL/FL Fluorometer attached to CTD (Conductivity, Temperature, and Depth) device. Whilst this instrument was lowered into the water using a crane, the device measures the fluorescent and uses it as a proxy to estimate the relative concentration of chlorophyll-a in the water.

Temperature and salinity

To determine the water mass characteristics in the area of study, parameters of temperature and salinity were measured per meter at the photic zone (up to 200 m depth). A CTD (Seabird 911-Plus) was used to measure these two parameters, and this instrument was lowered into the water using a crane. The collected data was then retrieved from the CTD using SBE Data Processing and corrected manually in Ms. Excel. The ready-to-use data of CTD (.cnv file) was then processed in the analysis step using Ocean Data View (ODV) Ver. 5.6.2.

Nutrients

The nutrients that were measured in this study were total nitrogen, phosphate, and silicate. Measurements of nutrients were carried out at six different depths, namely 5 m, 25 m, 50 m, 75 m, 100 m, and 200 m. The water samples were taken using a rosette sampler consisting of several 12-liter tubes that were controlled by the command room on the ship. Whilst this instrument was lowered into the water using a crane, it automatically collected water samples from the planned depth. After that, a 500 ml water sample was taken from each tube and was then filtered using cellulose paper with an MF-Millipore Cellulose Membrane Filter, 0.45 µm pore size, and 47 mm in diameter. However, due to several hindrances to the field conditions, the collection of water samples could not be carried out at all stations. Instead of 29 stations, the collection of water samples can only be done at 19 stations.

Table 1. Coordinates of the research stations

Station	Longitude (E)	Latitude (N)	Station	Longitude (E)	Latitude (N)
1	124.2546	3.6474	16	126.0290	3.5313
2	124.2533	3.1494	17	125.8745	2.9910
3	124.1929	2.5887	18	125.8019	2.4525
4	124.2527	2.1000	19	125.6055	1.8028
5	124.8060	3.8391	20	126.2553	5.3082
6	124.7510	3.1493	21	126.6526	4.8310
7	124.6762	2.6779	22	126.7295	3.5382
8	125.0892	4.6739	23	126.4529	2.9486
9	125.2516	4.0010	24	126.3514	2.4448
10	125.2504	3.6480	25	126.9230	5.7188
11	125.2423	3.1953	26	127.3025	5.0949
12	125.2157	2.6867	27	127.3722	4.3482
13	125.5894	4.8978	28	127.5045	3.5539
14	126.0003	4.5840	29	127.0080	2.9539
15	126.3200	3.9260			

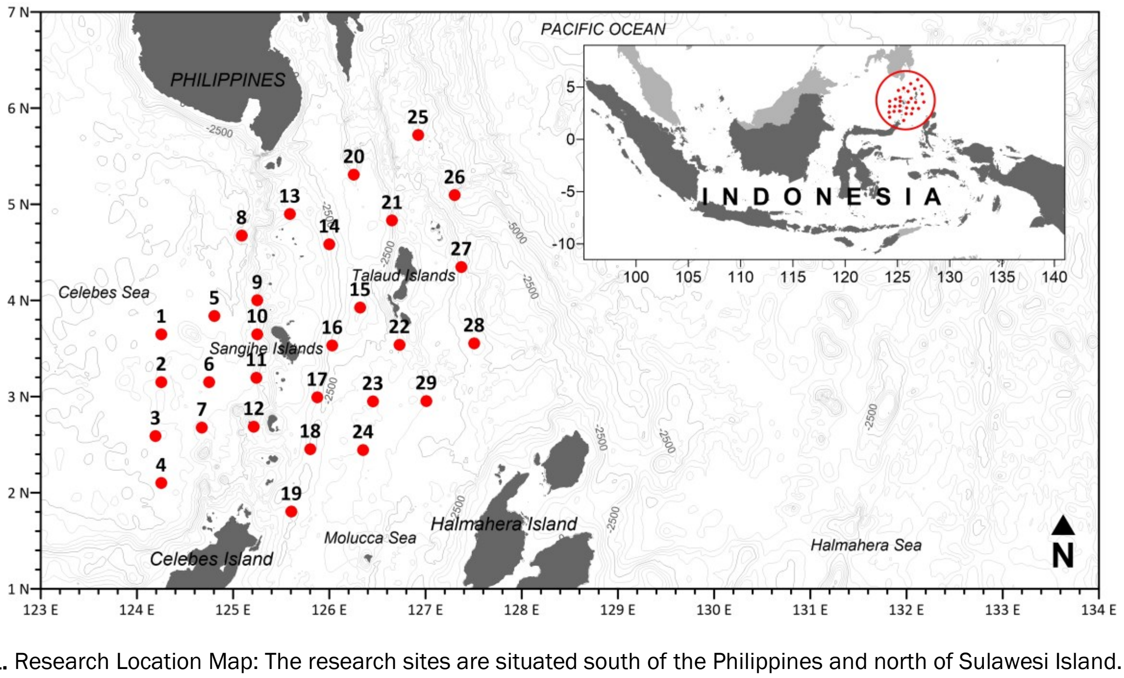

Figure 1. Research Location Map: The research sites are situated south of the Philippines and north of Sulawesi Island. The red dots indicate the research stations where data and samples were collected. This area is traversed by the majority of Indonesian Throughflow (ITF) water masses, which flow from the east (Pacific Ocean) to the west (Celebes Sea).

Data analysis

Several data analyses have been conducted to uncover the vertical and horizontal variability of chlorophyll-a in the study area and its correlation with environmental parameters. The distribution of temperature and salinity was assessed using the oceanographic software ODV (Ocean Data View) Ver. 5.6.2 to generate the Tpot-S diagram and ascertain the water mass characteristics at the research site. Spatial models for chlorophyll-a, temperature, salinity, and nutrients were created using geographic information system software Surfer Ver.11. Relationships between chlorophyll-a and water column parameters (temperature, salinity, and nutrients) were statistically examined using the Generalized Additive Model (GAM) in R-Studio, employing the "mgcv" package. The GAM model was constructed with a log-link quasipoisson family and REML (Restricted Maximum Likelihood) estimation. Response graphs were generated by incorporating the smoothing lines provided by LOESS and GAM prediction models using the "ggplot2" package.

Result and Discussion

Vertical and horizontal variability of chlorophyll-a

Overall, this study found that the distribution of chlorophyll-a in the waters of Sangihe-Talaud, Indonesia, showed vertical and horizontal variability. The minimum concentrations ranged from 0.0017 (station 19) to 0.0366 x 10^{-3} mg.L^{-1} (station 17), while the maximum concentration ranged from 0.4882 (station 8) to 1.2155 x 10^{-3} mg.L^{-1} (station 28) (Table 4). The concentration of chlorophyll-a near the surface ranged from 0.0039 to 0.1291 x 10^{-3} mg.L^{-1}, and at a depth of 200 m, it ranged from 0.0096 to 0.0482 x 10^{-3} mg.L^{-1}. The average concentration at each station went from 0.0982 (station 20) to 0.2646 x 10^{-3} mg.L^{-1} (station 11). Generally, the mean chlorophyll-a concentration in Sangihe-Talaud (0.21 mg.m^{-3}) was slightly lower than the mean chlorophyll-a in the global ocean (0.32 mg.m^{-3}) (Thornton, 2012). Additionally, the chlorophyll-a data (Table 4) indicates that most of the water column in Sangihe-Talaud was oligotrophic, with chlorophyll-a concentration <0.5 mg.m^{-3} (Ignatiades, 2005). Even so, the chlorophyll-a concentration (Table 4.) at some stations did indicate mesotrophic or slightly eutrophic water conditions. In that case, the chlorophyll-a at mesotrophic stations ranged between 0.5–1 mg.m^{-3}, while the eutrophic waters had chlorophyll-a concentration >1 mg.m^{-3} (Ignatiades, 2005).

Vertical and horizontal chlorophyll variability is a common feature in the oceans worldwide, especially in tropical waters such as the Indonesian Sea. For example, in the western part of the Indonesian seas, around the western coast of Northern Sumatra, chlorophyll-a ranged from 0.07–0.25 x 10^{-3} mg.L^{-1} (Iskandar *et al.*, 2022). In the south, in the waters of Bali Strait, chlorophyll-a ranged from 0.25–2.25 x 10^{-3} mg.L^{-1} (Rintaka and Priyono, 2020). In unique aquatic ecosystems such as the waters of Kawio Barat submarine volcano, Firdaus *et al.* (2019) found that the chlorophyll-a ranged from 0.003 to 0.602 x 10^{-3} mg.L^{-1}. Chlorophyll variability is influenced by many factors including temperature, salinity, nutrients, geographic location, water stratification, irradiance, season, zooplankton grazing, and so on (Moeller *et al.*, 2019; Cullen, 2015; Zhao *et al.*, 2019; Firdaus *et al.*, 2020; Rozirwan *et al.*, 2021; Yasunaka *et al.*, 2022; Wahyudi *et al.*, 2023; Firdaus *et al*., 2023).

The distribution of chlorophyll-a in the study area was concentrated in the subsurface layer (Figure 2A), which is a common phenomenon in tropical water and is known as a Deep Chlorophyll Maxima (DCM), Subsurface Chlorophyll Maximum (SCML), and Chlorophyll Maximum Layer (CML) (Cullen, 2015; Leach *et al.*, 2018; Cornec *et al.*, 2021a; Cornec *et al.*, 2021b). In the trophic region, the deep chlorophyll maxima permanently exist throughout the year due to continuous water stratification, and they commonly exist between 40–80 m (Leach *et al.*, 2018; Yasunaka *et al.*, 2022;). Not only does the deep chlorophyll maxima phenomenon occur in the ocean, but it also occurs in freshwater ecosystems, especially in lakes experiencing thermal stratification (Caballero and Vázquez, 2020; Reinl *et al.*, 2020; Li *et al.*, 2022; Zastepa *et al.*, 2022). In this study, the location of DCM in the water column varied at all stations; it occurred at a depth of between 46 and 101 m. The deepest DCM was found at station 14 (101 m), while the shallowest DCM was found at stations 2 and 6 (46 m) (Table 2.). On average, the DCM was located at a depth of 70.7 m (Table 2). As a comparison, in the water of western Northern Sumatera, DCM existed at a depth of 30–50 m; in the Bali strait, it was at the upper 50 m depth, and in the Kawio Barat submarine volcano, it was at around 90 m depth (Firdaus *et al.*, 2021). The DCM is an essential feature in the aquatic ecosystem; it is the hot spot of primary productivity in the water and holds almost half of the total productivity in the water column (Cullen, 2015; Leach *et al.*, 2018). The formation of DCM in the water is driven by nutrient supplies, phytoplankton and zooplankton composition, stratification of temperature and salinity, and light penetration (Ryabov and Blasius, 2014; Klausmeier and Litchman, 2001, Marañón *et al.*, 2020; Cornec *et al.* 2021b). Nevertheless, as per the findings of Masuda *et al.* (2021), the primary determinant of the DCM lies in the photoacclimation mechanism executed by phytoplankton, which involves adjusting their cellular chlorophyll content in response to changing environmental conditions.

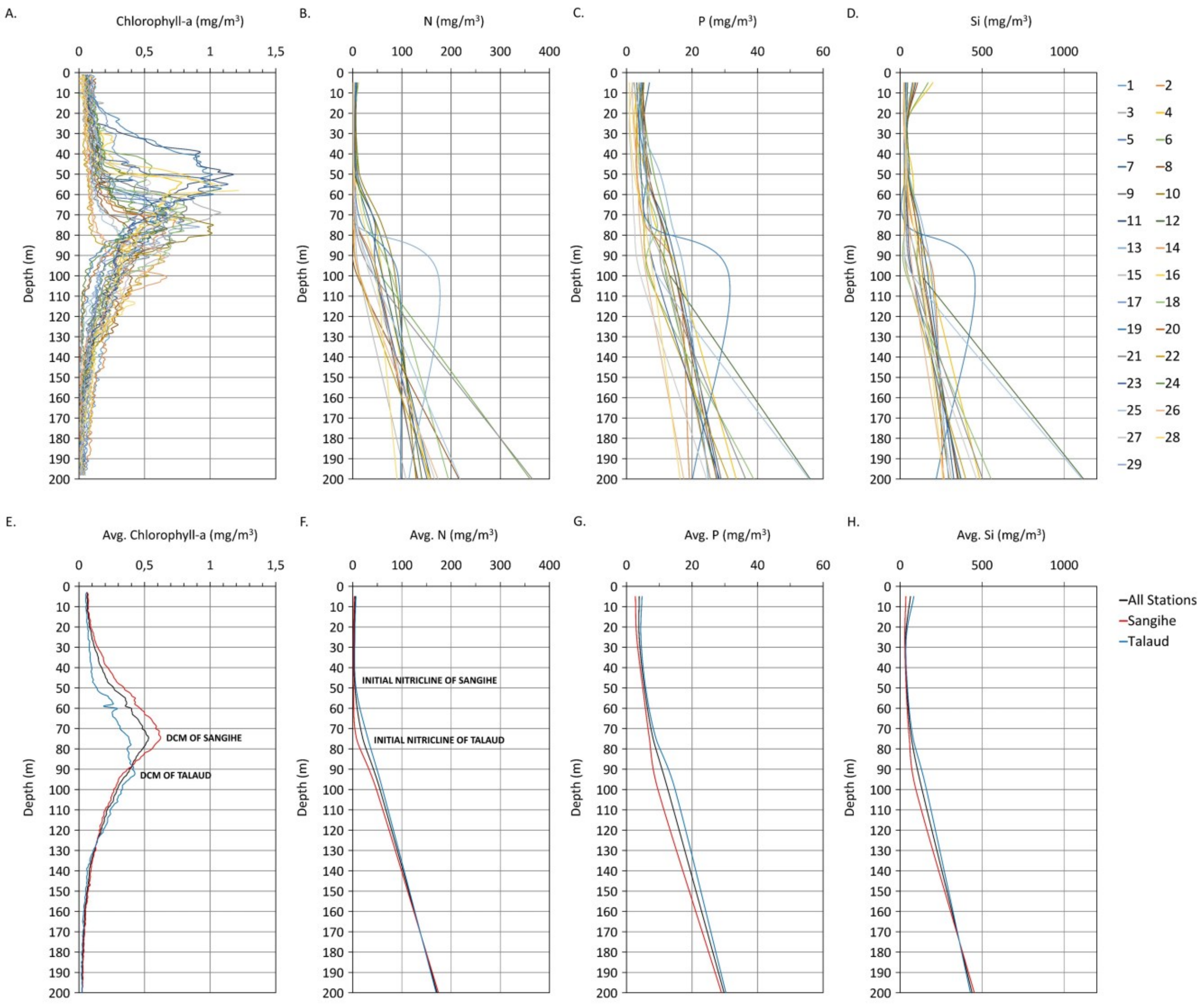

Figure. 2 Vertical distributions of chlorophyll-a (A), nitrogen (B), phosphate (C), and silicate (D) in the photic zone (1-200 MBSL) of all stations. The average value in all stations and separately in the Sangihe and Talaud waters was depicted in figures E, F, G, and H.

While the chlorophyll-a distribution displayed both vertical and horizontal variations, the primary patterns can be categorized into two main zones: west and east. The western region predominantly encompasses the waters surrounding Sangihe Island regency, while the eastern region mainly covers the waters around Talaud Island regency. Spatial modeling data indicate that, on average, the waters around Sangihe Island tend to have higher concentrations of chlorophyll-a compared to those around Talaud Island (see Figure 2.E.). This higher average concentration suggests that the waters around Sangihe Island are more productive than those around Talaud Island. Furthermore, the depth of the Deep Chlorophyll Maximum (DCM) gradually decreases from east to west in the waters of the Sangihe and Talaud Islands. Generally, stations in the eastern region exhibit a deeper DCM compared to the western region, indicating that the waters around Sangihe Island typically have a shallower DCM than the waters around Talaud Island. The location of the DCM can provide insights into the trophic status of the waters; in eutrophic waters, the DCM commonly appears near the surface, whereas in oligotrophic waters, it is found at deeper depths within the water column (Ryabov and Blasius, 2014).

Vertical and horizontal variability of environmental parameters

Several environmental parameters have been measured to determine how temperature, salinity, and nutrients (N, P, and Si) affect the distribution of chlorophyll-a in the waters of Sangihe-Talaud. This paper will focus solely on explaining the nutrient aspects since detailed descriptions of temperature and salinity in this study area have been published by Ismail *et al.* (2020). However, the statistical analysis of chlorophyll-a variability and its relationship with environmental parameters will include temperature and salinity.

During the study, the waters of the Sangihe and Talaud Islands generally displayed vertical and horizontal variability in nitrogen, phosphate, and silicate distribution. The concentration of nutrients tends to increase at greater depths in the water. The distribution of total nitrogen, phosphate, and silicate showed a similar pattern; stations with higher nitrogen tend to have a higher phosphate and silicate concentration. Nitrogen concentrations near the surface ranged from 0.34 to 11.59 $mg.m^{-3}$, meanwhile, the phosphate and silicate concentrations ranged from 0.86 to 6.97 $mg.m^{-3}$and 22–199 $mg.m^{-3}$. At the same time, nitrogen concentrations at a depth of 200 m varied from 90.02 to 365.15 $mg.m^{3}$, phosphate concentrations ranged from 16.36 to 56.07 $mg.m^{-3}$, and silicate concentration were 220 to 1118.8 $mg.m^{-3}$. Overall, the average concentration of nitrogen ranged from 21.87 (station 15) up to 97.7 $mg.m^{-3}$ (station 8), the phosphate ranged from 5.75 (station 28) to 20.08 $mg.m^{-3}$ (station 8), and the silicate ranged from 261.31 (station 33) to 1109.83 (station 28) $mg.m^{-3}$.

The horizontal distribution showed that the waters around the Sangihe Islands had a relatively higher concentration of nutrients than the Talaud Islands (Figure 3.). The highest average concentration of total nitrogen and phosphate occurred at the same station, station 8, and the lowest occurred at station 28. The waters of the Sangihe Islands have a higher concentration of nutrients, probably due to the high vertical mixing in this region since this region has steep bathymetry. This region is the location of internal tidal wave generation; therefore, it has a high local dissipation of tidal energy, contributing to higher local vertical mixing (Purwandana *et al.*, 2020; Purwandana *et al.*, 2021; Sani *et al.*, 2021). In addition, the recirculation in the western Talaud Islands waters is exposed by the retroflection of water mass flowing from the Celebes Sea to the Pacific Ocean, in which this water mass has experienced strong vertical mixing (enhanced nutrients) while crossing the Celebes Sea region (eastern north Kalimantan shelf) (Purwandana *et al.*, 2020; Purwandana *et al.*, 2021; Sani *et al.*, 2021). Tuerena *et al.* (2019) found the same condition in the waters of Mid-Ocean Ridges, where they observed that a spring-neap increase in diapycnal nitrate fluxes is a common occurrence across ridges and seamounts. Consequently, mid-ocean ridges assume a vital role in supporting the nutrient supply to the deep chlorophyll maximum (DCM). Vertical mixing has a role in nutrient supply since it can transport nutrients from the deep layer into the upper layer (Wihsgott *et al.*, 2019; Villamaña *et al.*, 2019; Olson *et al.*, 2020; Hopkins *et al.*, 2021).

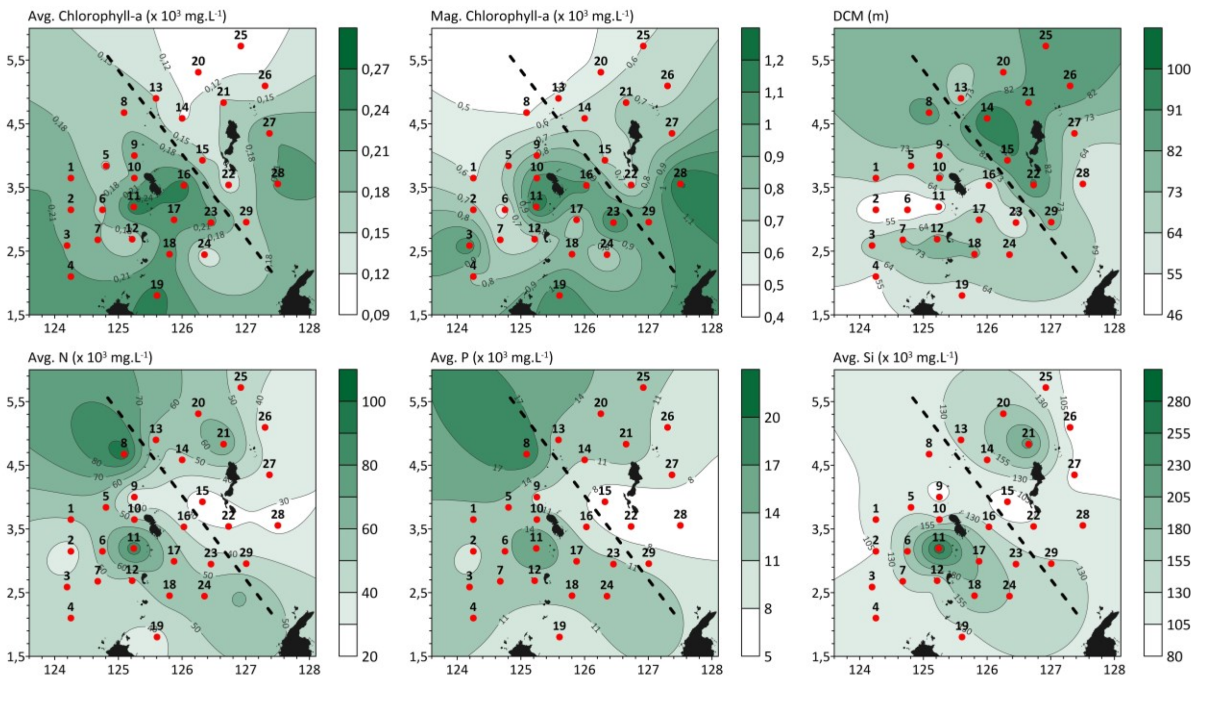

Figure 3. Horizontal distributions of chlorophyll-a (average, magnitude, and depth of maximum chlorophyll), and nutrients (N, P, and Si) in the research location.

Chlorophyll-a variability and its relationship with the environmental parameters

Generalized Additive Model (GAM) analysis was conducted to determine how environmental factors influence the variability of chlorophyll-a in the study area. This analysis generally indicates that the variability in chlorophyll-a concentration in the water column of the Sangihe-Talaud Islands was primarily influenced by temperature, salinity, phosphate concentration, N:P ratio, and N:Si ratio (Table 2.). Among these parameters, temperature, salinity, and N:P ratio was found to be highly significant (P< 0.001) in regulating chlorophyll-a concentration in the water (Table 2.). It's worth noting that phosphate concentration and the N:Si ratio was significant at a higher significance level (P<0.1) (Table 2.), suggesting weaker evidence of a regulatory relationship between these two parameters and chlorophyll-a in this study. The relationships between chlorophyll-a and the measured water environmental parameters are further explained by the response curve model based on the GAM analysis in Figure 4.

Based on the GAM analysis, the response models were constructed between the chlorophyll-a concentration and each explanatory variable, such as temperature, salinity, nutrient concentrations, and nutrient ratios (Figure 4.). Note that among all the water column parameters, the relationship between salinity and the Si:P ratio was close to a linear trend (Figures 4C and 4H.), unlike the other parameters, which exhibit non-linear and unimodal trends (Figure 4). Based on the GAM analysis, it was estimated that the optimum temperature to support high productivity in the water column of Sangihe-Talaud ranged between 24-26^{O}C (Figure 4A.). Any temperature that was lower or higher than the limits was predicted to have a significant negative impact on the chlorophyll-a concentration in the water column. Note that the very narrow temperature optimum range (Figure 4A.) suggested that the chlorophyll-a concentration was very sensitive to any water temperature deviation. Note that the study by Garcia-Corral *et al.* (2017) suggested that an increase in temperature beyond the 23^{O}C threshold would lead to a rapid decrease in chlorophyll-a concentration. In addition, the same model (Figure 4A.) also gives an insight into the effect of ocean warming on the primary productivity of the Sangihe-Talaud waters, in which increasing temperature results in a rapid decline in chlorophyll-a concentration in the water. With that, planktonic communities in the oligotrophic oceans could undergo a drastic shift towards heterotrophy under a warming ocean at temperatures above 21^{O}C (Garcia-Corral *et al.*, 2017). Furthermore, a warming oligotrophic ocean, which undergoes a shift into more heterotrophic conditions, could turn the planktonic communities in the sub-tropical and tropical oceans into a CO_2 source instead of a sink (Garcia-Corral *et al.*, 2017). Those conditions could cause a positive feedback loop that will accelerate the global ocean warming process.

The GAM model suggested a higher productivity, indicated by a higher chlorophyll-a concentration, at a higher salinity (Figure 4B.). Such a trend was also observed in other tropical oceans, like the Equatorial Pacific Ocean, where the maximum chlorophyll-a concentration is commonly observed along with the maximum sea surface salinity (SSS) and vice versa (Shi and Wang, 2021). Unfortunately, the data in this study was insufficient to determine the upper or lower limit of salinity to the chlorophyll-a

Table 2. Statistical summary table for GAM analysis, which includes all measured environmental parameters as explanatory factors without any interactions between them. GAM model was constructed using log-link quasipoisson family with REML estimation

Estimate (Intercept)	SE	t	value	Pr(>|t|)
	-2.096	0.05596	-37.45	<2e-16****
	edf	Ref.df	F	p-value
Temperature	6.46E+00	9	23.114	2.00E-16****
Salinity	5.91E+00	9	6.415	6.87E-10****
Phosphate (PO4)	1.15E+00	9	0.295	0.0687*
Nitrate, NO3	3.64E-05	9	0	0.6848
Silicate (SiO4)	4.95E-05	9	0	0.6345
N:P ratio	3.02E+00	9	2.025	7.16E-05****
N.Si ratio	6.39E-01	9	0.197	0.0591*
Si.P ratio	5.85E-04	9	0	0.3664
R-sq.(adj)	0.827	Scale est. =	0.024597	
REML	-119.75	n =	112	
Deviance explained	90%			
Signif. Codes **** 0.001; *** 0.01; ** 0.05; * 0.1				

concentration in the Sangihe-Talaud water column (Figure 4B.). As shown in Table 2, the salinity range measured in this study ranged between 33.9 and 35 PSU, which is considered high salinity (>30 PSU) but is typical for seawater. Despite the existence of some small islands, the study area consisted of oceanic waters, which are unlikely to have drastic and long-term changes in salinity. Even so, precipitation and evaporation do have a strong effect on the variability of sea surface salinity (SSS), in which precipitation leads to freshening (lowering the salinity) while evaporation leads to salting (increasing the salinity) of the surface layers (Durack, 2015). However, without any data on the chlorophyll-a concentration at lower or higher salinities measured in this study, it was not possible to generate a proper response model with lower and upper salinity limits.

Similar to temperature, the GAM analysis shows the optimum, lower, and higher limits of phosphate, nitrate, and silicate to support the high productivity in the water of the Sangihe-Talaud (Figure 4C-E.). The GAM model also suggested that the optimum chlorophyll-a concentration was estimated to occur at a concentration between 9–12 mg.m^{-3} for phosphate (Figure 4C.), 20–30 mg.m^{-3} for nitrate (Figure 4D.), and 90–100 mg.m^{-3} for silicate (Figure 4E.). As shown in the GAM analysis (Table 2.), only the phosphate concentration showed a weakly significant relationship with the chlorophyll-a in this study. The same analysis also suggested that interaction between nitrogen and phosphorus, in the form of the N:P ratio, was significantly more important as a regulatory factor for driving the variability of chlorophyll-a in the Sangihe-Talaud waters (Table 2.).

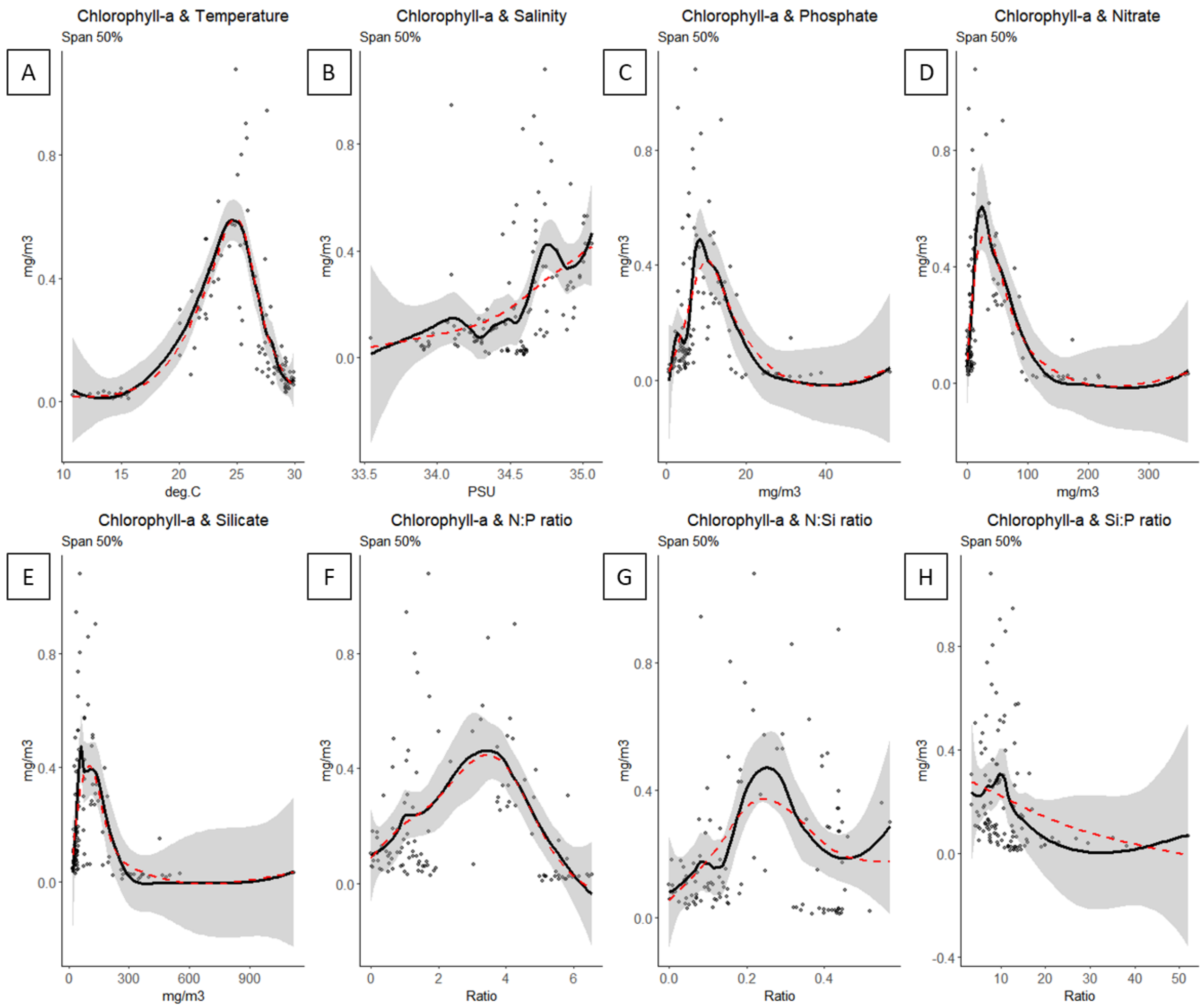

Figure 4. Response models between chlorophyll-a concentration and (A) temperature, (B) salinity, (C) phosphate, (D) nitrate, (E) silicate, (F) N:P ratio, (G) N:Si ratio, and (H) Si:P ratio in Sangihe-Talaud. Two smoothing lines based on GAM analysis (red dashed line) and LOESS smoother (black line) were incorporated in each response model. Grey area indicating standard error (se) for LOESS smoother. GAM line was constructed using predicted values from the GAM model. LOESS line was constructed using the values from the original dataset.

Based on the results, the N:P ratio in the water column of Sangihe-Talaud was far below Redfield's ratio of N:P < 16:1 (Geider and La Roche, 2002). Additionally, the results of the nutrient ratio indicate that the water columns in Sangihe-Talaud suffer from N-limitation, which is indicated by N:P < 16 and N:Si < 1 (Xu *et al.*, 2008). Note that a low N:P ratio could occur in waters where the nutrients, particularly nitrogen (N) and phosphorus (P), were replete due to deep mixing that delivered nutrients from the deeper layer to the surface (Geider and La Roche, 2002). Even so, the GAM model indicated that optimum water productivity, as shown by the maximum measured chlorophyll-a concentration, was observed at the N:P ratio between 3 and 4 (Figure 4F.). Considering that the chlorophyll-a concentration was comparably high as in some relatively productive waters, such as the Bali Strait (Rintaka and Priyono, 2020), it was suggested that the primary producers in Sangihe-Talaud could still thrive under N-limitation conditions. The unimodal pattern in the response model between chlorophyll-a and N:P ratio (Figure 4F.) did suggest that the primary productivity, indicated by chlorophyll-a concentration, was reduced under a higher N:P ratio, or N-enrichment condition. However, the reason why such a trend occurred was not clear. Interaction between the N:P ratio and other environmental parameters with significant effects, particularly temperature and salinity (Table 2.), might be the reason for the limited chlorophyll-a concentration under a lower or higher N:P ratio in Sangihe-Talaud waters.

Generally, the N:Si ratio in the water column of Sangihe-Talaud was low, although the optimum N:Si ratio to support the higher chlorophyll-a concentration was estimated between 0.2 and 0.3 (Figure 4.). Unlike N:P and N:Si ratios, the Si:P ratio shows a general negative relationship with chlorophyll-a concentration, in which the concentration of chlorophyll-a will be lower at a higher Si:P ratio (Figure 4.). The balance between the concentrations of silica (Si), nitrogen (N), and phosphorus (P) was important to determine the bioavailability of Si for the growth of photosynthetic microalgae, primarily diatoms (Armin and Inomura, 2022). With the high availability of Si, the diatoms will grow faster and might have denser or thicker frustules, but at the same time, they will also require more nitrogen to support their rapid growth (Armin and Inomura, 2022). Additionally, a shift in the N:Si ratio could also cause a shift in the N-limited to Si-limited condition, which will affect the diatom community and the primary productivity in the water (Fu *et al.*, 2012). Meanwhile, changes in the Si:P ratio could shift the phytoplankton community from a diatom-dominated to a flagellates-dominated community (Fu *et al.*, 2012). Because the water in Sangihe-Talaud was considered N-limited, the population of diatoms, as part of the primary producers, was unable to grow optimally despite their seeming to be an abundance of Si in the water column. Although the current studies did not identify the phytoplankton community structure, previous studies have shown that the phytoplankton community in Sangihe-Talaud was co-dominated by diatoms and cyanobacteria, such as Leptocylindrus, Chaetoceros, Nitzshia, and Trichodesmium (Thoha and Fitriya, 2010; Sriwijayanti *et al.*, 2019). The balance of the co-dominance between diatoms and cyanobacteria, as the primary producers in Sangihe-Talaud, most likely depends on the balance of the N:P and N:Si ratios in the water column, as shown by the results of this study.

Conclusion

This research has illuminated how the physical and chemical attributes of these waters impact the distribution of chlorophyll-a. The distribution of chlorophyll-a within the photic zone of these waters exhibits both horizontal and vertical variations. Additionally, the variability in chlorophyll-a concentration reveals a zoning pattern, where the eastern part of the study area (Sangihe Islands waters) exhibits a higher chlorophyll-a concentration compared to the western part (Talaud Islands waters). Furthermore, the deep chlorophyll maxima in the waters surrounding Sangihe Islands are situated at shallower depths compared to the waters around Talaud Islands. The analysis using the Generalized Additive Model (GAM) indicates that chlorophyll-a concentration in Sangihe-Talaud waters is primarily influenced by temperature, salinity, and the N:P ratio, with weaker effects from phosphate and the N:Si ratio. The N:P ratio suggests the potential for nitrogen limitation in the water column of Sangihe-Talaud, as chlorophyll-a concentration appears to be controlled by the balance and availability of nitrogen and phosphorus. On the other hand, an increase in salinity is proposed to boost chlorophyll-a concentrations. Nevertheless, due to data constraints, this study was unable to predict the specific upper and lower salinity limits. The narrow range of temperature tolerance indicated by the response model underscores the sensitivity of primary productivity in Sangihe-Talaud to temperature fluctuations, suggesting its susceptibility to future warming.

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