The Vertical Profile of Chlorophyll-a in the Waters of Submarine Volcano of Kawio Barat, Indonesia

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Abstract. The submarine volcano can release various materials into the waters and affect the distribution of chlorophyll. Nevertheless, studies in such kinds of exciting areas are rarely done. This study aims to determine the vertical profile of chlorophyll-a around the submarine volcano waters. A field survey was conducted in October 2018 in the photic zone (200 m) around the Kawio Barat submarine volcano waters, North Sulawesi Province, Indonesia. Chlorophyll fluorescence was measured using a sensor of WET Labs ECO-AFL/FL as a proxy of chlorophyll-a. The temperature, salinity, and depth were measured using a CTD. The nutrients, including nitrate, orthophosphate, and silicate, were measured using autoanalyzer Skalar SAN++. The average of chlorophyll-a values ranged between 0.098 - 0.175 mg/m3. The highest average chlorophyll-a was found around the waters of Kawio Barat submarine volcano. The vertical profile of chlorophyll-a indicated a forming of Deep Chlorophyll Maxima (DCM), located at a depth of 69 - 90 meters. In the Kawio Barat submarine volcano waters, the DCM is found in a depth of 90 m. It has chlorophyll-a concentration four times higher than the surface (5 m). The Principal of Component Analysis (PCA) shows that the temperature and salinity have a more substantial influence on the value of chlorophyll-a. Meanwhile, the nutrients are more influence firmly on the depth of DCM. This current study may conclude that the Kawio Barat submarine volcano waters are more productive than the other stations.

1. Introduction
The presence of an active submarine volcano in the sea can influence the environmental conditions around it. The active submarine volcano can release various materials into the waters, such as Fe, NO2-, NO3-, PO4, and Si(OH)4 [1] [2]. These nutrients could affect marine life, especially phytoplankton. The phytoplankton uses those nutrients to form the structure of their cells. For example, the class of Bacillariophyceacea needs silica (Si) to build its cell wall [3]. Phytoplankton obtains the energy (light) to form their cells through photosynthesis activity. During photosynthesis, phytoplankton absorbs sun-light energy using its chlorophyll pigment. Hence, the distribution of phytoplankton is manifested through the chlorophyll distribution in the waters. Therefore, the high distribution of chlorophyll in the seas also indicates the increased productivity of the seas. There are numerous types of chlorophyll, such as chlorophyll a, b, c1, c2, d, e, and f [4] [5] [6]. Chlorophyll-a is the primary photosynthetic pigment of phytoplankton. Hence, chlorophyll-a commonly used as a
proxy to estimates the photosynthesis and biomass of phytoplankton in the waters [7] [8] [9]. Chlorophyll-\(a\) in the water is widely measured using a fluorometer [8] [9]. The fluorometer measures the re-emitted light, called fluorescence, by chlorophyll-\(a\) during returns from excited to non-excited states.

The Kawio Barat is the submarine volcano that was discovered in 2010. However, the Kawio Barat Submarine Volcano was previously identified by the research expedition of AISHA 2003 (Indonesia-Australia Survey for Submarine Hydrothermal Activity). This expedition identified a high methane concentration and light transmission anomaly in the waters [10]. This expedition also found the rock's mineralization activity which is indicated by pyrite dissemination and marcasite. Hence, they concluded that there is a volcanic activity there, and it is still active. Their finding was followed up by the research expedition of INDEX SATAL 2010. This expedition used the ROV (remotely operated underwater vehicle) to directly observed the Kawio Barat. The Kawio Barat laid at a depth between 1890 m (the top) and 5400 m (the base) [11] [12]. Based on its size, the Kawio Barat is one of the enormous volcanoes in Indonesia.

Geographically, the Kawio Barat submarine volcano is located at the Sangihe-Talaud Islands, North Sulawesi Province. It is comprised of 105 islands and characterized by steep bathymetry [13]. It is also one of the three main gates of Indonesian Through-Flow (ITF) [14]. The ITF water masses originate from North Pacific Subtropical Water (NPSW) and North Pacific Intermediate Water (NPIW), flow into the Sulawesi Sea through Sangihe-Talaud waters, and then continues to the Makassar strait [15]. This pathway covers about 80 % of total ITF water transport with a volume reach around 11.6 SV (1 Sv = 1 x 10^6 m^3/ second ) [16] [17]. Therefore the Sangihe-Talaud waters are complex, dynamic, and supports fisheries. However, the chlorophyll distribution study conducted around The Kawio Barat submarine volcano is limited. This study aims to observe chlorophyll-\(a\) distribution around the waters of Kawio Barat Submarine Volcano. We also analyzed its correlations with environmental parameters.

2. Materials and Method
The research was carried out in October 2018 during the EWIN expedition. The study area is located around the Kawio Barat submarine volcano waters, Sangihe-Talaud Islands, North Sulawesi Province, Indonesia. Sampling was carried out at five research stations, which are arranged in such a way parallel with the direction of the Indonesian Through-flow (ITF) (Figure 1), and also the changes in chlorophyll concentration from each station before, during, and after crossing the underwater volcano can be observed. In contrast, the Kawio Barat submarine volcano is located at station 2. Distance between stations showed in Table 1.

| Stations   | Distance (km) | Distance accumulations (km) |
|------------|---------------|-----------------------------|
| ST 1 – ST 2| 108.6         | 108.6                       |
| ST 2 – ST 3| 62.8          | 171.4                       |
| ST 3 – ST 4| 86.9          | 258.3                       |
| ST 4 – ST 5| 87.1          | 345.4                       |

The hydrological parameters such as temperature and salinity were measured using the Conductivity, Temperature, and Salinity (CTD) SBE 911 sensors. The chlorophyll-\(a\) was measured using the fluorescence sensor of WET Labs ECO-AFL/FL attached to the CTD. The nutrients (orthophosphate, nitrate, and silicate) were collected using the rosette sampler and then analyzed autoanalyzer Skalar SAN++. The cross-section graphs of those parameters were generated using software Surfer 9. PCA analysis was used to know the correlations between a chlorophyll-\(a\) distribution and environmental parameters.
3. Results and Discussion

3.1. Temperature and Salinity

Table 2 presents the maximum, minimum, and average temperature and salinity values of the area study between 1-200 meters below sea level. Station 1 and 2 (submarine volcano) show a higher average temperature of about 1–2 °C than the station 3, 4, and 5. The cross-section diagram of temperature indicates that the station 1 and 2 have a deeper thermocline layer than the station 3, 4, and 5 (Figure 3). The thermocline depth at stations 1, 2, 3, 4, and 5 was 40 m, 40 m, 30 m, 5 m, and 10 m, respectively. The average salinity at all stations showed a relatively similar value ranging from 34.56-34.76 PSU (Table 2). Same as the temperature, the halocline at stations 1 and two shows a deeper depth than stations 3, 4, and 5 (Figure 3). The halocline center at stations 1, 2, 3, 4, and 5 was 40 m, 40 m, 30 m, 5 m, and 10 m, respectively. Based on the characteristic of temperature and salinity, the water masses in the thermocline zone of the area study mostly come from North Pacific Waters [16].

The diagram T-S shows two different water characteristics in the study area (Figure 2). The first water characteristic located at Sulawesi Sea zone covers the station 1, 2, and 3. The second covers the station 4 and 5 which located at the northern Molucca Sea. Several studies also confirmed the presence of two different water characteristics between the Sulawesi Sea and Northern Molucca Sea [18] [19] [20] [21]. The Sulawesi Sea was warmer than the northern Molucca Sea, with a temperature difference reached around 2 °C [19] [21]. Based on the direct measuring using CTD, Ismail et al. (2020) found the presence of surface temperature zoning between the Sulawesi Sea (>29.75°C) and the north of the Maluku Sea (<28.75°C). Furthermore, they also found the salinity distribution showed a low to high salinity gradient from the east to the west side of the Sangihe Talaud waters. Based on satellite observations, Wirasatriya et al. (2019) found Distinct Characteristics of SST Variabilities in the Sulawesi Sea and the Northern Part of the Maluku Sea During the Southeast Monsoon. This temperature gap was caused by the presence of the Gorontalo and Sulawesi mountains, which blocked the southeast winds to the Sulawesi Sea during the southeast monsoon season [19]. This causes the southeast winds to blow on the Sulawesi Sea (<3m/s) is weaker than the northern Molucca Sea.
(>6m/s). Conversely, the stronger winds which blow on the north of the Molucca Sea generate the eastward Ekman mass transport (EMT) that carries the water mass away from the coast and then inducing the upwelling [19].

Table 2. The temperature (°C), salinity (PSU), and chlorophyll-a (mg/m³) at the depth 1-200 meters at each station around the waters of Kawio Barat submarine volcano in October 2018.

| Stations | Parameters   | Minimum | Maximum | Average | Std. Dev. |
|----------|--------------|---------|---------|---------|-----------|
| 1        | Temperature  | 16.36   | 29.38   | 23.08   | 4.86      |
|          | Salinity     | 34.12   | 34.99   | 34.66   | 0.30      |
|          | Chlorophyll-a| 0.017   | 0.473   | 0.149   | 0.131     |
| 2        | Temperature  | 15.44   | 29.34   | 23.01   | 4.73      |
|          | Salinity     | 34.00   | 35.02   | 34.70   | 0.32      |
|          | Chlorophyll-a| 0.015   | 0.488   | 0.175   | 0.136     |
| 3        | Temperature  | 15.47   | 29.10   | 21.78   | 4.49      |
|          | Salinity     | 34.18   | 35.03   | 34.76   | 0.25      |
|          | Chlorophyll-a| 0.012   | 0.519   | 0.148   | 0.124     |
| 4        | Temperature  | 10.68   | 29.69   | 20.40   | 6.30      |
|          | Salinity     | 34.00   | 35.04   | 34.64   | 0.30      |
|          | Chlorophyll-a| 0.003   | 0.527   | 0.098   | 0.126     |
| 5        | Temperature  | 10.81   | 29.58   | 20.94   | 6.63      |
|          | Salinity     | 33.94   | 35.04   | 34.56   | 0.32      |
|          | Chlorophyll-a| 0.003   | 0.602   | 0.107   | 0.136     |

Figure 2. The diagram of temperature and salinity in the study area.

3.2. Nutrients
The vertical distribution of nutrients at the study area in the depth of 1-200 meters shown in Figures 4. The vertical distributions of orthophosphate, nitrate, and silicate appeared with a similar pattern at each station (Figure 4). The highest and lowest average orthophosphate values, nitrate, and silicate concentration were found at station 3 and station 1, respectively. The average value of orthophosphate,
nitrate, and silicate at station 3 in the depth of 1 - 200 meters was 12.15 µg/L, 50.76 µg/L, and 134.92 µg/L, respectively. Meanwhile, the average value of orthophosphate, nitrate, and silicate at station 1 in the depth of 1-200 meters was 7.97 µg/L, 24.74 µg/L, and 73.46 µg/L, respectively. The rapid increase of nutrients concentrations (nutricline) appeared from depths between 60 -100 meters. The nutricline is found around the thermocline layer. The depth of nutricline is one of the essential aspects of ocean biogeochemical. It can influence the carbon cycle in the sea. The nutricline reportedly correlated with the distribution of diatoms and coccolithophorids in the Atlantic Ocean [22]. Nutricline controlled the nutrient supply to the ocean upper mixed layer [22].

3.3. Vertical profile of chlorophyll-a
The average chlorophyll-a concentration in the depth of 1-200 meters ranged between 0.098 - 0.175 mg/m³ (Table 2). The lowest average chlorophyll-a concentration was found at station 4, while the highest was at station 2. Station 2 has higher chlorophyll-a than others due to the presence of the Kawio Barat submarine volcano. The active submarine volcano can release various materials into the waters, such as Fe, NO₂⁻ + NO₃⁻, PO₄³⁻, and Si(OH)₄ [1] [2]. These materials presumably enriched the waters around station 2. The Chlorophyll-a graph shows the rapidly elevated concentration of chlorophyll in the sub-surface water column and then decreased again (Figure. 4). This phenomenon has long been known and has several terms, such as Subsurface Chlorophyll Maximum (SCMLs), Chlorophyll Maximum Layer (CML), and Deep Chlorophyll Maxima/Maximum [23] [24] [25] [26]. Even Ryabov and Blasius (2014) distinguished three distinct locations of chlorophyll maxima, namely deep chlorophyll maximum (DCM), subsurface layers (SSLs), and surface layers (SLs). In this study, I use the term Deep Chlorophyll Maximum or abbreviated as DCM. Regardless of those terms, the DCM has essential roles in the aquatic ecosystem. It is the primary production hot spot in the waters, and it represents ecologically significant features of the planktonic ecosystem [25]. The DCM can covers over half of the total primary production in the water column, so they play essential roles in the nutrient and carbon cycles [22] [26]. The formation of DCM is influenced by many factors, such as resource supplies (nutrients), species requirements, and environmental parameters (temperature and salinity) [27] [28] [29].

The DCM in this study varies in the range of 69 - 90 meters (Figure 4). The shallowest DCM was observed at station 3, while the deepest DCM at station 2 (around 90 m). The DCM of station 2 was 0.488 mg/m³, this value is higher >4 times than the surface (0.11 mg/m³). The formation of DCM, as in this study, often indicated an oligotrophic water system [27] [30]. The formation of DCM in the eutrophic system often occurs near the surface [27]. The DCM in the lake ecosystem forms in the oligotrophic lakes but can also found in eutrophic to dystrophic lakes [26]. The formation of DCM often indicates the existence of stratification in the water column. In tropical water, thermal stratification and the DCM occurs throughout the year. Thermal stratification can regulate nutrients mixing from deep waters. Hence it determines the nutrient supply to the phytoplankton in the euphotic zone [26].

Figure 3 also indicates an upwelling event at the area study, especially station 3. Upwelling events are characterized by the presence of relatively higher Chl-a, nutrients, and salinity in the shallower depth, as well as low temperature. The nutrients also seemed in somewhat deeper water than other stations. However, the upwelling phenomena seemed weak because it probably has occurred several weeks before the sampling time. The intensive use of nutrients during upwelling leads to deficient nutrients in the DCM depth of stations 3, 4, and 5. Below this depth, the concentration of the nutrients rises again since the nutrients usage decreases. Atmadipoera et al. (2018) report that the upwelling at the Molucca Sea occurs during the Southeast Monsoon period from June to October, same as this study time. The upwelling is mainly forced by the southerly monsoon winds [31].
Figure 3. The cross-section distributions of chlorophyll-a, temperature, salinity, and nutrients in the depth of 1 – 200 meter at all stations around the waters of Kawio Barat submarine volcano in 2018.
Figure 4. The vertical profile of chlorophyll-α, temperature, salinity, and nutrients in the depth of 1–200 meter at all stations around the Kawio Barat submarine volcano waters. The grey line shows the locations of Deep Chlorophyll Maxima.
3.4. Chlorophyll-a and environmental factors analysis

The Principal Component Analysis (PCA) shows that all measured environmental parameters influence the vertical profiles of chlorophyll-a in the study area (Figure 4). However, all these environmental parameters did not show the same effect on the vertical profile of chlorophyll-a. Generally, the temperature and salinity affect much more the chlorophyll-a concentration than the Deep Chlorophyll Maximum (DCM). On the other hand, the nutrients affect much more the DCM than chlorophyll-a concentration. Furthermore, minimum and average temperature values show a strong positive influence on the maximum and average chlorophyll-a concentration values. This means that the warmer the waters, the higher relatively the average of chlorophyll-a concentrations. In this study, stations located in the Sulawesi Sea (ST 1, ST 2, and ST 3) have higher average chlorophyll-a concentration, and it coincides with higher average water temperature there (Table 2). Temperature is one of the primary factors which control the phytoplankton physiology, such as growth and photosynthesis rate [32]. In a specified range, increased temperature raises the photosynthesis rate. Hence, the increase in temperature enhances primary production. There is a high correlation between primary production and chlorophyll, so chlorophyll is widely used as a proxy to measured primary production [33]. Besides, the increase of temperature in non-limited nutrient conditions also increases the phytoplankton nutrient uptake [34] [35].

The salinity parameters show both positive and negative influences on the average chlorophyll-a concentration. In more detail, the minimum and average values of salinity show a strong positive impact, while the maximum value indicates a strong negative influence. The negative effect of maximum salinity value on the average chlorophyll-a possibly correlated with salinity stress. In an inevitable increase of salinity concentration, phytoplankton may suffer cellular osmotic pressure, uptake or loss of ions, and effects on the cellular ionic ratio in phytoplankton, so influence the phytoplankton community change [36] [37]. Sriwijayanti et al. (2019) report that the abundance of phytoplankton in the Sangihe-Talaud waters was lower at the station with relatively higher salinity. The strong correlation between nutrients and the DCM in this study possibly correlated with nutrient exploitation by the phytoplankton community. As in this study, the DCM is maintained by nutrient-light co-limitation of phytoplankton growth [38]. The DCM is regulated by more complex factors such as diatom aggregation, sea-ice retreat, eddies, subduction events, and photo-acclimation [38]. The micro-phytoplankton community in area study (Sangihe-Talaud waters) predominated by diatom includes at the surface, thermocline, and the deepwater (600 m) [39] [40] [41] [42]. The diatom is an r-strategist-species (opportunistic) that has high nutrients competitiveness [43]. For example, the diatoms can absorb phosphate 0.5 μmol/day, which is three times higher than dinoflagellates (0.17 μmol/day) [44]. Even the absorption rate of nitrate and ammonium, by diatoms, is ten times higher than dinoflagellates [44]. Hence, as an opportunistic organism, the diatom can exploits nutrients resources as much as possible then grow as much as possible. In the oceans, the nutrient content increases with increasing depth. Consequently, the phytoplankton community, especially diatom, must get to a deeper water column to reach higher nutrients resources. Despite this, it is not that simple due to the light attenuation also limited the shifting of the phytoplankton in the water column. It means the phytoplankton should adjust their position in the water column to get the best deal of nutrients and light. In this study, all DCM was found at the bottom of the mixed layer (Figure 4). Precisely around the commencement of the nutricline zone at all stations. Nutricline is the rapid elevation of nutrients concentration in a certain depth and is a proxy of nutrient supply to the upper mixed layer [22]. Richardson and Bendtsen found the universal relationship between nutrients (NO₃) with the depth of DCM. By numerical modeling, White and Matsumoto (2012) found that the presence of a nutricline influences both the depth and magnitude of the DCM [46]. The distribution of diatoms and coccolithophorids is correlated with the nutricline depth [22].
Figure 5. The Principal Component Analysis of chlorophyll-a and environmental parameters.

4. Conclusion
Based on the average value of chlorophyll-a concentration, we conclude that the Kawio Barat submarine volcano waters were more productive than other stations. This finding seems to be supported by the existence of an active Kawio Barat submarine volcano. Theoretically, the presence of an active submarine volcano enriches the waters with nutrients. So it can support the phytoplankton growth better. We find the nutrients in other locations precisely higher than the Kawio Barat submarine volcano waters. This finding may happen because there is an indicating of upwelling events in other stations. Besides, the Kawio Barat submarine volcano waters were more productive due to having warmer waters than others. The diagram T-S shows the disparity of water temperature between two zones, namely the Sulawesi Sea and Northern Molucca Sea. Sulawesi Sea, the Kawio Barat submarine volcano, is warmer than the Northern Molucca Sea. The Principal Component Analysis (PC) also shows that the average value of chlorophyll-a concentration is more associated with the temperature and salinity than nutrients. Nutrients precisely show a stronger positive influence on the depth of Deep Chlorophyll Maxima (DCM). The DCM appears below the mixed layer near the upper part of the nutricline.

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