Case study

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

ABSTRACT

Objective: Oil Company State of Indonesia - Refinery Unit IV Cilacap which processes crude oil into fuel oil, non-fuel oil and petrochemical products. This research analyzes the possible impact of residual waste from Waste Water Treatment that flowed into Donan river

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. H^2S 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), *Nitzchia 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

Which allows the carrying capacity of the environment to be unbalanced, resulting in increased pollution load. Around the location of Cilacap Unit Unit Plant Wax Unit (IV), 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 (BOD) 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 Bnethos are organisms that can live in ecological and adapt to environmental conditions so that if there is a change Planton 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 Bioindikator 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, Rhizosolonia sp., Nitschia sp., Oscillatoria sp. Nitzschia actinastroides and Spirulina sp. The α-mesosaprobic water is characterized by the development of algae from the Bacillariophyceae class, especially Nitzchia 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 study is purposive sampling with the location of research conducted in the area of the Donan River, Cilacap district - Central Java. Measurement of water quality was done in 2 locations, ie Location A = Donan River basin 39 holding output and Location B that Donan River basin 66 and 49 holding output

Analysis of heavy metal content using AAS (Atomic Absorption Spectrophotometry) method **[11,13],** while the plankton and benthos analysis as biological indicator is done by filtering the substrate of mud or river basin by using sample of Ekman Grab (benthos) and plankton net (plankton) and then analyzed At the Laboratory, with the standard Shannon - Wiener diversity index: [1, 16]

Materials on the study include Donan river water samples that are used to look at the concentration of water quality, 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 the Examination of Water and Wastewater [10, 14,15] Figure 1. below shows the sampling points of surface water, plankton and benthos, as follows:

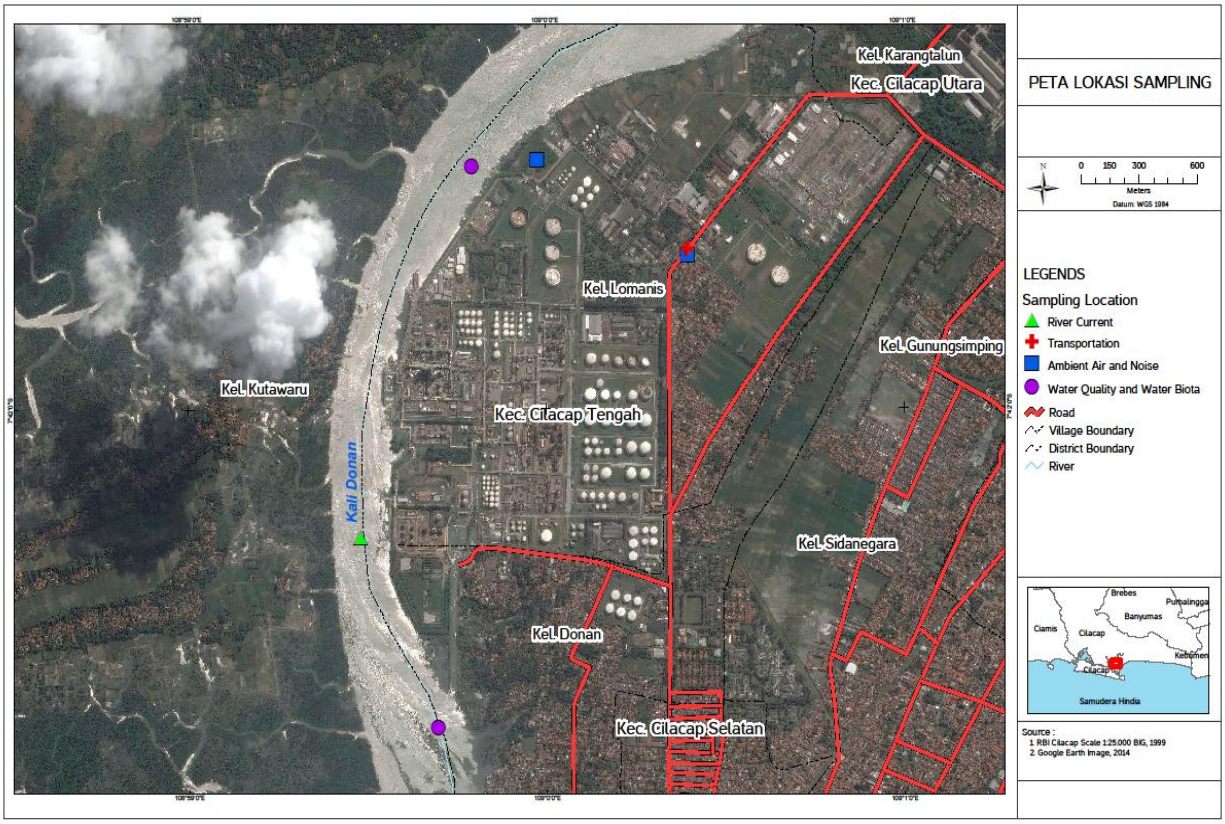

Figure 1. Water Sampling Point, Plankton And Benthos (Sampling A = Donan River Basin 39 Holding Output And Sampling B = Donan River Basin 66 And 49 Holding Output) (2)

RESULTS AND DISCUSSION

Water quality measurements were conducted in 2 locations with the following measurements:

Table 1. Water Quality Measurement Data (2)

No	Parameter	Unit	Sampling Location		Water Quality Criteria Based on Maximum Class Level (PP No. 82/2001) (12)			
			A	B	Class I	Class II	Class III	Class IV
	I. FISIKA							
1	Temperature	°C	31,7	31,9	Deviation 3	Deviation 3	Deviation 3	Deviation 5
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. KIMIA							
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. KIMIA ORGANIK							
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. MIKROBIOLOGI							
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 Source: Primary Data Analysis Result, 2014
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

1. Dissolved Residue (mg/L) 15.752 11.916
2. BOD (mg/L) 5,530 7,188
3. COD (mg/L) 33,64 33,73
4. DO (mg/L) 6,01 5,90
5. Fluoride (F) (mg/L) 0,878 1,007

While the other parameters are still below the specified threshold

Biological Oxygen Deman (BOD) is the Oxygen Needs required by all biological activities within a water. Biological imbalances in a waters cause the waters to become polluted [10]. The higher the BOD requirement, the worse the waters conservation. Based on the classification of the river, the Donan river belonging to class 4 is river with medium contaminated status (Government Regulation No. 82/2001) [12] also according to lee *at al* (1978) BOD value

5,530 ppm - 7,188 ppm included in range 5 ppm -15 ppm Waters with moderately polluted criteria. The COD figure is a measure for water pollution by organic substances that can naturally be oxidized 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, (Lakshmi, 1993). The COD value of the Donan river is about 33.64 ppm - 33.73 ppm with mild contaminated criteria, grade 3 (standard 50 ppm - 100 ppm). Based on the BOD-COD analysis of Donan river water status is a river with mildly polluted criteria, and retaltive PERTAMINA activity does not significantly affect

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

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.[3]

Plankton dan Bentos

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 Bentos sampling results in waters around the study area as follows:

Tabel 2. Plankton Analysis in Donan River Waters[2]

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	1,045	1,345
	Index dominance	0,482	0,306

	Uniformity index	0,208	0,250

Source: Primary data analysis results, 2014

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 H2S 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. 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 [8.17], The result of bentos analysis in the study area is presented in table 3 below:

Table 3. Bentos Analysis Of Sampling at Donan River [2]

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
	Index of diversity	1,352	1,321
	Index dominance	0,184	0,141
	Uniformity index	0,512	0,476

Source: Primary data analysis results, 2014

According to Lee, et.al, water quality criteria related to the Diversity Index are: (<1.0) heavily polluted; (1.0 - 1.5) is moderately polluted; (1.5 - 2.0) is lightly contaminated, and; (> 2) has not been polluted. Based on the result of plankton and benthos analyzes, [18] the condition of waters in the study area was categorized as mild to moderately contaminated. All identified benthos were clams (bivalves) living on mud substrate

and sandy mud. Common shellfish eat the remaining organic material in the bottom of the waters so that the contaminant contents can accumulate in the shell.

CONCLUSION

Based on data analysis of water quality, seagrass condition and coral reefs, the condition of harbor of legonbajak harbor is still categorized well, although the seagrass and coral reef conservation in the category of damaged.

Based On The Results Of The Analysis Of Water Quality And Planton / Benthos It Can Be Concluded That The Water Quality Can Be Categorized As Mild Contaminated, Pollutant Source Mostly Organic Material. Activity Of Operational Refinery Pertamina Unit IV Cilacap-Central Java-Indonesia Has No Significant Effect On Quality Of Donan Waters

REFERENCES

1. Kathleen A. Nolan and Jill E. 2005. Callahan Beachcomber Biology: The Shannon-Weiner Species Diversity Index St. ABLE 2005 Proceedings Vol. 27 Francis College 180 Remsen St. Brooklyn, NY 11201
2. Mitra Adhi Pranata, 2015. Addendum Andal & RKL RPL ◊ Development of Wax Plant Unit at Ru Iv Cilacap Plant.
3. Chinoy, NJ , et al, 1994, Transient and reversible fluoride toxicity in some soft tissue of female mice, ahmedabad, india.
4. Indonesian National Standard. 2017. SNI 06-6989.3-2004 Water and waste water- Part 3: Total suspended solids (TSS) suspension method gravimetrically
5. Anonymous, 1990, Government Regulation no. 20 of 1990 on the Control of Water Pollution
6. UNESCO/WHO/UNEP. (1992). Water Quality Assesment-Aguide to Use of Biota, Sediment and Water in Environmental Monitoring, Second Editon. .
7. Anonymous, 1995. Decree of the Minister of Environment no. 51 / MENLH / 10/1995 on Industrial Liquid Waste Quality Standard
8. Onyema, I.C 2013. Phytoplankton Bio-indicators of Water Quality Situations in the Iyagbe Lagoon, South-Western Nigeria . Department of Marine Sciences, University of Lagos, Akoka, Lagos, Nigeria.
9. Anonymous, 2010, Minister of Health Regulation no. 492 / MENKES / PER / IV / 2010 About Persyartan Water Quality.
10. APHA, 1992. Standard Methods for the Examination of Water and Wastewater, 18th edition. American Public Health Association. Washington D.C.
11. Varian, AAS Spectra AA 220FS Varian, Stevens Creek Blvd Santa Clara, CA 95051 United States.2015
12. Government of the Republic of Indonesia, 2001. Government Regulation No. 82 of 2001 on Water Quality Management and Water Pollution Control, Jakarta
13. Letter J., A.M. Teeter, B.P. Donnel. 2003. Users Guide to SED2D Version 4.5. US Army Engineer Research and Development Center. Waterways Experiment Station. Coastal and Hydraulics Laboratory. New York.

14. National Standardization Agency. 2017. SNI 6964.8: 2015 Sea water quality - Part 8: Seawater sampling method. Building I BPPT, floor 9 - 14. Jl. M.H Thamrin No. 8 Kebon Sirih - Central Jakarta 10340 – Indonesia
15. Ministry of Environment, 2004. Decree of State Minister of Environment Number 51 Year 2004 concerning Water Quality Standard of Sea
16. Poole, R.W. (1974) An Introduction To Quantitative Ecology. McGraw-Hill, New York.
17. Ernest Hodgson (Ed) 2004. A Textbook Of Modern Toxicology Third Edition Department of Environmental and Biochemical Toxicology North Carolina State University John Wiley & Sons, Inc
18. Lee, C.D et al. 1978. Benthic Macroinvertebrates and Fish as Biological Indicators of Water Quality, with Reference to Community Diversity Index. International Conference on Water Pollution Control in Developing Countries, Bangkok. Thailand. Hal. 172.