Case study

WATER QUALITY STATUS OF RIVER DONAN DUE TO OPERATIONAL REFINERY PERTAMINA UNIT IV CILACAP-CENTRAL JAVA-INDONESIA

ABSTRACT

Objective:Indonesian State Oil Company processes crude oil into fuel oil, non-fuel fuel and petrochemical, this activity produces waste that allows pollution of the Donan river. herefore, this study aims to analyze the quality of Donan streams based on water chemical - physical quality, and the plankton and benthos diversity conditions, due to the impact of waste discharged from the installation of wastewater treatment units from cilacap state oil companies.

Methodology: This research was conducted by analyzing water samples with Atomic Absorption Spectrophotometer method. Water sampling is done at point 2 sampling points is at sampling point A = holding basin output 39 and B = holding basin output 66 - 49.**Results**: Based onBiological Oxygen Demand (ppm) analysis between 5.5 ppm - 7.2 ppm. Chemical Oxygen Demand concentration (ppm) between 33.6 ppm - 33.7 ppm. While the concentration of Dissolved Oxygen (ppm) between 6.0 ppm - 5.9 ppm. The results of heavy metal chromium analysis with concentrations between 0.04 ppm - 0.05 ppm. Free chlorine concentration with concentration of 0.04 ppm - 0.05 ppm. While the concentration of H_2S was 0.2 ppm . and the fluoride concentration was 0.88 ppm - 1.01 ppm. Based on the quality standards stipulated by Regulation of the Minister of Environment No. 19 of 2010 and Regional Regulations of Central Java, No. 5 of 2012 shows that the Donan river on the verge of polluted. Plankton analysis was found as the dominant species of *Coscinodiscus sp* and *Nitzschia sp* which is a bio-indicator of pollutant.the waters are contaminated lightly

Keywords: Biological Oxygen Demand,Dissolved Oxygen, Chemical Oxygen Demand, Atomic Absorption Spectrophotometer *Nitzschia sp, Coscinodiscus sp*

Competing Interests: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

Comment [A1]: donan's front word has been replaced by Donan

Comment [A2]: mg / L has been replaced with ppm

INTRODUCTION

Oil and Gas Refinery Unit is an Indonesian owned company located in cilacap city. Thecompany is processing crude oil into petroleum and petrochemical fuel. In the process would produce waste that could disrupt the ecological balance to the surrounding environment, especially the Donan river (Directorate General of Water Resources 2015).

The entry of the remaining production can cause disruption to the river's ecological system.The oxygen content will decrease in Donanriver waters bodies, which means the dissolved oxygen content and the amount of oxygen needed to oxidize organic matter are also reduced. (Directorate General of Water Resources 2015).Pollution waters is the entry of pollutant materials into water bodies due to human activities, so the quality of the waters to some extent causes water can not function in accordance with its appointment. From the formula can be that. Thereforesaid that pollution waters is a decrease in water quality due to the entry of pollutant components of human activities or natural processes, thereforethe water is not feasible or even disrupt its utilization. (Government of the Republic of Indonesia, 2001) `

Biological components (Dissolved Oxygen, Biochemical Oxygen Demand nd Chemical Oxygen Demand) are often used as indicatorsthereforechanges in water quality. Similarly, biological components can adapt to occupied environments to be bio-indicators of aquatic environments.Benthos is one of the organisms that can be used as bio-indicator because it has three properties that are very helpful. in indicating the level of pollution waters , namely: a) Has a different level of sensitivity to various types of pollutants and provide rapid reactions to changes that occur. b) Have a low mobility , so it is very easily influenced by in the circumstances surrounding environment. c) Easy to be catch and identified.Therefore, these indicators are often used to assess quality of river waters(Wilhm, J.L.1975)

Benthic invertebrates are one of the groups of animals that can survive in a bad environment and where pollution buildup of waterthereforе, this group of animals other than a component to balance the aquatic animal community, can also be used as an indicator of water quality of aquatic.. Similarly plankton is a marine organism whose existence can be serve as an indicator of changes in biological quality of river waters. Plankton which has the nature of always moving can also be used as indicators of pollution waters. It is therefore the diversity and dominance of plankton on river waters is very important. The diversity of plankton and benthos shows the level of river water quality, the higher the diversity of plankton and benthos mka the better the quality of the water (Shuh-Sen Young et al., 2014)

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Oil and Gas Refinery Unit is an Indonesian owned companyin accordance with the EPA Standard Industry Classification can be defined as a company engaged in producing gasoline, kerosene, distillate fuel oil, spent fuel oil, and lubricants, by fractionation, crude oil refining, unfinished petroleum derivatives redistilation. The Environmental Protection Agencyis also considering and selecting the Petroleum Refining category for further review as it ranks fourth highest among all point source categories for both toxic and non-conventional pollutants. Ha is possible to contain vanadium, mercury, and selenium, and also affects the composition of Biochemical Oxygen Demand and Chemical Oxygen Demand on river flows (Wilhm, J.L. 1975). Similarly, research on the oil company Cilacap needs to be in-depth research in assessing the impact on the water quality of the Donan river. The Donan river body is the final disposal of the Pertamina crude oil processing plant. (Mitra Adi Pranata, 2015). The environmental aquatic components expected to be affected by the development of the Wax Unit Plant. Aquatic ecological limits taking into account potential spreading of waste water spill during transport to vessels and mixing the discharge of liquid waste from activities with the Donanriver waters bodies. The waters in the study area, including the type of tidal force and semi-diurnal movement pattern that is currently in the tidal period with the current flow of waters of the southern Donan river.The main river that flows in the research area is the Donan River which has a small gradient and is affected by tides. The influence of sea water can reach as far as 5 km upstream. This pattern is influenced by local rainfall and the addition of water from sea to river. even in Donan rivers often show puddles. Free ground water is present in very unfragmented quarter deposits that lead to high graduation rates(Boyd, C.E. 1990.)

The River pollution is a situation where the ecological conditions become unbalanced so that the water function changes and does not does not regulate its function.Based on Government Regulation no. 20/1990 on pollution waters control that pollution waters is the entry or the entry of living creatures, substances, energy and other components into the water by human activities and the quality of the water down to a certain extent which causes the water no longer function in accordance with the appointment and utilization. (IndonesianGovernment Regulation, 1990). This causes changes in bio indicators in the river, among others, changes in Dissolved Oxygen conditions, oxygen demand in water, chemical oxygen demand and plankton-benthos diversity index.Among others, benthos because it has three properties that are very helpful in indicating the level of pollution of waters, namely:a. Has a different level of sensitivity to various types of pollutants and provide rapid reactions to changes that occur, b. Have a low mobility , so it is very easily influenced by in the circumstances surrounding environment and easy to be catch and identified. (Onyema, I.C 2013)

Dissolved oxygen is needed by organisms in the metabolism process, this is because with the decrease of oxygen content in water causes the process of catabolism of organic material by organism becomes disturbed. The result of aerobic imperfect catabolism will turn into anaerobic to produce toxic compounds such as H_2S and NH_4.(Christy E, et al. 2013).The need for Oxygen (BOD_5) is the amount of oxygen required by organisms in the aerobic metabolic process, whileChemical Oxygen Demand is the chemical oxygen content, required fordegradation of organic material by chemical reaction.

Chemical Oxygen Demand can also be defined as a parameter to estimate the amount of organic material present in water and utilized by organisms in the process of catabolism of organic matter into energy.Based on the UNESCO / WHO / UNEP (1992)The Biological Oxygen Demand (BOD5) content is allowed to drink water and the maintenance of living organisms ranges from 3.0 ppm to 6.0 ppm. While based onministerial ministerial decree number 51 / Ministry of Environment and Forestry / 10/1995 that the Biological Oxygen Demand (BOD_5) value for quality raw wastewater for industrial purposes Group I is 50 ppm and Group II was 150 ppm andChemical Oxygen Demandvalues for non-contaminated waters have a value of <20 ppm.

The Plankton or benthos can be used as bio-indicators of water quality, the presence of certain species may indicate the conditions of pollution levels, therefore if there is a change of environmental condition. The plankton or benthoswill beadapt to environmental changes.The water quality index is closely related to the saprobity index as measured by the number of species (plankton and benthos) found, as each species (plankton and benthos) is a constituent of a particular saprobic group that will affect the value of water saprobitas

Based on the saprobik index divided into 3 categories are oligosaprobik, mesosaprobik and oligosaprobik. . The Oligosaprobik category is a classification of waters that have not been contaminated or contaminated lightly, commonly found species from the Class of Chlorophage (Trishala K. Parmar, Deepak Rawtani & Y. K. Agrawal, 2016). The mesosaprobic category is waters with mild to moderate contamination levels, its levers are inhabited by *Spirogyra sp, Desmidium sp, Melosira sp, Spyrogira sp, Rhizosolonia sp., Nitschia sp., Oscillatoria sp. Nitzschia actinastroides and Spirulina sp,* while the Polysaprobic waters category, are more inhabited by Spirulina sp of the genus of*Chrysophyceae* (Onyema, 2013 and Edward and David C, 2010).

This study aims to determine the condition of Donanriver waters before and after the project footprint of State Oil Company, so it can be an effort to manage and monitor the environment in the area. especially if the area will be developed in the future.

Comment [A5]: In line 126: Please divide this sentence to two sentences as follows:
... in the process of metabolism. Absence..... . In addition, move "interrupted" after water and delete causes..... Then, this sentence will be: Absence of oxygen in water interrupted metabolic process

Comment [A6]: •In line 129: Please write aerobic not Aerobic.

Comment [A7]: • . In line 132: please delete "or water which is

Comment [A8]: •In line 133: please move maximum to be between the and content

Comment [A9]: •In line 143: please do not use plankton or benthos type and use species or genera

Comment [A10]: • . In line 148: please delete "are the spirogyra and desmidium genera"
•In line 150 - 151: please delete divisions of algae and move Nitzschia actinastroides to be between spirogyra sp, and Rhizosolonia sp.,
•In line 152: please delete "the" before Bacillariophyceae and "class" after Bacillariophyceae.
•In line 153: please rewrite saprobic as not italic and write cyanobacteria instead of Chrysophyceae.

APPLICATION METHODS IN SAMPLE

1. The sampling has been done on December, 2017. The onsite temperature were 28℃, with air pressure 765 mmHg, humidity 74.4 %– 78.8%. The wind speed were 0.4 m/s – 1.3 m/s with northwest to soutwest direction.
2. Water sampling is carried out at two sampling points, at a point of sampling (A) near the North Holding Basin outlet and at sample point B near Unit 49 and 66 Holding Basin outlets. The exact location is shown in Figure 1. The sampling methods for surface water qualitywere based on Indonesian National Standard (SNI) No. 06-6989.57:2008 of The Methods of Surface Water Sampling. The analysis of heavy metal content was used Atomic Absorption Spectrophotometry Method (Varian, 2015)and whileTotal Suspended Solid (TSS)analysis was used gravimetric method (Indonesian National Standard. 2017, Letter,Teeter and Donnel. 2003)
3. Sampling of plankton and benthos is done at the same point.The fitoplankton and zooplankton sample were taken using plankton net with mesh size of 30-50 µm for fitoplankton and 0.2 mm for zooplankton. Then, the sampel were preserved with 4-5% formalin solution (Goswami, S.C., 2004). The identification of planktonwere usedidentification key such as Bold & Wynne (1978)and APHA (1992)and benthos sample were taken by grab sampler. The sediment that had been taken were sifted in water by 5 mesh sieve (254mm). The filtered material then preserved by 10% formalin solution that had been added with coloring solution. The sample were identified by identification key.The plankton and benthos that had been identified then analyzed with standard Shanon-Wiener diversity index.

Figure 1. Below shows the sampling points of surface water, plankton and benthos, as follows:

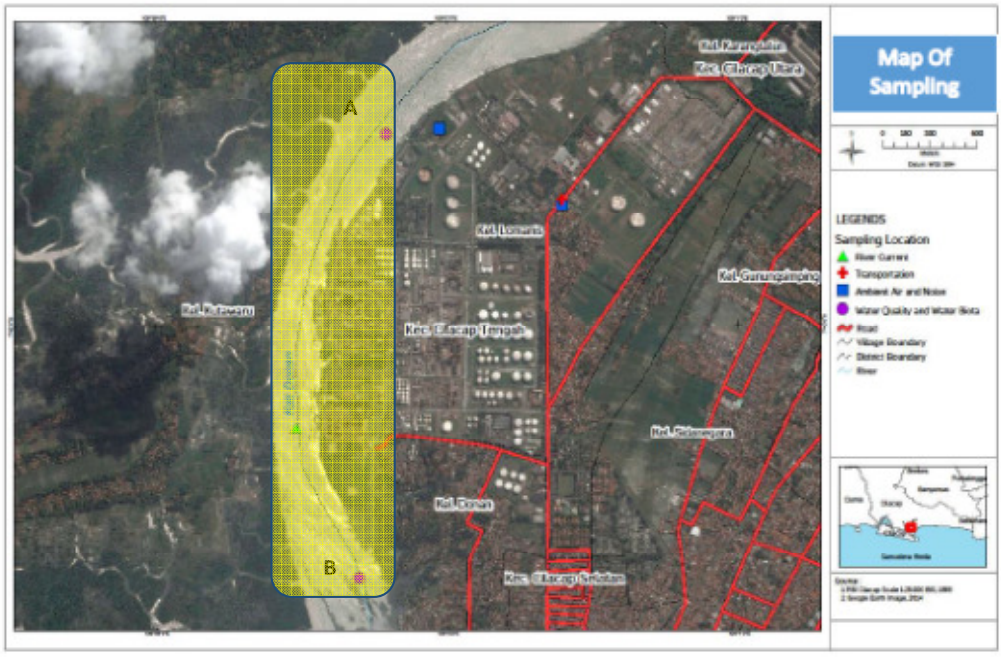

Figure 1. Water Sampling Point, Plankton and Benthos (Sampling A = Donan River,near outlet of north Holding Basin and Sampling B = Donan River, near outlet of holding Basin 66 And Holding Basin 49)[2]

RESULTS AND DISCUSSION

Based on the analysis results Measurement of water quality is done in 2 locations as follows:

Table 1. Water Quality Measurement Data (Mitra Adi Pranata, 2015)

No	Parameter	Unit	Sampling Location		Water Quality Criteria Based on Maximum Class Level (PP No. 82/2001)			
			A (sampling before project)	B (sampling after project)	Class I	Class II	Class III	Class IV
	I. PHYSICS							
1	Temperature	℃	31.7^0	31.9^0	Deviation+/- 3	Deviation +/- 3	Deviation+/- 3	Deviation+/- 3
2	Dissolved Residue	ppm	15,752	11,916	1,000	1,000	1,000	1,000
3	Suspended Residue	ppm	22	32	50	50	400	400
	II. CHEMICAL							
1	pH	-	7,9	7,8	6 - 9	6 – 9	6 – 9	6 – 9

2	BOD	ppm	5.5	7.2	2	3	6	12
3	COD	ppm	33.7	33.7	10	25	50	100
4	DO	ppm	6.0	5.9	6	4	3	0
5	Total Phosphate as P	ppm	< 0.001	< 0.001	0.2	0.2	1	5
6	NO3 as N	ppm	0.018	0.161	10	10	20	20
7	Arsenic (As)	ppm	< 0.003	< 0.003	0.05	1	1	1
8	Cadmium (Cd)	ppm	< 0.010	< 0.010	0.01	0.01	0.01	0.01
9	Chromium (Cr +6)	ppm	0.004	0.005	0.05	0.05	0.05	1
10	Copper (Cu)	ppm	< 0.010	< 0.010	0.2	0.2	0.2	0.2
11	Lead (Pb)	ppm	< 0.030	< 0.030	0.3	0.3	0.3	1
12	Mercury (Hg)	ppm	< 0.001	< 0.001	0.001	0.002	0.002	0.005
13	Zinc (Zn)	ppm	< 0.001	< 0.001	0.05	0.05	0.05	2
14	Cyanide (CN)	ppm	< 0.002	< 0.002	0.02	0.02	0.02	-
15	Fluoride (F)	ppm	0.88	1.01	0.5	1.5	1.5	-
16	Nitrit as N (NO_2)	ppm	< 0.001	< 0.001	0.06	0.06	0.06	-
17	Free chlorine	ppm	0.02	0.02	0.03	0.03	0.03	-
18	Sulfur as H2S	ppm	< 0.002	0.002	0.002	0.002	0.002	-
	III. ORGANIC CHEMICALS	ppm						
1	Oil and fat	ppm	250	500	1000	1000	1000	-
2	Detergent as MBAS	ppm	12	21	200	200	200	-
3	Phenol compounds as Phenol	ppm	< 1	< 1	1	1	1	-
	IV. MICROBIOLOGY							
1	Faecal Coliform	number/100 mL	330	270	100	1,000	2,000	2,000
2	Total Coliform	number/100 mL	330	270	1,000	3,000	10,000	10,000

Description: ource: Primary Data Analysis Result, 2014
A = Donan River basin holding output 39
B = Donan River basin holding output 66 and 49

a) First class, water which can be used for drinking water, and / or other designations that require the same water quality as that purpose;
b) Secondary classes, water which may be used for recreational water facilities, cultivation of freshwater fish, farms, water to irrigate crops, and or other designations that require the same water quality as those uses;
c) Class three, water whose designation may be used for the cultivation of freshwater fish, farms, water to irrigate crops, and or other designations that require the same water quality as those uses;
d) Class four, the water of which the designation may be used to irrigate crops and / or other designations which require the same water quality as those uses

Based on the analysis of the water sample then some parameters have exceeded the specified limit is are as follows : Biological Oxygen Demand(ppm) value range 5.5- 7.2 ppm, Chemical Oxygen Demand (ppm) value range 33.64- 33.73, a.Dissolved Oxygen(ppm)value range 6.01-5.90 ppm, Fluoride (ppm) value range 0,878 -1,007 ppm while the other parameters are still below the specified threshold base on Government of the Republic of Indonesia, 2001. Indonesia Government Regulation No. 82 of 2001 on Water Quality Management and pollution waters Control . (Indonesia Government Regulation, 2001)

a. Dissolved Oxygen

The need for dissolved oxygen in the waters of the Donan river will increase as the oxygen demand of water organisms increases to metabolize organic matter. Therefore, an increase in organic matter will increase the oxygen demand in Donan river waters. The quality of Donan river waters on Dissolved Oxygen parameters are classified as mild contamination streams, based on measurement results show that a. Dissolved Oxygen(ppm) has a value between 6.01 - 5.90ppm (Indonesia Government Regulation, 2001)

b. Biochemical Oxygen Demand and Chemical Oxygen Demand

Biological Oxygen Demandcondition is very related to the content of Dissolved Oxygen inwaters, this is linear,If Biological Oxygen Demandneeds increase then dissolved oxygen will also rise. Biological Oxygen Demand is the Oxygen Needs required by all biological activities in water. Biological imbalances in the waters cause water to become polluted (APHA, 1992). The higher the Biological Oxygen Demand requirement, the worse the water conservation. also according to lee *at al* (1978)Biological Oxygen Demandvalue 5.53 ppm - 7.19 ppm included in the range of 5 ppm -15 ppm waters with fairly polluted criteria. The Chemical Oxygen Demand number is a measure for water pollution by organic substances that can be oxidized naturally through microbiological processes, and result in reduced oxygen in water (Poole, R.W., 1974) . The**Chemical Oxygen Demand**value is always higher than the Biological Oxygen Demand value. The differences between the two values Biochemical Oxygen Demand and Chemical Oxygen Demand are caused by many factors such as chemicals that are resistant to biochemical oxidation but are not resistant to chemical oxidation, such as lignin, (Environmental Protection Agency, 2001)

Based on the analysis withBiological Oxygen Demandparameter, the Donan river is included in the category of medium polluted river (Government Regulation No. 82/2001)**,** While based on the analysis with Chemical Oxygen Demand parameters then the Donan river with Chemical Oxygen Demand value : 33.64 ppm – 33.73 ppm (Table 1) , included in the category of mild contaminated streams that are class 3 categories based on government regulations on the quality of river waters(standard 50 ppm - 100 ppm).

c. Flouride

Based on Indonesia Government Regulation no. 82 of 2001 on the Management and Control of Water Quality for First Class Water Pollution that is water that can be used for drinking water requires maximum permissible fluoride level of 0.5 ppm. Effect of

fluoride may be detrimental to health if at high exposure, Fluoride compound mechanism in the body it is possible to inhibit nerve impulses and inhibit resistance chains so as to cause necrosis, if fluorescent fluids range from 3 ppm to 10 ppm (WHO, 2004)

Based on the measurement results that the content of fluoride from the Donan flow is in the range of 0.88 mg - 1.01 ppm included in the category of mild contamination therefore the waters of the Donan river belonging to Class 1 category is mild contamination therefore water category can be used as raw drinking water source after cooking (Chinoy, NJ , et al, 1994and Government of the Republic of Indonesia, 2001)

d. Plankton and Benthos

The quality of Donan river can be known based on the plankton diversity index and benthos. The plankton diversity index is the ratio value of the number of an individual of each type to the total number of individuals of all species found. The plankton diversity index is the ratio value of the number of an individual of each type to the total number of indi- viduals of all species found. The diversity index (H) represents the species diversity of plankton and benthos inhabiting a community, where the value of diversity is closely related to the small number of species present in the community denoted by H.

Plankton and benthos are organisms that can be used as bioindicators of water pollution, therefore plankton and benthos sampling are important parameters.(Onyema, I.C 2013). Sampling of plankton and benthos was conducted at the same location as water quality sampling. Sampling is done at two points, namely the Donan River output from North Basin Holding, and Donan River output from Holding Basin Units 66 and Unit 49. Table 2 shows plankton and Benthos sampling results in waters around the study area as follows:

Tabel 2. Plankton Analysis in Donan River Waters(Mitra Adi Pranata, 2015 and Kathleen A. Nolan and Jill E. 2005)

No	Species (Type)	Sampling after Project (ind/L)	Sampling before Project (ind/L)
1	*Asterionella sp*	1	-
2	*Biddulphia sp*	-	1
3	*Chaetoceros sp*	2	9
4	*Codonellopsis sp*	3	-
5	*Coscinodiscus sp*	3	79
6	*Cyclops sp*	64	6

7	*Nauplius sp*	76	80
8	*Nitzchia sp*	1	-
9	*Peridinium sp*	2	39
10	*Thalasiothrix sp*	-	2
	Number of types	8	7
	Number of individuals	152	216
	Index of diversity (H)	1.05	1.35
	Index dominance	0.49	0.31
	Uniformity index	0.21	0.25

Source: Primary data analysis results, 2014

Water quality based on plankton and benthos diversity is calculated by using the shannon winner diversity index as follows (Kathleen A. Nolan and Jill E. 2005)

$H = - \Sigma \, pi \ln pi$

Information:
pi = comparison of the number of individuals of a type with the whole type
The pollution index is divided into four categories:
> 2.0 = Unaffected
2.0 - 1.6 = Pure Light
1.5 - 1.0 = Medium Medium
<1.0 = Seriously Weight

Most of the identified plankton are diatoms. Some types of diatoms can be used as environmental bioindicators. Type *Coscinodiscus* is a type of plankton that can survive in waters that contain lots of calcium while the type of *Nitzchia* can survive at high H_2S levels. From the result of measurement of water quality of H_2S parameter shows the value of 0.002 ppm and has been on the threshold of water quality standard for class I, II and III. The value of the diversity index shows that the quality of the waters is contaminated lightly therefore the plankton community in the waters is quite good. The stability of the plankton community is supported by a dominant index value ranging from 0.114 to 0.156. Based on shannon winner diversity index indicating that no species dominates other species therefore the plankton community structure becomes stable (Onyema, 2013)

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Benthos are organisms that live in the bottom of the water (substrate) either sleazy, creep or dig a hole. Bentos live in sand, mud, rocks, broken corals or dead corals. The aquatic substrates and depths affect the pattern of dispersal and functional morphology as well as the behavior of benthic animals. This is related to the characteristics and types of food benthos. Bentos is an organism that lives on the seabed or river either attached to sand or mud. Some examples of bentos include

shellfish, sea urchins, starfish, sea whips, coral reefs and others. Animals bentos live relatively settled, so good used as a guide of environmental quality, because it is always in contact with waste into its habitat(Ernest Hodgson, 2004)The result of bentos analysis in the study area is presented in table 3 below:

Table 3. Bentos Analysis Of Sampling at DonanRiver(Mitra Adi Pranata, 2015)

No	Species (Type)	Sampling after Project (ind/L)	Sampling before Project (ind/L)
1	*Macoma sp*	4	6
2	*Macula sp*	4	2
3	*Prothothaca sp*	2	4
4	*Tagelus sp*	4	4
	Number of types	4	4
	Number of individuals	14	16
	Diversity index	1.35	1.32
	Dominance index	0.19	0.14
	Uniformity index	0.51	0.48

Source: Primary data analysis results, 2014

According to Lee*, et.al*, (1978) water quality criteria associated with the Sannon winner Diversity Index are: (<1.0) highly polluted; (1.0 - 1.5) is sufficiently polluted; (1.5 - 2.0) is lightly contaminated, and; (> 2) has not been polluted. Based on benthos analysis, sample diversity index A = 1.35 and sample B = 1.32 indicating that benthos diversity index in Donan river is mild-moderate contaminated category (**Lee, C.D et al. 1978)**

The condition of waters in the mild-moderate category of contamination is usually dominated by shrubs (bivalves) that live in mud substrate and sandy mud, because their shells (bivalves) are able to utilize the remaining organic material as a source of energy. Therefore, bivalves may be used as an indicator of bio-water contaminated with organic matter under moderate-to-moderate category (Kaushik Gupta*et al*, 2015)

CONCLUSION

Research with title Water Quality Status of River Donan Due To Operational Refinery Pertamina Unit IV Cilacap-Central Java-Indonesiaindicates that the Pertamina Refinery Operational Activity of IV Cilacap has no significant impact on the quality of Donan river waters when viewed from chemical, physical and biological reviews. the Donan river is still in the category of mild to moderate contamination.

Comment [A12]: Has been fixed

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