Total organic carbon and dissolved organic nitrogen in the upper water column of Keunekai Waters, Weh Island, Indonesia: an overview of mass coral mortality impacts

U J Wisha*1, K Ondara1

1Research Institute of Coastal Resources and Vulnerability, Ministry of Marine Affairs and Fisheries. Jl. Raya Padang-Painan Km. 16 Bungus, Padang, West Sumatera 25245 Indonesia
E-mail: ulungjantama@gmail.com

Abstract. Keunekai waters located in the southern Weh Island are directly bordered by the Indian Ocean. Due to the climatic anomaly occurred in the Indian ocean in 2016 where the temperature raised dramatically, resulting in mass-bleached coral colony. This study aims to evaluate the impact of carbon organic resulted from mass coral mortality on the availability of dissolved nitrogen in Keunekai waters. Non-dispersive infrared – supercritical water oxidation (NDIR-SCWO) and Kjeldahl methods are employed to analyze the total organic carbon (TOC) and dissolved organic nitrogen (DON) that the concentrations respectively ranged 9.67 - 14.19 mg C/L and 0.13-0.53 mg N/L. The ratio of C:N shows the N-relative content which the observation station with higher TOC indicates the N limitation probably influenced by the competition between autotroph biota and microbes indicating the decomposition level variation and the water fertility. In several stations, the N concentration is slightly low in accordance with the higher TOC concentration identified. The relatively high C:N ratio indicates that Keunekai water is in the imbalanced condition.

1. Introduction

Indonesia has a lot of coastal resources that are tremendously rich utilized as marine tourism, aquaculture, capture fisheries and many others [1]. In the opposite side, the over exploration of coastal area induces several major issues such as mass tourism, environmental degradation, and damaged ecosystem as well [2] that become the major factor in elevating the carbon stock in the water that directly influences carbon emission in the atmosphere related to global warming issues [3].

One of the enriched water areas is Weh Island located in the northern Indonesia directly bordered by the Indian Ocean, Andaman Sea, and Bengal Bay where the water condition is heavily influenced by the climatic behavior of the Indian Ocean [4]. In 2016, EL-Nino Phenomenon effects were suffered by Indonesian waters which it triggers high-temperature anomaly resulting in mass-bleached coral reefs in the Indian Ocean [5]. Weh Island becomes one of areas impacted. The most damaged area is Keunekai water where mass coral bleaching is observed. This condition is worsened by the utilization of fish-bomb to catch the coral fishes effortlessly which really contributes to demised coral and damaged ecosystem in this area where the rehabilitation is severe necessary.

The accumulated organic carbon and other nutrients in the coral and sediment can release and dissolve again in the water column [6]. The redemption mechanism is depended on the diffusion process according to its concentration between the water column and the source that is supported by several physical factors such as tidal current and water quality parameters (Salinity, pH, Dissolved oxygen) [7].
The determination of organic carbon is an important part of site characterization and ecological assessment because the presence of organic carbon tremendously influences the binding of chemical compounds including other nutrient compounds (phosphate, nitrate and their derivatives) [8]. C:N ratio can be used for determining the processes occurred in the environment. The mass mortality of corals caused by fish-bombing and the raising of temperature may contribute to the enhancement of carbon accumulation. This study aims to evaluate the impact of carbon organic resulted from mass coral mortality on the availability of dissolved nitrogen in Keunekai waters.

2. Materials and Methods
2.1. Study site
This study was conducted on March 14th-16th, 2017 in Keunekai waters (Figure 1). The sampling point consists of 12 observation stations which represent the area of demised coral and the normal area so that it can be well-compared the organic carbon and nitrogen concentrations in those two areas. The sampling was done twice each station.

![Figure 1. Research location map](image)

Sampling time was conducted during the displacement time of high toward low tidal condition considering the land-sourced carbon and nutrient dominations. Water sampling accomplished using Rosette sampler equipped with Niskin bottles [9]. The samples of water were taken only on the surface due to the relatively shallow water. However, it sufficiently represents the study area.

2.2. Coral cover assessment
Coral cover was observed using Point Intercept Transect (PIT) method. PIT is employed to define the benthic community based on life form developed. Coral community is characterized by life form categories which obviously gives the information regarding coral community morphology [5, 10].

Firstly, the site location was surveyed using manta tow method to make sure the perfect area that will be monitored. PIT survey is applied twice both 3-5 m and 6-10 m. Benthic habitat and the length of the transitional cover which are observed along the transect line (10x10 m) are grouped by their growth form. Percent cover calculation is defined according to [11] as follow:

\[
\text{% cover} = \frac{\text{Total length of life form (cm)}}{\text{The length of btransect (cm)}} \times 100
\]
2.3. TOC and DON analysis
Non-dispersive infrared – supercritical water oxidation (NDIR-SCWO) is employed to analyze the TOC[12]. The organic and CuSO\textsubscript{4} solutions with a certain concentration, super pure water and oxidizer were mixed proportionally using the low-pressure gradient mixer, and then pumped into the reaction tube by a high-pressure metering pump (redox reaction). The liquid after the reaction is cooled by a water bath cooling device and then released to normal pressure by the back-pressure valve. The effluent then flowed into the gas-liquid separation device. The mixed gas of N\textsubscript{2} and CO\textsubscript{2} flowed through an electronic dehumidifier to remove residual water. At last the gas mixture flowed into the NDIR detector to get the amount of CO\textsubscript{2} generated. As the signal intensity of NDIR reflects the concentration of CO\textsubscript{2}. There is a linear relation between TOC and CO\textsubscript{2} generated, as well as between TOC and NDIR signal. Then the amount of TOC in water can be obtained by such a relation.

The dissolved organic nitrogen (DON) is obtained from the Kjeldahl method analysis. Generally, this method of obtaining the nitrogen content uses H\textsubscript{2}SO\textsubscript{4}, K\textsubscript{2}SO\textsubscript{4}, HgO, and CuSO\textsubscript{4}. After that, Na\textsubscript{2}S is added to settling the mercury which the process was running in the alkaline condition by adding NaOH. The nitrogen in the form of ammonia is distilled into the boric acid solution. Then, Ammonia is titrated with standard solution H\textsubscript{2}SO\textsubscript{4} and purple methyl as an indicator[13].

3. Results and Discussions
3.1. TOC and DON concentrations and their possible impact in the water
The highest TOC value is observed at station P5 reaching 14.19 mg C/L, while the lowest one is identified at station P6 reaching 9.67 mg C/L (Figure 2). Station P5 is located in the area of fish-bombing-impacted coral which obviously induces the higher accumulation of carbonate due to the demised coral. The carbon concentration is slightly different in all station with the carbon average reached 12.17 mg C/L. Commonly, in the damaged area, the carbon concentration is relatively higher than the normal area.

![Figure 2. TOC (red) and DON (black) concentrations in Keunekai waters](image)

The concentration of dissolved organic nitrogen (DON) ranges from 0.13-0.53 mg N/L (Figure 4). The higher concentrations of DON are observed at station P6, P7, P9, P10, and P11, whilst the lower concentrations are observed at station P1, P2, P3, P4, P6, P8, and P12 which is located in the damaged area (Figure 1). In the damaged area, the demised coral redounds more organic carbon in the form of CaCO\textsubscript{3} settled in the sediment in which this condition contribute into the reduction of organic nitrogen that is probably influenced by the competition of microbe and autotroph biota.

Based on the comparison (Figure 3), the organic carbon condition influences the organic nitrogen availability that has an opposite condition in all stations, the higher the carbon concentration, the lower the nitrogen concentration even though in the small scale. This condition induces the imbalanced condition in Keunekai waters in which the organic nitrogen is not optimally utilized by autotroph biota due to the lack of ecosystem. Carbon and nitrogen in the water are influencing each other even though they can support the nutrient availability for photosynthesis.

The process of carbon accumulation is also controlled by the water quality condition (Table 1). The levels of dissolved oxygen (DO) ranged from 3.83 up to 5.49 mg/L are categorized into medium
polluted waters [14]. The extremely low level of DO indicates that the activity of microorganism utilizing oxygen to break down the organic matter to become inorganic substances is very maximal [15].

The low salinity and the relatively high temperature influence the nutrient concentration in the water. According to Juneja et al. [16], the nutrient concentration will increase when the salinity value is lower. Temperature conditions are responsible for controlling efficient carbon and nitrogen utilization which may play a key role in photo inhibition known to impact algal growth rate [17]. Total suspended solids (TSS) ranged 12-24 mg/L. The concentration of TSS mainly associated with the level of solid content in the water that disrupts the penetration of light entering the water bodies, resulting in reduced nutrient utilization for photosynthesis by autotroph biota. As a result, the nutrients will enrich in the water [15].

Table 1. Descriptive statistic of water quality parameters in Keunekai waters

| Parameters               | Min | Max | Mean | ST dev |
|-------------------------|-----|-----|------|--------|
| pH                      | 8.3 | 8.43| 8.34 | 0.02   |
| Salinity (‰)            | 30.1| 31.52| 31.1 | 0.33   |
| Dissolved oxygen (mg/L) | 3.83| 5.49| 4.4  | 0.39   |
| Temperature (℃)         | 29  | 30.3| 29.75| 0.22   |
| Total suspended solid (mg/L) | 12 | 24 | 17.2 | 3.59 |

3.2. C:N ratios of Keunekai waters

C:N ratios ranged from 2-11:1 with the mean ratio of 5.8 (Figure 3). A carbon-nitrogen ratio is obtained from the comparison between the mass of carbon against the mass of nitrogen [18]. C:N ratio becomes an indicator for nitrogen limitation of autotroph biota which can determine the main source of the nutrient. If the C:N ratio ranges from 4-10:1, the nutrient mainly comes from sea-sourced, whereas the higher ratio can be determined that the nutrient sources from the terrestrial area[18]. Generally, based on the ratios obtained in Keunekai waters, carbon sources from marine itself. It is clear why the damaged ecosystem has a bigger influence contributing to the carbon stock than the terrestrial sources.

The elevated C:N signature is preserved in the sediment, until another form of diagenesis, post-depositional diagenesis, alters its C:N signature once again. Post-depositional diagenesis occurs in organic-carbon-poor marine sediments where bacteria can oxidize organic matter in aerobic conditions as an energy source. C:N condition is a significant rule controlling the process of nitrogen cycle (denitrification) [20].

![Figure 3. C/N ratios at all observation stations](image)

3.3. C and N limitations and their relationship with the coral cover condition

The composition of coral colony impacted bleaching is almost 35%, pale condition reached 6%, normal condition reached 8% (Figure 4). Whilst, the demised coral determined by (nutrient indicator
alga) NIA and rubble reached 6% and 45% respectively. The highest demised coral colony is observed in Keunekai waters reaching 51%.

Figure 5 shows the correlation between percent coral cover, TOC and DON contents in Keunekai waters are mainly determined by the supply ratios of C:N. A high C content reflects situations in which the high C is available relative to N, in such situation the total C is not necessarily high. Probably, Total organic C availability mainly affects N availability, photosynthesis and biogeochemical cycle mechanisms indicating that C has a special limitation on nitrogen cycle[21].

TOC will increase in accordance with the lower percent cover of coral, whilst, generally, the nitrogen increases when the percent cover is higher (Figure 5). The declination of percent covers triggers the accumulation of carbon in the bottom that induces the nitrogen cycle disruption so that in the area with a higher damaged ecosystem, the nitrogen may decrease due to its cycle disruption [3]. Thus, the N-limitation will predominant. It can be concluded that Keunekai waters are in the imbalanced condition due to the damaged ecosystem.

4. Conclusion
Total organic carbon concentration is relatively higher in the damaged area which induces by the carbon accumulation due to mass mortality of coral ecosystem caused by both anthropogenic pressure and climatic behavior. The ecosystem destruction directly influences the nutrient availability such as nitrogen and its derivatives which is also decreasing in accordance with the higher carbon stock because the organic carbon contributes to ammonification processes so that N and C relate each other. Moreover, the C:N ratio contributes to the decomposition level and the fertility of Keunekai waters. In several stations, the N concentration is slightly lower in accordance with the higher TOC concentration identified. The relatively high C:N ratio indicates that Keunekai water is in the imbalanced condition.

5. Acknowledgments
Acknowledgments and gratitude are given to Research Institute of Coastal Resources and Vulnerability (RICRV) for DIPA budget 2017 for Weh Island research, to the Local government of Sabang, and for those who support the completion of this paper, as well as for every institute which supports to complete the main data.

6. References
[1] Patlis J 2007 Bulletin of Indonesian Economic Studie 43 201-226
[2] Worm B, Barbier E B, Beaumont N, Duffy J E, Folke C, Halpern B S, Sala E 2006 Science 314 787-790
[3] Bauer J E, Cai W J, Raymond P A, Bianchi T S, Hopkinson C S, Regnier P A 2013 Nature 504 61-70
[4] Wisha U J, Al-Tanto T, Ridwan N N H, Dhiauddin R 2018 Jurnal Kelautan Nasional (In press)
[5] Wisha U J, Khoirunnisa H 2017 *International Journal of Civil Engineering and Technology (IJCIET)* 8 725-734
[6] Maslukah L., Wulandari S Y, Yasrida A 2017 *Buletin Oceanografi Marina* 6 (1) 39-45
[7] Warnken K W, Gill G A, Santschi P H, Griffin L L 2000 *Estuaries* 23 647-661
[8] Deming J W, Yager P L 1992 Natural bacterial assemblages in deep-sea sediments: towards a global viewIn *Deep-sea food chains and the global carbon cycle* (pp 11-27) Springer Dordrecht
[9] Pesant S, Not F, Picheral M, Kandels-Lewis S, Le Bescot N, Gorsky G, Dimier C 2015 *Scientific Data* 2 15-23
[10] Miller J, Muller E, Rogers C, Waara R, Atkinson A, Whelan K R T, Witcher B 2009 *Coral Reefs* 28 (4) 925
[11] Annas R A, Muchlisin Z A, Sarong M A 2017 *Biodiversitas* 18(2): 524-529.
[12] Indrayani E, Nitimulyo K H, Hadisusanto S, Rustadi R 2015 *Jurnal Manusia dan Lingkungan* 22 217-225
[13] Chen B, Westerhoff P, Zhang L, Zhu A, Yang X, Wang C 2015 *Critical Reviews in Environmental Science and Technology* 45 249-276
[14] Lee G F, Jones R, Saleh F, Mariani G, Homer D, Butler J, Bandyopadhyay P 1978 Evaluation of the Elutriate Test as a Method of Predicting Contaminant Release During Open Water Disposal of Dredged Sediment and Environmental Impact of Open Water Dredged Disposal Vol II: data report Technical Report D-78-45 US Army Corps of Engineers WES Vicksburg MS
[15] Wisha U J, Maslukah L 2017 *Indonesian Journal of Marine Sciences* 22 37-45
[16] Juneja A, Ceballos R M, Murthy G S 2013 *Energies* 6 4607-4638
[17] Geider R J, La Roche J 2002 *European Journal of Phycolology* 37 1-17
[18] Aschenbroich A, Marchand C, Molnar N, Deborde J, Hubas C, Rybarczyk H, Meziane T 2015 *Science of the Total Environment* 512 296-307
[19] Yoon S, Cruz-Garcia C, Sanford R, Ritalahti K M, Loffler F E 2015 *The ISME Journal* 9 10-13
[20] Doetterl S, Berhe A A, Nadeu E, Wang Z, Sommer M, Fien P 2016 *Earth Science Reviews* 154 102-122
[21] Ciais P, Sabine C, Bala G, Bopp L, Broykin V, Canadel J, Jones C 2014 Carbon and other biogeochemical cycles In *Climate change 2013: the physical science basis* Contribution of Working Group I to Fifth Assessment Report of the Intergovernmental Panel on Climate Change (pp 465-50) Cambridge University Press