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Water Quality and The Heavy Metal Occurence of Fish in Polluted Watershed

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Abstract

The clean river is very important for human life and river's biota. However, many rivers are polluted from both domestic and industrial waste today. Domestic waste comes from households and industrial wastes from nearby industrial activities. One of the biotas of the river is the fish. The objective of the research was to evaluate pollutant and pollutant index in the watershed and the present of Pb in fish in the watershed. The location of this research was a long *Garang* watershed Semarang, namely from upstream to downstream of the river. The sampling area was divided into 7 segments based on Central Java Governor Regulation No. 156/2010 based on water designation. The studied parameters in this research were heavy metal in fish and water quality. The studied fish was Nila fish (*Oreochromis sp.*). Results show that Cu was the main pollutant in water river class 1, 2, 3 and 4. DO exceed the limit parameter in water river class 3 and 4. Finally, the highest heavy metals found in fish were found in Pb, while the water pollution index was due to exceeding Cu, all of which came from industrial waste.

Keywords: *Oreochromis sp.*; heavy metal; lead; copper; river.

Introduction

The fishery sector in public waters, for example in the watershed, has a large contribution and could be one of the sources of world food security. Fisheries in the watershed region both nationally and regionally have a very important role, such as supporting food security, livelihood for the community, and providing a source of life for the surrounding population. Plankton biodiversity plays a major role in the uniqueness of the river ecosystem and is different from one river to other rivers. Another potential of fisheries in the watershed is to provide fishery resources, both on fishing and aquaculture. The favorite biomarker research is fish, because of its to changes in temperature, natural environment, and degradation of water quality. Additionally, aquatic contamination is bad for fish and aquatic biotas, which can lead to ecosystem mortality and degradation (Skouras et al., 2003; Sabullah et al., 2015). It is hoped, by knowing the results of the following research can provide an overview for stakeholders for the management of river-based fisheries so as to minimize the possibility of heavy metal toxicity. The main use of lead in the industry is for example as fuel and lead pigments in paints, which give a major cause of an increase in Pb levels in the environment. One of the fish species, found in these waters, was the Nila Fish (*Oreochromis sp.*). This fish was divided into two sizes, namely large and small fish.

According to Central Java Governor Regulation No. 156/2010, *Garang* Watershed is divided into 7 segments which aim to maintain the preservation of water function and recovery of water quality so that it can be utilized according to its allocation. This segment is used for residential, estuary, fishery, and port loading and unloading. Utilization of this river location is for recreation, industry, aquaculture activities, domestic industry, and is the meeting point of two rivers whose activities have an effect on the decrease of river water. The estuary area, which is the tidal area of the sea, is used to measure the whole water quality. Upstream and upstream water quality data will be compared to the objectives to be policy recommendations for river management strategies and food security for fisheries. The results of the study have been expected to provide an overview for stakeholders of river-based fisheries management, so it could be minimized the possibility of heavy metal toxicity.

Materials and Methods

Water Quality

Parameters of water quality are acidity level, Total Dissolve Solid (TDS), Fe, Cr, Cu, Nitrate, and Dissolved Oxygen (DO). Acidity level was measured using Schott Lab 850 pH meter. TDS was analysed using conductivity meter 3210. Fe, Cr, Cu, and nitrate, were analysed using spectrophotometer DR 2800. DO was analysed using titration method. Data analysis based on Minister of Environment Decree No. 115/2003 on Guidelines for Determination of Water Quality Status (Effendi, 2016). The procedure are:

(i) Selection of parameters.
(ii) Calculation of C_i/L_i for each parameter for each sampling location. C_i is the measured water quality parameter. L_i is standard water quality for each parameter.
(iii) The usage of value $(C_i/L_i)_{\text{measurement}}$ if the value is smaller than 1.0, and the use of (C_i/L_i) new if the value of $(C_i/L_i)_{\text{measurement}}$ greater than 1.0. (C_i/L_i) new = 1.0 + P log $(C_i/L_i)_{\text{measurement}}$
(iv) Determination of the average value and the maximum value of the overall C_i/L_i $[(C_i/L_i)_R$ and $(C_i/L_i)_M]$.
(v) Determination of water pollution index using the following equation:

$$P_{ij} = \sqrt{\frac{\left(\frac{C_i}{L_{ij}}\right)_M^2 + \left(\frac{C_i}{L_{ij}}\right)_R^2}{2}} \qquad (1)$$

where P_{ij} is pollution index for a specified water quality purpose (j); C_i is the measured water quality parameters; L_{ij} is standard water quality parameter for each parameter at specified water quality purpose (j); $(C_{ij}/L_{ij})_M$ is C_{ij}/L_{ij} maximum; and $(C_{ij}/L_{ij})_R$ is C_{ij}/L_{ij} is the average.

Criteria shown in **Table 1.**

Table 1. Pollution Index and Water Quality Status Criteria

Pollution Index	Water Quality Status
$0 \leq P_{ij} \leq 1.0$	Meet quality standards (good)
$1.0 < P_{ij} \leq 5.0$	Lightly polluted
$5.0 < P_{ij} \leq 10$	Moderately polluted
$P_{ij} \geq 10$	Heavily polluted

Ministry of Environment Decree No. 115/ 2003 (Effendy, 2016).

Sampling Location

The research was performed in *Garang* Watershed, Semarang Central Java Indonesia, during January - October 2017. This research location was in the coordinate 6˚59’32,5” S and 110˚24’10,0” E. According to Central Java Governor Regulation No. 156/2010, *Garang* Watershed is divided into 7 segments segments (**Fig. 1**), which aim to maintain the preservation of water function and recovery of water quality so that it can be utilized according to its allocation. The location of this research is located in Segment 7 which is the area between downstream and middle of the river, so there is much pollution in this area from domestic and coastal. The water of Semarang estuary is not deep and muddy in the bottom, dirty and has suspended solids. Pollution comes from domestic, industrial waste, and marine waters and that comes from two main canals (Tjahjono et al., 2017). Segment 7 is located in Banjir Kanal Barat River, Semarang Central Java Indonesia; and it is near the estuary and freshwater ecosystem.

Heavy Metal Analysis in *Oreochromis sp*.

Approximately 25 g (to nearest 0,1 g) test portion was put into crucible, and was dried at 135˚C to 150˚C for 2h. It was then transferred to a temperature-controlled furnace and slowly raised the temperature to 500˚C overnight (16h). The crucible was removed, let cool to room temperature, cautiously added 2 mL HNO_3, and swirled. It was carefully evaporated on a warm hot plate or steam bath. Samples were then transferred to the furnace, slowly increased the temperature to 500˚C, and held at this temperature 1 h. Afterwards, the dish was removed and cooled down. If necessary, the HNO3 ashing was repeated in order to obtain clean and practically C-free ash. 10 mL of 1M HCl was added and followed by heating cautiously on the hot plate to dissolve the ash. Samples were then transferred to 25 mL volumetric flask, related to two 5 mL portions 1M HCl, cooled, and, diluted with 1M HCl and mix (Latimer, 2012). A dilution series of Pb 0, 0.2, 0.6., 1.0, 3.0, 5.0 and 10.0 µg Pb/mL in 1 mL HCl respectively). A Spectrophotometer was set to previously established optimum conditions for maximum signal at 283.3 nm.

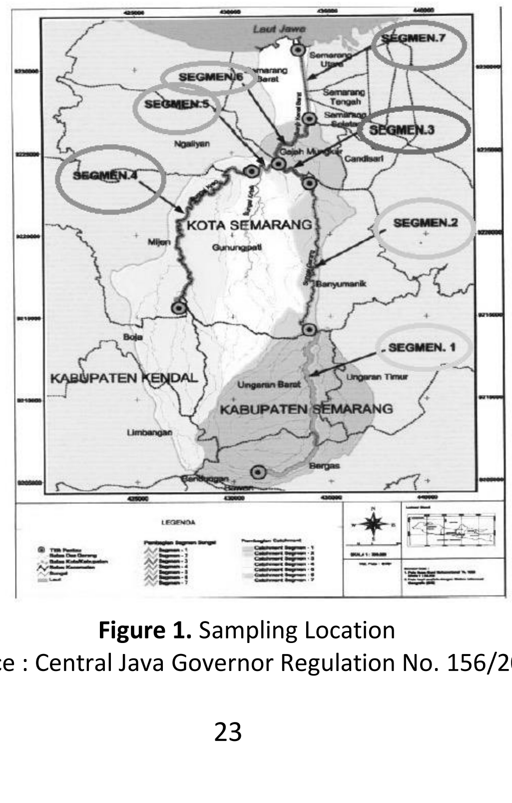

Figure 1. Sampling Location
(Source : Central Java Governor Regulation No. 156/2010)

Use air–C_2H_2 flow rates was recommended by the manufacturer for standard conditions for Pb. For digital concentrations readout, calibrated in concentration mode with solutions containing 0,2 and 10,0 µg Pb/mL. The concentration was directly recorded after calibration of the instrument. For strip chart readout, set amplification to give ≥1% absorption reading for 0,2 µg Pb/mL working solution and prepared standard curve against µg Pb/mL (Latimer, 2012).

Results and Discussion

The results were evaluated by pollution index method, which was analyzed by Government Regulation No. 82/2001 on Water Quality Management and Water Pollution Control, in which class 1, class 2, class 3 and class 4 are shown in Table 2 to 5 respectively.

Pollution Index in Water Quality Standard Class 1

In class 1, water that can be used for drinking water, and/or other designations that require the same water quality as those uses (Government Regulation No. 82/2001 on Water Quality Management and Water Pollution Control). **Table 2** is the comparison between the pollution index and the water quality standard class 1. The parameter exceeding the limit was Cu. This may be due to the effluent of polluting agricultural pesticides in the upstream area. The upstream area in *Garang* Watershed was located on Gebugan Village, Bergas, Central Java, Indonesia. This farmland area in this area was 392,418 ha, furthermore, there are many pesticides which polluted the water flow in the area.

Table 2. The Comparison of Pollution Index and Water Quality Standard Class 1

No	Parameters	Ci	Lix	(Ci/Lix)	(Ci/Lix) $_{measurement}$
1	pH	8,01	6.0-9.0	0.51	0.51
2	TDS	183	1000	0.18	0.18
3	Fe	0.28	0.3	0.93	0.93
4	Cr	0.025	0.05	0.50	0.50
5	Cu	0.11*	0.02	5.50	2.48
6	Nitrate	0.14	10	0.01	0.01
7	DO	6.4*	6	1.07	1.06
				(Ci/Lix)M	2.48
				(Ci/Lix)R	1.24
				PI	1.96
				Status	lightly polluted

*Concentrations exceeding the limit

Pollution Index in Water Quality Standard Class 2

Table 3 is the comparison between the pollution index and the water quality standard class 2. In class 2, water can be used for water recreation facilities, freshwater fish farming, livestock, water to irrigate crops, and or other designations that require the same water quality as those uses (Government Regulation No. 82/2001 on Water Quality Management and Water Pollution Control). Another parameter that was also quite high is DO (**Table 3**). Another parameter in water pollution control is Cr. Cr was from mining, electroplating, textile, and tannery industries. Many industries were located near rivers or the fresh water streams. Textile, tofu, bakery, canning drinks, tofu, and biscuits industries were responsible for discharging their untreated effluents into rivers, like highly toxic heavy metals. *Garang* watershed received wastes from these industries. Water quality in this area were pH, TDS, nitrate, DO. The relationships between fish larvae occurrence, biotic (zooplankton and phytoplankton) and abiotic factors (TDS and pH) reveal strong relations (Hussain et al., 2013). Nitrate may be associated with storm water run off, increased industrial development and caused by discharging waste water from human activities (Pham, 2017).

Table 3. The Comparison of Pollution Index and Water Quality Standard Class 2

No	Parameters	Ci	Lix	(Ci/Lix)	(Ci/Lix) $_{measurement}$
1	pH	8.01	6.0-9.0	0.51	0.51
2	TDS	183	1000	0.18	0.18
3	Cr	0.025	0.05	0.50	0.50
4	Cu	0.11*	0.02	5.50	2.48
5	Nitrate	0.14	10	0.01	0.01
6	DO	6.4*	4	1.60	1.41
				(Ci/Lix)M	2.48
				(Ci/Lix)R	1.38
				PI	2.01
				Status	lightly polluted

*Concentrations exceeding the limit

Pollution Index in Water Quality Standard Class 3

Table 4 is the comparison between the pollution index and the water quality standard in class 3. In class 3, water can be used for the cultivation of freshwater fish, farms, water for cropping, and/or other designations that require water equal to those uses (Government Regulation No. 82/ 2001 on Water Quality Management and Water Pollution Control). The parameters exceeding the limit were Cu and DO. This area was utilized as aquaculture, fishing, human activities example bath, tourism etc. Domestic waste can cause water pollution and microbiological contamination in this river.

Table 4. The Comparison of Pollution Index and Water Quality Standard Class 3

No	Parameters	Ci	Lix	(Ci/Lix)	(Ci/Lix) $_{measurement}$
1	pH	8.01	6.0-9.0	0.51	0.51
2	TDS	183	1000	0.18	0.18
3	Cr	0.025	0.05	0.50	0.50
4	Cu	0.11*	0.02	5.50	2.48
5	Nitrate	0.14	20	0.01	0.01
6	DO	6.4*	3	2.13	1.66
				(Ci/Lix)M	2.48
				(Ci/Lix)R	1.47
				PI	2.03
				Status	lightly polluted

*Concentrations exceeding the limit

Pollution Index in Water Quality Standard Class 4

Table 5 is the comparison between the pollution index and the water quality standard in class 4. This water can be used for irrigation, planting and or other designations that require the same water quality as those uses (Government Regulation No. 82/2001 on Water Quality Management and Water Pollution Control). This research area was near to downstream and used for aquaculture. They were many aquaculture activities in this area, so there are many fish food waste and ammonia from fish caused bad aquatic environment. The parameters exceeding the limit were Cu and DO (Table 5). DO greatly affected the stability of fish life. Water contains contaminants that enter the gill slit are toxic to fish; it will directly affect the gills and damage the gill cells. DO is an important water quality parameter because the value of DO can indicate the level of pollution in the waters or the level of waste water treatment. The amount of dissolved oxygen value in water determined the suitability of water quality as a source of life (Sunu 2001; Dewi et al., 2014). DO in water was affected by the process of photosynthesis of aquatic plants. The amount of the DO in water depended on temperature, atmospheric pressure and mineral content in water (Argawala 2006; Miller 2007; Dewi et al., 2014).

Table 5. The Comparison of Pollution Index and Water Quality Standard Class 4

No	Parameters	Ci	Lix	(Ci/Lix)	$(Ci/Lix)_{measurement}$
1	pH	8.01	5.0-9.0	1.02	1.02
2	TDS	183	2000	0.09	0.09
3	Cr	0.025	0.01	2.50	1.80
4	Cu	0.11*	0.2	0.55	0.55
5	Nitrate	0.14	20	0.01	0.01
6	DO	6.4*	0	0.14	0.14
				(Ci/Lix)M	1.80
				(Ci/Lix)R	0.72
				PI	1.36
				Status	lightly polluted

*Concentrations exceeding the limit

The Occurrence of Heavy Metals in *Oreochromis sp.* Fish

Table 2 - 5 show that Cu was exceeding the quality standards. Cu was high due to the presence of mining industry, electroplating industry, and pesticides (Paul, 2017). The highest heavy metal in fish was Pb. This may be because the area was polluted by the industrial activities; the industrial activities and the anthropogenic pollution were also from local people activities (Jayaprabha et al., 2014), in the upstream and the middle-stream river areas.

Pb is very dangerous for the health, such as: affecting cognitive function, decreasing learning ability, short posture, decreasing hearing, affecting person intelligence or reducing the intelligence, damaging the kidneys, damaging the nervous system, affecting reproduction, high blood pressure, affecting brain development, anemia for pregnant women, affecting the fetus and poison the organs. Heavy metal residues in the contaminated sediments can accumulate in microorganisms, such as aquatic flora and fauna, which may enter to the food chain and lead in human health problems (Cook et al., 1990; Deniseger et al., 1990; Upadhyay et al., 2006). Lead is more widespread than most other toxic metals.

Levels in the environment are increasing due to industry (Lu, 2010). The pattern of distribution and bioaccumulation of heavy metals in organisms was not only influenced by the environmental sorption-desorption characteristics, but also by physiological status, feeding strategy, biochemistry, and capacity to accumulate heavy metals in their bodies (Noegrohati, 2005). Highest Pb concentration was found in the downstream zone pollutants flows from urban runoff and municipal sewage that increased the concentration of Pb in stream water (Malik, 2011). A good monitoring program is an essential program for managing the coastal areas based on ecological and sustainability (Jayaprabha et al., 2014). In addition to publishing Government Regulation No. 82/2001 on Water Quality Management and Water Pollution, many government's departments participate in controlling this pollution, such as the Ministry of Forestry and Environment, the Environment and Forestry of Central Java province. Environmental section is responsible for protecting this water quality from heavy metal and the community development in the watershed area. In forestry section, they work on the forest and land rehabilitation, conservation and community development in the watershed area to protect the watershed area. It is suggested that Government participation in the above - mentioned ways may help to reduce the problem of waste that can cause harmful toxic effects for humans with the food intermediaries that they consume.

Table 6. Heavy Metal in *Oreochromis sp.*

No	Parameters	Result		Indonesian National Standard (SNI)	Method
		Small Fish (<100gr)	Big fish (>100gr)		
1.	Lead (Pb)	0.63	0.68	0.3	SSA
2.	Copper (Cu)	1.35	1.35	0.1-150	SSA

Conclusion

In this study, Cu was the main pollutant in water river class 1, 2, 3 and 4. Cr in water river class 2 due to mining, electroplating, textile, and tannery industries along the river. On the other hand, DO exceed the limit parameter in water river clas 3 and 4. Finally, the highest heavy metals found in fish were found in Pb, while the water pollution index was due to exceeding Cu, all of which came from industrial waste.

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