



Coastal Acidification as Nutrients Over Enrichment Impact: A Case Study in Ambon Bay, Indonesia

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ABSTRACT

Ambon Bay is a silled bay on Ambon Island consisting of two regions, Inner Ambon Bay (IAB) and Outer Ambon Bay (OAB) that are separated by shallow sill. Ambon bay and its surrounding have economically important ecosystem since the utilization for many activities. The bay is affected by anthropogenic impacts associated with urbanization, climate change, and nutrients over enrichment. The “deep water-rich nutrients” from Banda Sea that enter the bay during Southeast monsoon also contribute to this enrichment as well as the nutrients transport from the land. The high concentration of nutrients increases carbon dioxide level and promotes acidifications. There are literatures about nutrients over enrichment in Ambon Bay, however, little is known about coastal acidification as nutrients over enrichment impact. In order to study the effect of nutrients distribution on the acidity of Ambon Bay, the researchers measured pH and concentrations of nutrients {nitrate + nitrite (N+N) and Soluble Reactive Phosphate (SRP)} from water samples collected in 7 stations on both IAB and OAB during Southeast monsoon. The results showed that in surface water, nutrients concentrations is increased from May to June due to the “deep water flushing” occurrence on May and increased precipitations from May to June. From July to August, the nutrients concentrations on surface layer decreased, due to the decreased precipitations. In column and bottom water, the nutrients concentrations were increased consistently from May to August. While the acidity has a reverse response to the nutrients, when nutrient concentrations increased the acidity was decreased. Statistically, pH was not significantly correlated with the concentrations of nutrients on surface water, but showed significantly correlated on column and bottom water. The results indicated that the distribution of nutrients on column and bottom water might be an important environmental factor affecting the acidification of the Ambon Bay in Southeast monsoon.

Keywords: *coastal acidification, nutrients, Ambon coastal bay, pH, southeast monsoon.*

1. Introduction

In many coastal areas around the world, nutrients over-enrichment is a major environmental problem (Seitzinger et al., 2005; Heisler et al., 2008; Wallace et al., 2014; Zhang and Gao, 2016, Ikhsani et al. 2016). The rapid increase of human activities transport large amount of nutrients from land to coastal areas trough the rivers (de Jonge et al., 2002; Seitzinger et al., 2005). Another reason of nutrients over-enrichment in coastal area is upwelling induced by wind and/or topography (Feely et al., 2008). Upwelling brings the deep water onto surface layer. The characteristic of the deep water was cool, dense, and rich in nutrients. The impact of upwelling is nutrients

enrichment in euphotic area. The high concentration of nutrients in coastal ecosystem promotes algal productivity and reduced oxygen level, but increases carbon dioxide level (Wallace et al., 2014; Aparicio et al., 2016, Zhang and Gao, 2016). Carbon dioxide which enters the waters can form carbonic acid (H_2CO_3) dissociating into bicarbonate ions (HCO_3^-), carbonate ions (CO_3^{2-}), and hydrogen ions (H^+) that can decrease the seawater pH. In addition, some nutrients may exist in the form of weak acid, for instance N may exist as HNO_3 , which may affect the acidity of seawater directly.

The effect of nutrients distribution on coastal acidification may be evidence in Ambon Bay area. Ambon Bay is semi-enclosed bay on

Ambon Island in Moluccas Province, Indonesia. The bay consists of inner and outer region that is separated by narrow sill (about 17 m deep and ½ km wide). The inner Ambon Bay is at average 30 m deep while the outer Ambon Bay opens into Banda Sea. Ambon Bay and its surrounding have several functions and purposes, like fishery and aquaculture areas, port harbor of Indonesian Navy and Water Police, fishery harbor, hot water waste disposal from State Electricity Company, ship docking, recreations and settlements areas (Pello et al., 2014). In Ambon area, the northwest monsoon is the dry hot season while the southeast monsoon is the rainy wet season. Ambon Bay is part of Banda Sea, where the water mass and nutrients distribution in that sea was affected by monsoon. Wyrki (1961) determined that during northwest monsoon from about September to March, occurred water mass sinking in Banda Sea. Meanwhile during southeast monsoon from about April to August, occurred water mass upwelling.

Upwelling in Banda Sea causes the increasing of thermocline up to ± 70 m, and bringing the deep water from Banda Sea to inner bay through tidal upwelling mechanism (Anderson and Sapulete, 1981; Wenno and Anderson, 1984; Zijlstra et al., 1990). The deep water from Banda Sea will sink after through the sill since it was denser and cooler than resident deep water of inner Ambon Bay. This is often referred to as deep water "flushing" (Anderson and Sapulete, 1981). Flushing has important impact of nutrient distribution in Ambon Bay, because it brings the rich nutrient from bottom to surface layer. Besides of upwelling, excessive nutrients from land that are transported to the coastal area at rainy season can cause nutrients enrichment in Ambon Bay (Ikhsani et al., 2016). This condition provided the opportunities to analyze the interaction between nutrients distribution and coastal acidification.

This study aims at determining the vertical profile of temperature, salinity, nitrite plus nitrate (N+N), Soluble Reactive Phosphate (SRP) and pH during southeast monsoon in the Ambon Bay with a purpose of attempting to analyze the interaction between the distribution of nutrients and coastal acidification.

2. Materials and Methods

Sample collection

The survey was carried out during southeast monsoon from May to August 2012.

The sampling stations were arranged as a straight line from inner bay to outer bay. There are 7 sampling stations, 3 stations in inner bay, 1 station in sill and 3 stations in outer bay, as seen in Figure 1. Stations locations were recorded using a Garmin GPS data logger 76CSX type. At each station, the distributions of temperature and salinity were recorded with Compact conductivity-temperature-depth (CTD) recorder model ASTD 687.

During each survey, water samples of outer bay were collected for multiple depths including surface layer (0 m) and water column (10, 25, and 50 m). While for inner bay, that shallower from outer bay, the water samples were collected for surface layer (0 m), water column (10 m and 25 m for station 3, the deepest station in inner bay with 45 m depth) and bottom water of inner bay (0.5 m near the sea bed). Sub sampling collected using Nansen bottle and vertically profiled the water column at seven stations across the Ambon Bay. A total of 25 water samples for each survey were collected using well cleaned polyethylene bottles. The samples were stored in cooler box and refrigerated at 4 °C for further analysis. All the samples were filtered with cellulose acetate membrane filters (Whatman, 0.45 μ m) before nutrients determinations. Concentration of nutrients; nitrite plus nitrate (N + N), and Soluble Reactive Phosphate (SRP) were determined on P2LD laboratory. Additional meteorology data, such as precipitation, has been collected from Meteorology, Climatology, and Geophysics Agency, Ambon.

Analytical method

Nitrite and nitrate was determined by standard pink azo dye method (Strickland and Parsons, 1972). Soluble Reactive Phosphate (SRP) was determined with the standard phosphomolybdenum blue method (Strickland and Parsons, 1972).

The pH values were determined by in situ using a portable pH meter model HI 9126 that provided pH measurements on the NIST scale. Prior to each survey, a three point calibration was conducted on the pH sensor using commercial buffer solution. The vertical profiling of the physical and chemical data carried out using Ocean Data View (ODV) software version 4.6.2.

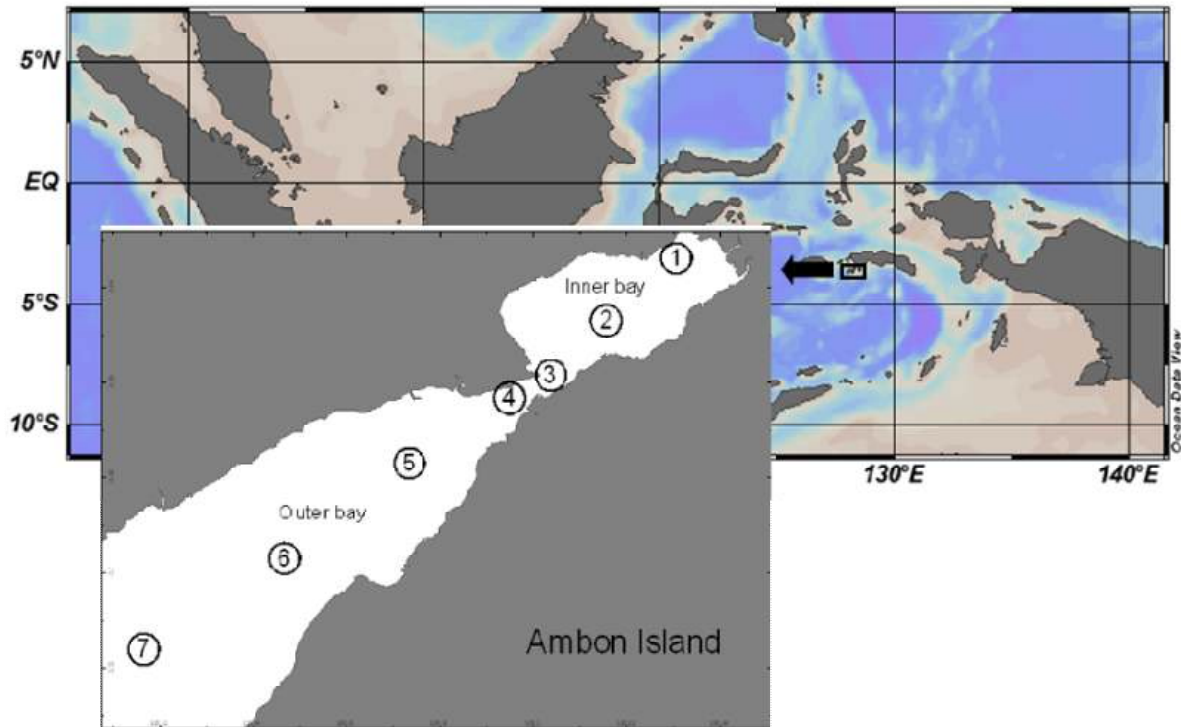


Figure 1. Station map in Ambon Coastal Bay, Moluccas Province, Indonesia

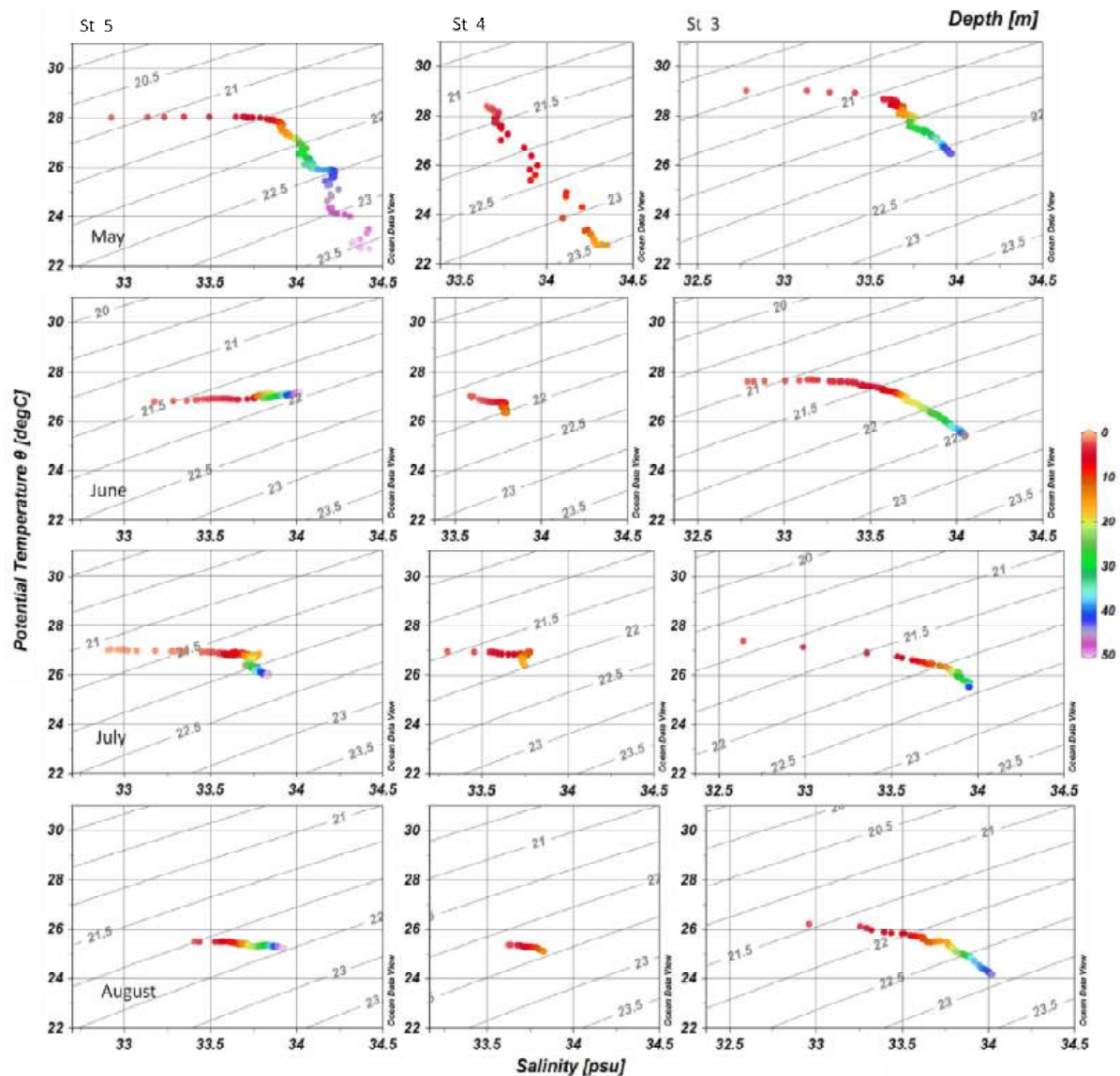
3. Results and Discussion

Seawater mass characteristic during southeast monsoon

Based on the measurement during southeast monsoon in both of inner and outer Ambon Bay, it could be seen that the vertical profile of temperature and salinity changes gradually from May to August as seen in Figure 3. From the temperature-salinity (T-S) diagram on May (see Fig.2), it could be seen that the water mass with high density (salinity > 34 psu) was identified in inner (represented by station no. 3), sill (represented by station no. 4), and outer bay (represented by station no. 5). The high density water mass with salinity > 34 psu was the character of Banda Sea's water mass (Zjilstra et al., 1990). The existence of Banda

Sea's water mass in inner bay showed deep water "flushing" occurrence (Anderson & Sapulete, 1981). The Banda Sea's water mass from outer bay, climbing up the sill and sinking to the bottom of inner bay. The flushing process was replacing resident deep water in the bottom of inner bay.

Based on the measurement of temperature and salinity variability, the authors expect that the deep water flushing occurred only in May. The T-S diagram from June to August showed that water mass in outer bay have lower density than that of inner bay. Therefore, the water mass from outer bay could not replace the deep water in inner bay. In July, the surface salinity of outer bay was very low, due to mixing with fresh water from the river along the coast in Outer Ambon Bay.



Note: St: Station

Figure 2. The Temperature-salinity (T-S) Diagram

Nutrients distribution

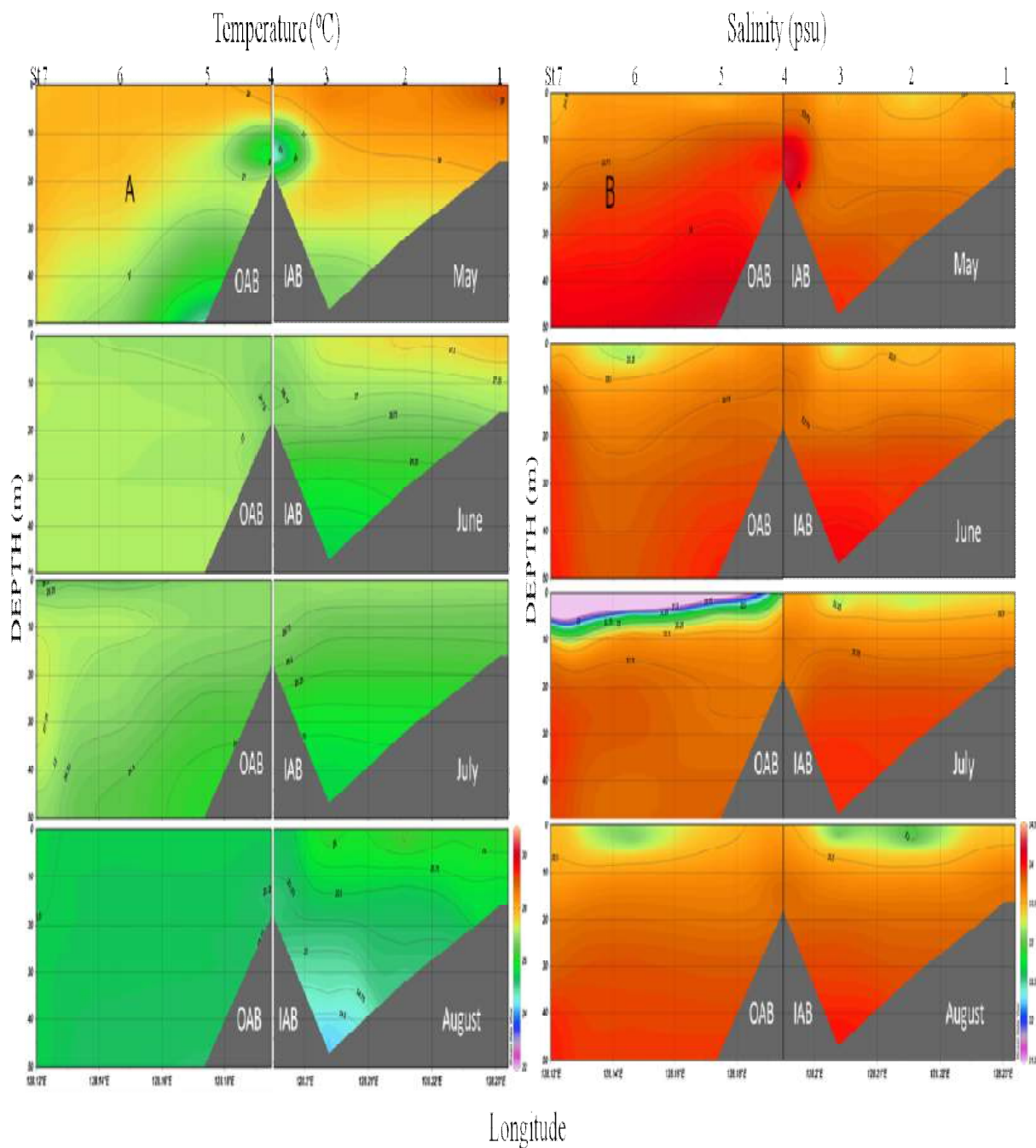
The vertical distribution of both N+N and SRP in Ambon Bay showed low concentration in surface water and increased with increasing depth. Nutrients taken up by marine organism in surface waters and returned to solution as the organism die, sink to depth and decompose (Sarmiento & Gruber, 2004; Cochran, 2014). The vertical distribution of N+N and SRP during May to August in both of inner and outer bay was seen in Figure 4 A. During May survey, the concentration of N+N on surface and column water was in range 2.3 – 52.9 and 10.3 – 51.8 $\mu\text{g L}^{-1}$. From Figure 4A, it can be seen that rich N+N water mass climbs up the sill then sink into the bottom of inner bay, replacing the resident deep water. Based on Figure 3B, this rich N+N

water mass was upwelling water mass from Banda Sea with high salinity character, >34 psu. The renewal deep water caused nutrients enrichment in both of bottom and column water, because the former deep water is displaced upwards and a net outflow will occur in the upper portions of the sill water column (Anderson & Devol, 1973; Anderson & Sapulete, 1981; Gargett et al. 2003).

From May to June, the concentration of N+N on surface layer and water column in both of outer and inner bay was increased to 15.3 – 47.2 and 16.4 – 52.4 $\mu\text{g L}^{-1}$. The highest increasing N+ N concentration occurred in surface layer of stations no.3, from 2.3 to 26.7 $\mu\text{g L}^{-1}$. The surface salinity of this stations was 33.39 psu, it means that N+N enrichments could be influenced more by river discharge

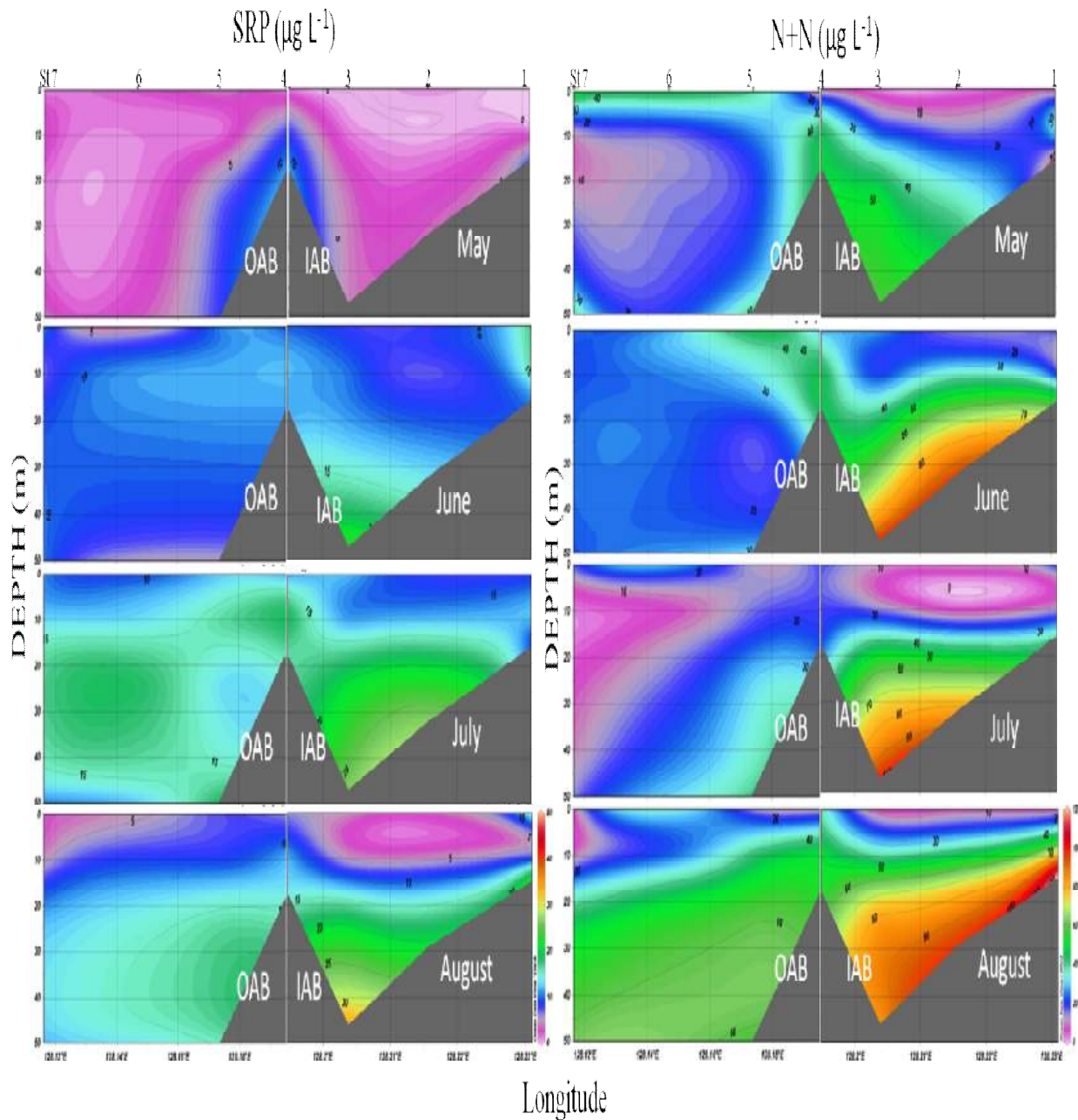
than Banda Sea upwelling. Station 3 was located on Ferry harbor that connected both sides of Ambon Island and to other Islands. Besides that, rivers that were flowed through high population settlements streamed down in

this station. In June that precipitations were higher (1252 mm) than those in May (908 mm). Larger amount of nutrients transport from the land through the rivers and caused enrichments on this stations.



Note: St: Station OAB: Outer Ambon Bay, IAB: Inner Ambon Bay

Figure 3. (A) The Vertical Profile of Temperature (°C) and (B) and Salinity (psu) in Ambon Bay during Southeast Monsoon



Note: St: Station OAB: Outer Ambon Bay, IAB: Inner Ambon Bay

Figure 4. (A) The Vertical Profile of N+N ($\mu\text{g L}^{-1}$) and (B) SRP ($\mu\text{g L}^{-1}$) in Ambon Bay during Southeast Monsoon

In July and August, the N+N concentration on surface water decreased to $11.2 - 29.7 \mu\text{g L}^{-1}$ and $6 - 36.4 \mu\text{g L}^{-1}$. It was influenced by the decreasing of precipitation in June and August became 1157 and 639 mm (Source: Meteorological, Climatological, and Geophysical Agency, 2016). A much wider N+N concentration in water column range of $2.6 - 64.2$ and $9.2 - 85.4 \mu\text{g L}^{-1}$ was occurred in July and August. The concentration of N+N in

bottom water of inner bay increased from May to August with varied from $10.1 - 56.1$ in May, $46.3 - 92$ in June, $22.2 - 94.9$ in July and $52.7 - 116.6 \mu\text{g L}^{-1}$ in August. The highest increasing N+N concentration on bottom water, more than 10 times occurred from May to June in station 1. From May to June, the salinity of bottom water in station 1 was increased from 33.7 to 33.8 psu, and stable up to August. Increasing salinity together with N+N concentration on May

might be caused by flushing process. Another reason were that this station was surrounded by high density settlements, sea grass and mangrove area, many rivers that were flowed through agriculture area also streamed down to this station. Therefore, the high N+N concentration in this station was also caused from mineralization of sea grass and mangrove litter as well as agricultural fertilizer (Sims et al., 1998; Kristensen et al., 2000; Homer & Olsen, 2002, Ray et al., 2015).

The concentration of SRP in surface layer has the same pattern as N+N in surface water, increased from May ($0 - 4 \mu\text{g L}^{-1}$) to June ($3.5 - 17 \mu\text{g L}^{-1}$), but decreased in July ($8 - 12.3 \mu\text{g L}^{-1}$) to August ($3 - 14.9 \mu\text{g L}^{-1}$). The highest increasing SRP concentrations from May to June were found in station 1, which was probably associated with the fact that many rivers flows through agricultural area and transported large amounts of phosphate fertilizer to this station. The concentration of SRP in water column in May to August varied from $0 - 7.9$ in May; $5.2 - 15.3$ in June; $12.1 - 20.8$ in July and $4.5 - 20.9 \mu\text{g L}^{-1}$ in August. Same as N+N, the SRP concentration in bottom of inner bay increased from May to August. The SRP concentration was ranged from $3 - 10.9$ in May, $11.4 - 22$ in June, $9.7 - 25.7$ and $13.4 - 32.7 \mu\text{g L}^{-1}$. From May to August, the highest increasing SRP concentration in bottom water was founded on station 3. The high concentration of SRP could be explained by the higher precipitations in southeast monsoon that caused accumulation in bottom water of station 3. Another reason was no occurrence of deep water flushing by upwelling water mass from June to August. As seen in Figure 4, from May to August the inner bay has higher both of N+N

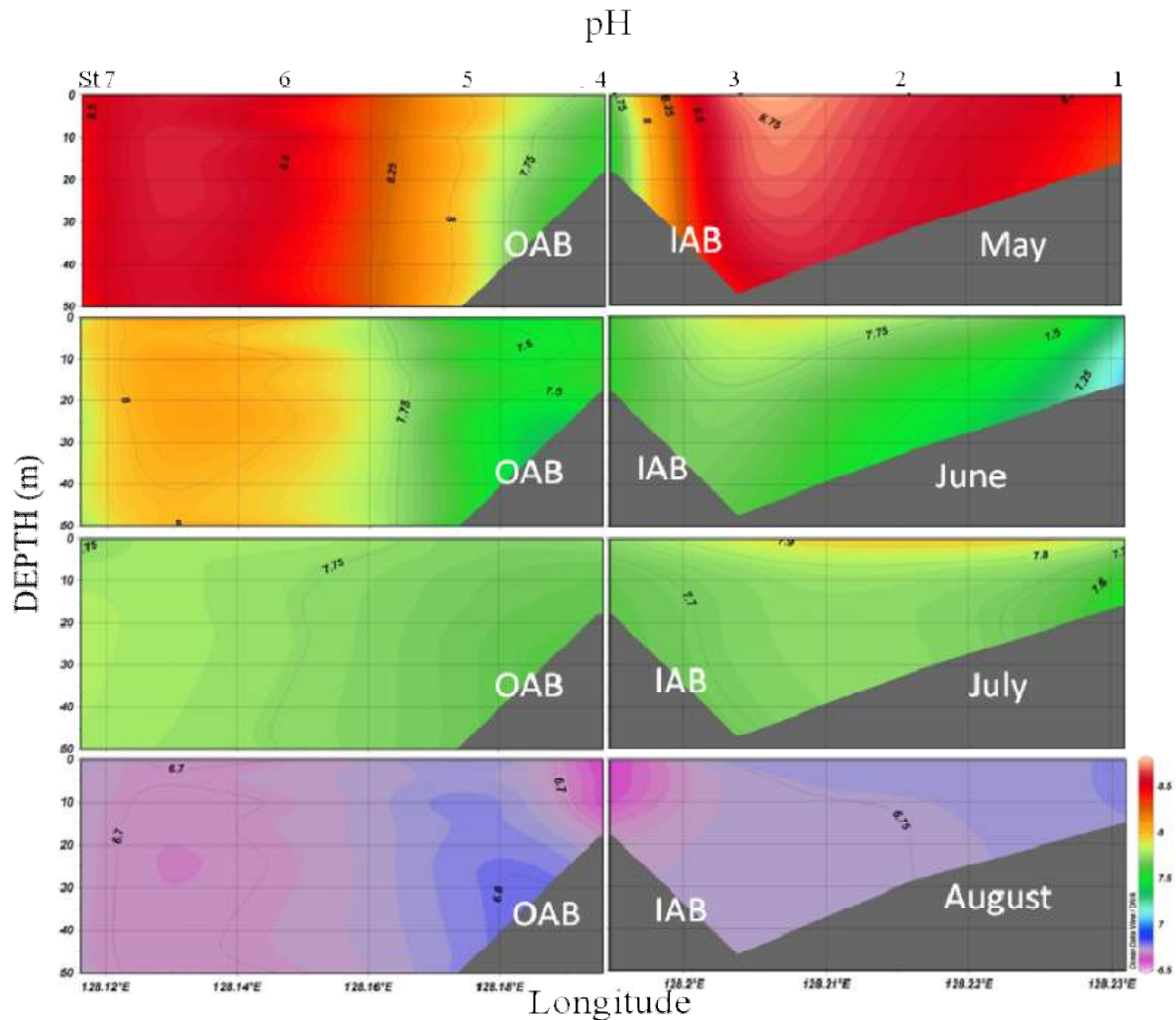
and SRP concentration than those of outer bay. These differences were mainly caused by the existence of sill located between the inner and outer bay that restricts water mixing process (Anderson & Sapulete, 1981; Basit et al. 2012), so that the nutrients accumulation was occurred in the bottom area of inner bay, especially in station 3. Whereas, the "upper sill water mass" can undergo water mass mixing that induced by wind (Ruiz-Castillo, 2016; Disbiolles, 2016). This "upper sill water mass" mixing explained the uniformity of N+N and SRP concentration in both of inner and outer bay.

The acidity (ph) of Ambon bay

In contrast to the increasing nutrients concentration, the acidity of Ambon bay was decreasing gradually during southeast monsoon. The pH value (on NIST scale) from May to August was declined by more than 1.0 pH units in both of inner and outer bay. The pH value in surface layer were varied from $7.71 - 8.64$ in May, $7.32 - 8.02$ in June, $7.72 - 7.96$ in July and $6.62 - 6.78$ in August. In water column, the pH ranged from $7.57 - 8.68$ in May, $7.13 - 8.04$ in June, $7.56 - 7.8$ in July and $6.64 - 6.79$ in August. While in bottom water of inner bay, the pH ranged from $7.56 - 8.58$ in May, $7.09 - 7.64$ in June, $7.52 - 7.69$ in July and $6.7 - 6.77$ in August. It could be seen that pH value in surface layer and water column decreased from May to August. While in bottom layer, pH value decreased from May to June, increased slightly in July and decreased again in August. The slightly increasing pH value of bottom water in July maybe associated with the wide range of N+N and SRP concentration (Zhang & Gao, 2016).

Table 1. The Summary of correlation test between nutrient distribution and acidity

Distribution	Significance	
	N+N	SRP
Surface	0.616	0.097
Column	< 0.001	< 0.001
Bottom	0.048	0.016



Note: St: Station, OAB: Outer Ambon Bay, IAB: Inner Ambon Bay

Figure 5. The vertical profile ph in Ambon bay during southeast monsoon

The pH value of bottom was smallest than column and surface water from May to August. It means that the bottom water was most acidified than another area. This trend could be associated with N+N and SRP concentration that showed highest concentrations on bottom water. To analyze the correlation between nutrient distribution and acidity, the data was tested using SPSS Statistic 17.0 software, the summary of this test given in Table 1. The result showed that no correlation between N+N and SRP concentration in surface water with acidity, but significant correlation in column and bottom water. The acidity of surface water may be mainly caused by atmospheric CO₂ adsorption than CO₂ release from respiration process (Feely, 2010). While for column and bottom water, the enrichment of nutrients during Southeast monsoon may enhance acidification

in Ambon Bay. A common phenomenon that was accompanying acidification by nutrients enrichment is oxygen depletion (Gilbert et al. 2010; Zhai et al., 2012; Wallace et al, 2014). The consequence of nutrient enrichment was algal blooming and stimulated acidification (Smith et al., 1999; Gilbert et al., 2008; Loureiro et al, 2011).

4. Conclusion

In this research, the N+N and SRP concentrations generally increased during southeast monsoon due to the increased precipitations and the influx of "deep water-rich nutrient" from Banda Sea. The influx of "deep water-rich nutrient" from Banda Sea caused deep water flushing in IAB on May. From June to August there is no occurrence of deep water flushing in IAB, therefore the nutrients

enrichment cause by land transport. While the pH value of Ambon Bay decreased during southeast monsoon, indicating a sign of acidifications.

The bottom water of IAB is most acidified area because the existence of sill that restricts water mass mixing. In surface water, there is no correlation between nutrients concentrations and pH value. While the significant correlation showed in column and bottom water. This result indicated that CO₂ uptake from atmosphere may be the main reason of acidification in surface water. For column and bottom water, the high concentrations of nutrients promote high primary production and increased CO₂ level may be the main reason of acidification.

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