

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

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Authors' contributions

This work was carried out in collaboration between both authors. Author SI designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SI and PSO managed the analyses of the study. Author PSO and INA managed the literature searches. Both authors read and approved the final manuscript.

ABSTRACT

Objective: State Oil Company of Indonesia - Unit IV Cilacap Refinery which process crude oil into fuel oil, non-fuel and petrochemical fuel, the activity produces waste that will make possible contamination on the Donan river body. Therefore this study aims to analyze the quality of donan rivers due to the impact of waste discharged from the installation of waste water treatment plant unit IV of the State Oil Company

Methodology: This research was conducted by analyzing water samples with Atomic Absorption Spectrophotometer method. Water sampling is done at point 2 sampling points that is A = holding basin output 39 and B = holding basin output 66 – 49.

Result: Based on the analysis of BOD (mg / L) between 5,530 (mg / L) - 7,188 (mg / L). The concentration of COD (mg / L) between 33.64 (mg / L) - 33.73 (mg / L). While the DO concentration (mg / L) between 6.01 (mg / L) - 5.90 (mg / L). The results of heavy metal analysis detected chromium with a concentration of between 0.04 ml / L - 0.05 ml / L. Free chlorine concentration with concentration of 0.04 ml / L - 0.05 ml / L. H₂S concentrations +/- 0.2 (mg / L) and Fluoride concentrations between 0.878 (mg / L) - 1.007 (mg / L). Based on the quality standard set by the Government in Per. Men. LH No. 19 of 2010 and the Regional Regulation of Central Java. No. 5 of 2012 that the Donan river on the verge of polluted medium. The plankton analysis was found to be the dominant species of *Coscinodiscus sp* and *Nitzschia sp* which is a pollutant bioindicator

Keywords : Biological Oxygen Demand (BOD), Dissolved Oxygen (DO), Chemical Oxygen Demand (COD) Atomic Absorption Spectrophotometer (AAS), *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.

INTRODUCTION

Refinery Unit Oil and Gas, Mining Company IV Cilacap is one of Indonesia's state-owned companies that process crude oil into petroleum and petrochemical fuel. In the face of the challenges of the world's increasingly competitive oil processing industry, innovation is needed to develop new technologies to produce better products, in addition to the need to apply the cleaner industry and not negatively affect the environment. The impact of these activities is very necessary to monitor and manage well, so as not to cause environmental damage, especially in Donan river water bodies exposed to direct refinery activity. ⁽²⁾

Location Unit of Refinery (IV) Cilacap located on Donan River with length 19,5 km. The Donan River is a river mouth bordering the sea estuary of the Indian Ocean so that it is hydrogeologically influenced by freshwater and seawater conditions. Donan River serves as a natural drainage channel and a network of water transportation lines and various companies located in this region, therefore Donan river is very important for the surrounding community. The introduction of organic and inorganic materials due to refinery industry activities and domestic activities can cause ecological imbalances in Donan river water bodies ^(2, 22). Which allows the carrying capacity of the environment to be unbalanced, resulting in increased pollution load. Around the location of Plant Wax Unit (IV) State oil company, the Donan River characteristic has been affected by the hydrocarbon condition in the water body and the water level of the river will vary according to tidal conditions. The direction of river flow is also influenced by the current pattern of Cilacap marine waters. The environmental components expected to be affected by the development of the Wax Unit Plant in this case are aquatic components. 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 Donan River water bodies. In 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 this sea water can reach as far as 5 km upstream. This pattern is influenced by local rainfall, addition of water from river to river rivers Donan is not so great, even in rivers often show marsh or puddles. Free groundwater is present in very unfragmented quarter deposits leading to high graduation rates. ⁽²⁾ River pollution is a situation where the ecological conditions of attachment are so unbalanced that the water function changes. Based on Government Regulation no. 20/1990 on Water Pollution Control that "water pollution 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 ⁽⁵⁾, it causes changes in bio-indicators in the river, among others, changes in the condition of dissolved oxygen, the oxygen demand in the water, the demand for chemical oxygen under conditions of diversity of water and plankton-benthos. dissolved oxygen (oxygen) oxygen is needed by the organism in the process of metabolism absence of oxygen in water causes metabolic process is interrupted, so that the organic solute is not degraded completely, this causes metabolic processes become anaerobic and produce toxic compounds such as H₂S and NH₄. the need for oxygen (BOD₅) is the amount of oxygen required by organisms in the

metabolic process Aero Bik, While COD is a chemical oxygen content. Required in degradation of organic material by chemical reaction. COD can also be defined as a parameter to estimate the amount of organic material present in water or water, which is degraded and difficult to degrade. Based on the UNESCO / WHO / UNEP, 1992.⁽⁶⁾ The content of BOD₅ maximum allowed for drinking water and maintenance of aquatic organisms life is 3.0 to 6.0 mg / L, while based Kep.51 / Ministry of Environment and Forestry / 10/1995 that the BOD₅ value for Quality Raw wastewater for industrial purposes Group I is 50 mg / L and Group II was 150 mg / L and COD values for non-contaminated waters have a value of <20 mg / L.⁽⁷⁾ Plankton and benthos can be used as bio-indicators of water quality, the presence of certain species may indicate that the conditions of pollution levels. Plankton and Benthos are organisms that can live in ecological and adapt to environmental conditions so that if there is a change Plankton and benthic environment will adapt to environmental changes. The water quality index is closely related to the water sapometry index as measured by the type of plankton and benthos found, since each type of plankton and benthos is a constituent of a particular saprobic group that will affect the saprobity value of water. Oligosaprobik Bio-indicator Air is a classification of waters that have not been contaminated or contaminated lightly, class chlorophage, generally bioindicators that can multiply well. Genera of the Chlorophyceae class of the Spirogyra and Desmidium genera commonly used as water bioindicators are the Spirogyra and Desmidium genera. Waters - Mesosaprobik is waters with mild to moderate contamination levels. Bioindicators that can develop are divisions of Algae Melosira sp, Spyrogira sp, Rhizosolenia sp., Nitzschia sp., Oscillatoria sp. Nitzschia actinastroides and Spirulina sp. The α-mesosaprobic water is characterized by the development of algae from the Bacillariophyceae class, especially Nitzschia sp and Rhizosolenia sp and from the Polysaprobic waters dominated by the Chrysophyceae class, in particular Spirulina sp⁽⁸⁾

APPLICATION METHODS IN SAMPLE

The sampling technique used in this research is purposive sampling with research location conducted in Donan River area, Cilacap regency - Central Java. Water quality measurements were carried out in 2 locations, namely A = DAS of the Donan River 39 holding output (location before project) and Location B that the Donan River is flowing 66 and 49 holding output (after project location).

Analysis of heavy metal content using AAS (Atomic Absorption Spectrophotometry)^(11,13), suspension suspended suspendeds suspension (TSS) with gravimetric method⁽⁴⁾, Research using survey method and data analysis done descriptive qualitative, that is by explaining what

happened. by providing sufficient explanation based on facts obtained in the field and the results of laboratory analysis. While plankton and benthos analysis as biological indicator was done by filtering the substrate of mud or river basin by using sample of Eckman Grab (benthos) and plankton net (plankton) and then analyzed in laboratory, with standard Shannon - Wiener diversity index method. : (1, 16)

Sampling was done on December 16, 2017. at temperature 28 o Celcius, air pressure 765 mmHg, humidity 74,4 -78,7% H2O with wind direction northwest to southeast, wind speed 0,4-1,3 m / s with cloudy weather

The materials in this study include the Donan river water samples used to see the water quality concentration, while the water quality parameters measured were temperature, TSS, pH, DO, BOD, COD, chromium and phosphate. Measurements of TSS, BOD, COD, Phosphat and Chromium parameters (Indonesian National Standard No. 06-6989.3: 2004) and APHA Standard Methods for Water and Wastewater Inspection (10, 14,15)

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

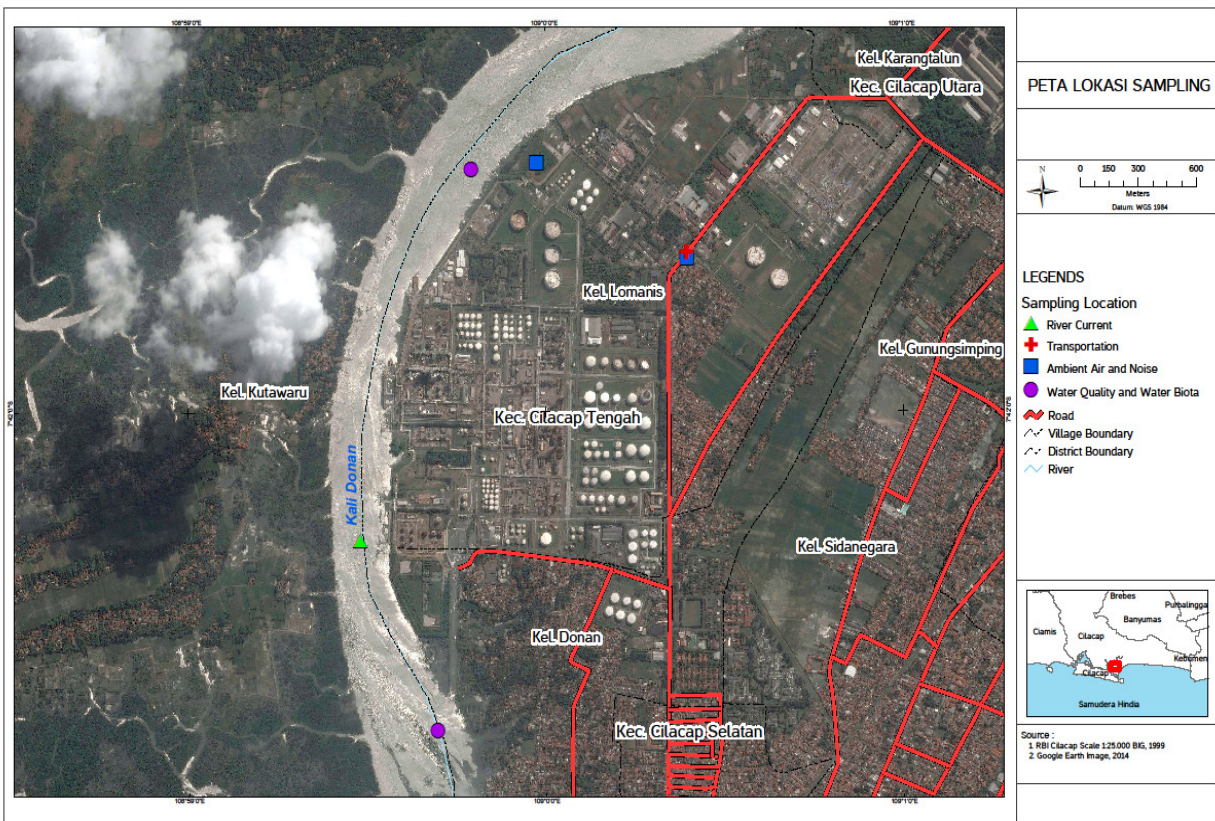


Figure 1. Water Sampling Point, Plankton And Benthos (Sampling A = Donan River Basin 39 Holding Output And Sampling B = Donan River Basin 66 And 49 Holding Output) (2)

RESULTS AND DISCUSSION

The state-owned mining company Cilacap is Southeast Asia's largest crude oil refinery, with a production capacity of 348,000 barrels / day and supplying 34% of Indonesia's fuel needs. This oil refinery process crude oil (crude oil) into non-fuel products and fuel products. Crude oil as the main raw material of oil processing consists of various hydrocarbon compounds which are then treated with a sewage treatment plant and stored in a Clean Water Tank such as waste water. with better quality. Furthermore, waste water is discharged through an outlet on the Donan River. Based on the analysis results Measurement of water quality is done in 2 locations with the following measurements:

Table 1. Water Quality Measurement Data ⁽²⁾

| No | Parameter | Unit | Water Quality Criteria Based on Sampling Location Maximum Class Level (PP No. 82/2001) (12) | | | | | |
|------------------------|--------------------------------|------------|---------------------------------------------------------------------------------------------------|-----------------------------|-------------|-------------|-------------|-------------|
| | | | A | B | Class I | Class II | Class III | Class IV |
| | | | (sampling before project) | (sampling after project) | | | | |
| I. PHYSICS | | | | | | | | |
| 1 | Temperature | °C | 31,7 ^o | 31,9 ^o | Deviation 3 | Deviation 3 | Deviation 3 | Deviation 3 |
| 2 | Dissolved Residue | mg/L | 15.752 | 11.916 | 1.000 | 1.000 | 1.000 | 1.000 |
| 3 | Suspended Residue | mg/L | 22 | 32 | 50 | 50 | 400 | 400 |
| II. CHEMICAL | | | | | | | | |
| 1 | pH | - | 7,9 | 7,8 | 6 - 9 | 6 – 9 | 6 – 9 | 6 – 9 |
| 2 | BOD | mg/L | 5,530 | 7,188 | 2 | 3 | 6 | 12 |
| 3 | COD | mg/L | 33,64 | 33,73 | 10 | 25 | 50 | 100 |
| 4 | DO | mg/L | 6,01 | 5,90 | 6 | 4 | 3 | 0 |
| 5 | Total Phosphate as P | mg/L | < 0,001 | < 0,001 | 0,2 | 0,2 | 1 | 5 |
| 6 | NO3 as N | mg/L | 0,018 | 0,161 | 10 | 10 | 20 | 20 |
| 7 | Arsenic (As) | mg/L | < 0,003 | < 0,003 | 0,05 | 1 | 1 | 1 |
| 8 | Cadmium (Cd) | mg/L | < 0,010 | < 0,010 | 0,01 | 0,01 | 0,01 | 0,01 |
| 9 | Chromium (Cr +6) | mg/L | 0,004 | 0,005 | 0,05 | 0,05 | 0,05 | 1 |
| 10 | Copper (Cu) | mg/L | < 0,010 | < 0,010 | 0,2 | 0,2 | 0,2 | 0,2 |
| 11 | Lead (Pb) | mg/L | < 0,030 | < 0,030 | 0,3 | 0,3 | 0,3 | 1 |
| 12 | Mercury (Hg) | mg/L | < 0,001 | < 0,001 | 0,001 | 0,002 | 0,002 | 0,005 |
| 13 | Zinc (Zn) | mg/L | < 0,001 | < 0,001 | 0,05 | 0,05 | 0,05 | 2 |
| 14 | Cyanide (CN) | mg/L | < 0,002 | < 0,002 | 0,02 | 0,02 | 0,02 | - |
| 15 | Fluoride (F) | mg/L | 0,878 | 1,007 | 0,5 | 1,5 | 1,5 | - |
| 16 | Nitrit as N (NO ₂) | mg/L | < 0,001 | < 0,001 | 0,06 | 0,06 | 0,06 | - |
| 17 | Free chlorine | mg/L | 0,02 | 0,02 | 0,03 | 0,03 | 0,03 | - |
| 18 | Sulfur as H2S | mg/L | < 0,002 | 0,002 | 0,002 | 0,002 | 0,002 | - |
| III. ORGANIC CHEMICALS | | | | | | | | |
| 1 | Oil and fat | µg/L | 250 | 500 | 1.000 | 1.000 | 1.000 | - |
| 2 | Detergent as MBAS | µg/L | 12 | 21 | 200 | 200 | 200 | - |
| 3 | Phenol compounds as Phenol | µg/L | < 1 | < 1 | 1 | 1 | 1 | - |
| IV. MICROBIOLOGY | | | | | | | | |
| 1 | Faecal Coliform | Jml/100 mL | 330 | 270 | 100 | 1.000 | 2.000 | 2.000 |
| 2 | Total Coliform | Jml/100 mL | 330 | 270 | 1.000 | 3.000 | 1.000 | 10.000 |

Description: A = Donan River basin holding output 39
B = Donan River basin holding output 66 and 49

Source: Primary Data Analysis Result, 2014

- 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
BOD (mg/L) value range 5,530- 7,188, COD (mg/L) value range 33,64- 33,73, DO (mg/L) value range 6,01- 5,90,
Fluoride (F) (mg/L) value range 0,878 -1,007, while the other parameters are still below the specified threshold
base on Government of the Republic of Indonesia, 2001. Government Regulation No. 82 of 2001 on Water Quality
Management and Water Pollution Control ⁽¹²⁾

a. Dissolved Oxygen

The increase in DO due to the need of dissolved oxygen in the waters of the donan river will increase due
to the oxygen demand of aquatic organisms become high to metabolize organic material metabolism.
Therefore, with the increase of ingredient ingredients, especially organic ingredients will increase the need
for oxygen in the waters of the river donan. The quality of donan river waters at Dissolved Oxygen parameter
is classified as mild contaminated. The measurement results indicate that DO (mg / L) has a value between
6.01 - 5.90 and belongs to the category First class, water which can be used for drinking water, and / or
other designs that require the same water quality as that purpose ⁽¹²⁾

b. Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

Biological Oxygen Demand (BOD) condition is very related to the content of Dissolved Oxygen (DO) in a waters, this
is linear. If BOD needs increase then DO will also rise. Biological Oxygen Demand (BOD) is the Oxygen Needs
required by all biological activities in water. Biological imbalances in the waters cause water to become polluted (10).
The higher the BOD requirement, the worse the water conservation. also according to lee et al (1978) BOD value
5,530 ppm - 7,188 ppm included in the range of 5 ppm -15 ppm Waters with fairly polluted criteria. The COD 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 (18). The COD value is always higher than the BOD value. The
differences between the two values (BOD and COD) are caused by many factors such as chemicals that are
resistant to biochemical oxidation but are not resistant to chemical oxidation, such as lignin, ⁽¹⁹⁾.
Based on the analysis with BOD parameter, the donan river is included in the category of medium polluted river
(Government Regulation No. 82/2001) ⁽¹²⁾ , While based on the analysis with COD parameters then the Donan river

with COD value = 33.64 ppm - 33,73 ppm, including in the category of mild contaminated river, class 3 (standard 50 ppm - 100 ppm). Based on the BOD-COD analysis on the status of the Donan river waters is a river with mildly polluted criteria, and the retention of the State Oil Company Retentive activity has no significant effect.

c. Floride

Based on Minister of Health Republic Indonesia regulation 492 / Menkes / Per / IV / 2010 ⁽⁹⁾ about drinking water quality requirements, fluoride including parameters that are directly related to health. The maximum allowable fluoride content is 1.5 mg / l, whereas based on Government Regulation No. 82 of 2001 on Water Quality Management and Control of First Class Water Pollution ie water which can be used for drinking water water requires maximum permissible fluoride levels is 0.5 mg / l. The influence of floride can be detrimental to health if at high exposure, The fluoride mechanism in the body is possible to inhibit nerve impulses and inhibit the resurgence chain so that it can cause necrosis, if floride exposure ranges from 3 to 10 mg ⁽²⁰⁾

The fluoride content of the Donan stream is in the range of 0.878 mg - 1.007 mg, included in the category of mild contaminated contamination so the donan stream belongs to the category of class 1 (First class, water which can be used for drinking water, and / or other designations that require the same water quality as that purpose) ^(3, 12)

d. Plankton and Benthos

Plankton and benthos are organisms that can be used as bioindicators of water pollution, therefore plankton and benthos sampling are important parameters. ⁽⁸⁾ 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 ^(1, 2)

| No | Species (Type) | Sampling after Project (ind/L) | Sampling before Project (ind/L) |
|----|-------------------------|-----------------------------------|------------------------------------|
| 1 | <i>Asterionella sp</i> | 1 | - |
| 2 | <i>Biddulphia sp</i> | - | 1 |
| 3 | <i>Chaetoceros sp</i> | 2 | 9 |
| 4 | <i>Codonellopsis sp</i> | 3 | - |
| 5 | <i>Coscinodiscus sp</i> | 3 | 79 |
| 6 | <i>Cyclops sp</i> | 64 | 6 |
| 7 | <i>Nauplius sp</i> | 76 | 80 |
| 8 | <i>Nitzchia sp</i> | 1 | - |
| 9 | <i>Peridinium sp</i> | 2 | 39 |
| 10 | <i>Thalasiothrix sp</i> | - | 2 |
| | Number of types | 8 | 7 |
| | Number of individuals | 152 | 216 |
| | Index of diversity | 1,045 | 1,345 |
| | Index dominance | 0,482 | 0,306 |

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 ⁽¹⁾:

$$H = - \sum p_i \ln p_i$$

Information:

p_i = 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 ⁽⁸⁾. From the result of measurement of water quality of H_2S parameter shows the value of 0,002 mg / l 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 so that 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 indicating that no species dominates other species so that the plankton community structure becomes stable. ⁽⁸⁾

Benthos are organisms that live in the bottom of the water (substrate) either sleazy, creep or dig a hole. Benthos 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. Benthos is an organism that lives on the seabed or river either attached to sand or mud. Some examples of benthos include shellfish, sea urchins, starfish, sea whips, coral reefs and others. Animals benthos live relatively settled, so good used as a guide of environmental quality, because it is always in contact with waste into its habitat ^(8.17). The result of benthos analysis in the study area is presented in table 3 below:

245

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Table 3. Benthos Analysis Of Sampling at Donan River ^(1,2)

| No | Species (Type) | Sampling after Project (ind/L) | Sampling before Project (ind/L) |
|----|-----------------------|-----------------------------------|------------------------------------|
| 1 | <i>Macoma sp</i> | 4 | 6 |
| 2 | <i>Macula sp</i> | 4 | 2 |
| 3 | <i>Prothothaca sp</i> | 2 | 4 |
| 4 | <i>Tagelus sp</i> | 4 | 4 |
| | Number of types | 4 | 4 |
| | Number of individuals | 14 | 16 |
| | Index of diversity | 1,352 | 1,321 |
| | Index dominance | 0,184 | 0,141 |
| | Uniformity index | 0,512 | 0,476 |

247 Source: Primary data analysis results, 2014

248 According to Lee, et.al, 1978, water quality criteria related to the Diversity Index are: (<1.0) heavily
 249 polluted; (1.0 - 1.5) is moderately polluted; (1.5 - 2.0) is lightly contaminated, and; (> 2) has not been
 250 polluted. Based on the result of benthos analysis, the result of diversity index on sampling A = 1.352 and
 251 sampling B = 1,321, it shows that benthos diversity index in donan river is included in moderately polluted
 252 category; (index diversity = 1.5 - 2.0). ⁽¹⁸⁾

253 In the condition of waters in the category of polluted medium is usually dominated by shellfish species
 254 (bivalves) that live in the substrate of mud and sandy mud, this is because the shell (bivalvia) is able to
 255 utilize the remaining organic material as a source of energy therefore bivalves can be used as bio-
 256 indicators waters are contaminated with organic materials of moderate-to-moderate category ⁽²¹⁾

257 **CONCLUSION**

258 Based on the Result of Donan River Water Quality Analysis where the donan river is the waste disposal site of
 259 Operation Refinery Indonesian state oil mining company Unit IV Cilacap Pertamina Unit IV Cilacap-Central Java, is
 260 as follows:

- 261 1. The DO- BOD and COD parameters indicate that the quality of the donan streams including the polluted
 262 category is in accordance with Government Regulation no. 82/2001
- 263 2. Floride Parameters, indicate the quality of donan river included in the category of class 1, based on Minister of
 264 Health Republic Indonesia regulation 492 / Menkes / Per / IV / 2010 ie water which can be used for drinking
 265 water, and / or other designs that require the same water quality as that purpose
- 266 3. Planton and benthos parameters, the quality of donan streams were included in the mild-moderate polluted
 267 category based on the diversity index with values of 1.352 (sampling A) and 1.321 (sampling B) (index diversity
 268 standard = 1.5 - 2.0, base on lee et al, 1978)

This shows that the operational activity of PERTAMINA Refinery Unit IV Cilacap Indonesian state oil mining company Unit IV of Cilacap-Central Java does not show significant impact to the water quality of the river donan

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