Cu metal concentration in the water and sediment of Surabaya's flowed-Jagir River Estuary

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Abstract. Cu is one of the few metals that predominate in water. In addition, Cu potentially pollutes to any aquatic organisms due to bioaccumulation and biomagnification. One of the estuaries that experienced pressure due to the presence of Cu is Jagir River estuary in Surabaya. The objective of this study was to determine Cu metal concentration in the water and sediment of Jagir River estuary. The sample was purposively taken from the estuary area and its surroundings, in general grouped in three locations: station 1 (before entering the estuary), station 2 (inside estuary), and station 3 (flowing beyond the estuary). The results indicated that the concentration of Cu in the water at station 1 was <0.004 mg L^{-1} while station 2 and 3 had the same concentration of 0.05 mg L^{-1}. Cu concentration at stations 2 and 3 exceeded the standard limits set by the government. In terms of sediments, Cu concentrations were still below the standard quality limits with an average of 44.73 mg kg^{-1}. Therefore, the water of Jagir River estuary had been already polluted by Cu metal, however Cu concentration in the sediment still meets the criteria of the government.

1. Introduction

As time goes, the water pollution problem in Surabaya is not shrinking but increasing. Palar described pollution as a worsen changing conditions from the original circumstances [1]. Government Regulation Number 82 (2001) defines that water pollution is substances, energy, living things or other elements that enter and lead to a decrease of water quality. Mainly, degrading the quality of water is caused by anthropogenic activity. Unfortunately, as anthropogenic activities intensifies, increasment of water pollution mostly is inevitable. These contributing activities to water pollutions, such as: settlements, tourism, agriculture, marine transportation, fisheries, and industry.

The Jagir river, especially in the estuary area, experiences water pollution. Jagis River estuary is situated as one of the estuary in the eastern part of Surabaya City, in the Province of East Java. Together with other estuaries, Jagir estuary is under high pressure of water pollution. As for some of the contaminants present in the estuary of Jagir River, heavy metals are the pollutants that pose a threat to the life of living beings. Because, heavy metals hardly degrade, can accumulate in the body of organisms, and have high toxicity [2]. Some metals, according to EPA (Environmental Protection

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Agency), should be monitored throughly, such as Hg, Pb, Cu, Cd, Cr, Ni, Zn, and As because these metals have a high toxicity rate and can cause environmental damage.

Minamata tragedy, well-known for "*itai-itai* disease", in Japan was one of the cases caused by heavy metal contamination on living things [3]. As for some heavy metals contained in the water of the Jagir River estuary, Cu metal are concentrated in high quantity and highly toxic for aquatic organisms. In the preliminary study, it was noted that the concentration of Cu metal in the sediment and water were 51.62 mg Kg^{-1} and 0.04 mg L^{-1} respectively, whereas according to previous research conducted [4] the estuary of the Jagir River had 41.9 mg Kg^{-1} heavy metals in the sediment. Compared with the previous research, the concentration of the Cu metal in the Jagir River estuary positively increased.

With the Cu metal contained in the Jagir River estuary, its concentration must always be monitored both in water and in the sediment. Hence, Cu concentration will not adversely affect the life of living things through its toxicity potency along the estuary of the Jagir River. Therefore, the objective of this study was to determine the concentration of the Cu metal in the water and in the sediment along the Jagir River estuary. Later, a further handling of the Cu metal pollution can be conducted.

2. Research method

2.1. Research site description

This research was conducted on November 27 2016 at 09:00am – 03:00pm (local time, UTC + 07:00) at Jagir River, or commonly referred by local people as Wonokromo River, which is one of several rivers, flowing through Wonorejo Village, Rungkut Sub-district, Surabaya City (eastern coastal area). The coordinate point of this research was on 7°18'21.73"-7°18'20.12" S, 112°49'14.30"-112°50'35.81" E (figure 1). Monographic Data at 2014 showed that environmental conditions at the estuary of the Jagir River, Wonorejo Village has an average temperature of 32ºC, 13300 mm $year^{-1}$ rainfall, average soil elevation from sea level (2.5 m) and topography conditions included into the medium topography category of the Jagir River, Wonorejo Village bordering the northern Keputih Village, South Medokanayu Village, Madura Strait in the east and Medokan Semampir Village.

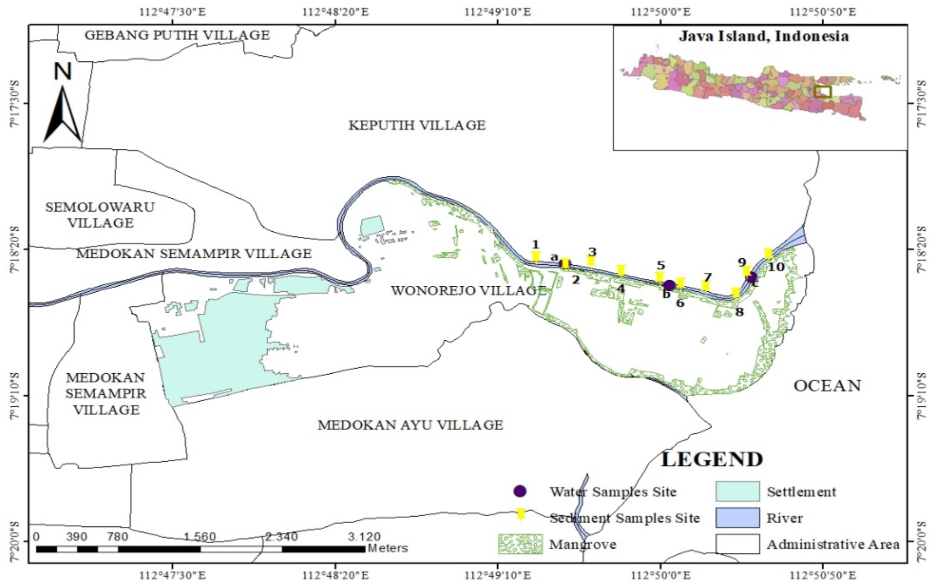

Figure 1. Research site.

2.2. Instruments and materials
We used several instruments in this research, such as: thermometer, DO meter, salinometer, pH meter, pipette, washing bottle, GPS (Global Positioning System), polyethylene bottle, Ekman grab and a water sampler. Several supporting materials were used during the research: water samples, sediments, aquadest, tissues, paper labels, plastics, HNO_3.

2.3. Sampling methods
There were three water sampling points along the estuary of Jagir River, Wonorejo Village: before entering estuary, right inside the estuary, and after the river estuary. Each coordinate point was documented in table 1. As for sediment sampling, there were 10 sampling points, where each point was made in intervals of ± 300 m and each coordinate point could be found in table 2.

Table 1. Coordinate of water sampling.

Station	Coordinate	
	S	E
a	7°18’25.79”	112°49’29.61”
b	7°18’32.38”	112°50’03.99”
c	7°18’29.49”	112°50’28.06”

Table 2. Coordinate of sediment sampling.

Station	Coordinate		Station	Coordinate	
	S	E		S	E
1	7°18’23.82”	112°49’38.03”	6	7°18’34.05”	112°50’06.01”
2	7°18’26.49”	112°49’28.19”	7	7°18’34.36”	112°50’12.49”
3	7°18’26.79”	112°49’39.05”	8	7°18’38.37”	112°50’19.11”
4	7°18’30.58”	112°49’49.00”	9	7°18’32.97”	112°50’25.21”
5	7°18’31.06”	112°49’58.83”	10	7°18’25.65”	112°50’32.64”

A water sampler was used for taking samples of the water from the river. This device was placed at half the depth of the estuary of Jagir River. Water sampling was conducted in three replicates, then composited into one sample per point. Afterwards, the sample was stored into a polyethylene bottle where it was previously washed with detergent then rinsed with clean water. After the rinsed using HNO_3 1: 1 liquid and rinsed again with aquadest 3 times and dried [5]. After the water sample was inserted into the polyethylene bottle then 3 mL HNO_3 was added 3 for 1 L [6]. The polyethylene bottle later was stored into the cool box and was ready to be analyzed for Cu content using AAS (Atomic Absorption Spectroscopy). In addition to water sampling, data collection of environmental parameters, such as water temperature, water pH, salinity, and dissolved oxygen (DO) had been performed 3 times with an interval ± 10 minutes.

Sediment sampling was done by using Ekman grab with a 0-10 cm depth from the bottom surface of the Jagir River estuary (3 replicates) at different points. Samples later were put into clear plastic and then stored into the cool box. Then, the Cu content of the sediment was analyzed by using AAS.

2.4. Data analysis
The observation data were compared to the predefined quality standard. We used Government Regulation No. 82/2001 on the Management of Water Quality and Control of Water Pollution and Decree of the Minister of Environment No. 51/2004 on Water Quality Standard Appendix III for marine biota, as the water standard. Meanwhile, National Water Quality Management Strategy-ANZECC (Australian and New Zealand Guidelines for Fresh and Marine Water Quality) Volume 1/ 2000 was referred for the sediment standard [7].

3. Result and discussion

3.1. Environmental parameters

3.1.1. Water temperature. Temperature is a very important physical factor for life because it can affect the life process. Here is the average temperature at each station along the estuary of Jagir River in figure 2. As shown in the graph, the water temperature range along the Jagir River estuary was 30.2-30.6ºC with an average temperature of 30.3ºC during the time of measurements. Compared with the natural temperature in the Indonesian rivers, the temperature at the research location was still normal. The natural water temperature in Indonesia ranges from 28-32ºC [8]. Comparing to the standard quality of the Government Regulation No. 82/2001 and the Decree of the Minister of Environment No. 51/2004 Annex III, the temperature of the waters at the research location was still relatively normal and could support the life of organisms living along the downstream of the Jagir River. The previous research [9], water temperature in 2014 reached 37.4ºC while another research reported the temperature of waters which ranged from 29.91ºC-31.82ºC [10].

Water temperatures may vary over time and in general the water temperatures in the tropical area are higher compared to the sub-tropical and the polar regions. There are several factors that affecting the temperature change of water, rainfall, the flow of the river, and the current circulation pattern in the waters [11]. Changing the temperature of water in a region may affect the rate of the fundamental biochemical processes in the aquatic organism inside it [12]. The existence of heavy metals in waters is also influenced by water temperature. The higher the temperatures in the water will cause a higher solubility rate of heavy metals [13].

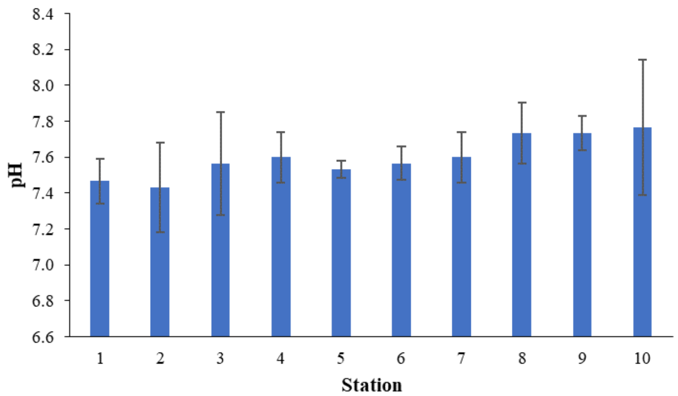

Figure 2. Average pH distribution in the waters at the estuary of the Jagir River, Surabaya

3.1.2. pH distribution. The acidity rate or so-called the pH is the intensity of the acidity or alkalinity of a solution or liquid that can represent the concentration of hydrogen ions. The average pH measurements along the Jagir River estuary can be seen in figure 3. Based on figure 3, the average pH at the downstream area of the Jagir River was 7.6 with a pH range of 7.4-7.8 during the time of measurements. Comparing to the standard quality issued in the Government Regulation Number 82/2001 and the Decree of the Minister of Environment Number 51/ 2004 Annex III, the condition of pH in the waters of the study location was still quite normal. Water with a relatively normal pH [1] and classified in highly productive water body. In 2013, pH value at the estuary of the Jagir River was between 6.8–8.0 [14], while in 2014 the average pH value at the study site was 8.37 [9].

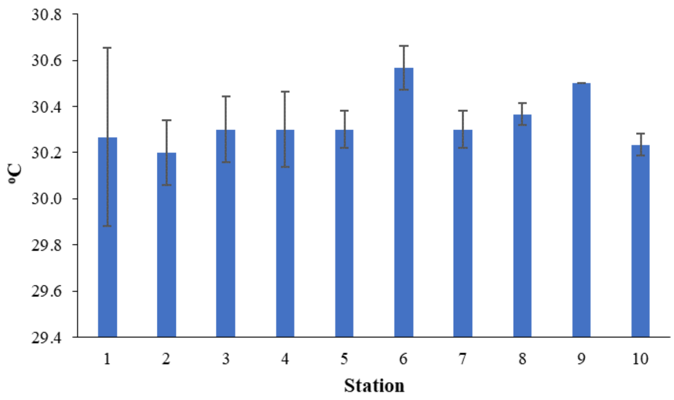

Figure 3. Average water temperature distribution at the estuary of the Jagir River, Surabaya.

If there is a change in pH, therefore the physiological function of aquatic organisms including the ion exchange process with water and respiration will be affected [15]. The pH also causes the deposition process of heavy metals. As the value of a pH gets higher, heavy metals tend to easily settle to the sediment [1]. Changes in pH in the waters may occur due to the process of photosynthesis, organic nitrogen fixing, sulfate reduction, and denitrification [16].

3.1.3. Salinity. Salinity is defined as the amount of salts contained in one kilogram of water and it is usually expressed in parts per thousand (ppt) [17]. The result of measuring the salinity along the estuary of the Jagir River is illustrated in figure 4. Figure 4 displays that the salinity at the estuary of the Jagir River is still relatively normal for living organisms living in the study sites when compared to the Decree of the Minister of the Environment Number 51 of 2004 Annex III. Salinity at the study sites is known to have a range between 1.0 g L^{-1}-2.7 g L^{-1} and an average salinity of 1.7 g L^{-1}. The average salinity later classified as oligohalone or brackish waters [18]. Previous research revealed that the salinity in 2015 at the estuary of the Jagir River was 36 g L^{-1} [9], while in the same year salinity was observed at the study sites between 5.26 g L^{-1}-11.95 g L^{-1} [10].

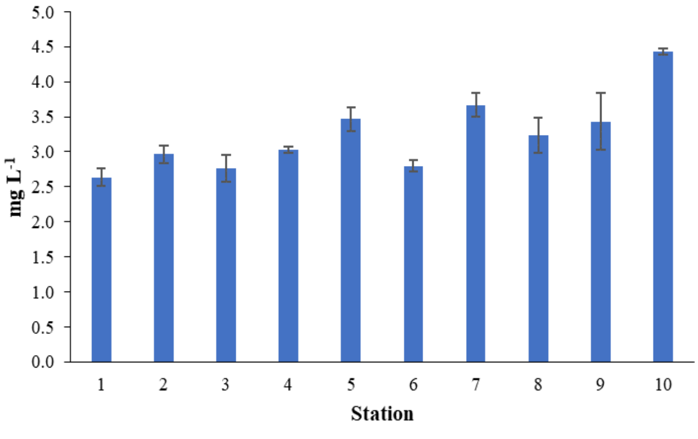

Figure 4. Average dissolved oxygen distribution at the estuary of the Jagir River, Surabaya.

The differences in the salinity rate due to the different types of freshwater and sea water inputs annually. The salinity level in the estuary will be much lower when compared to the salinity in the sea because in the estuary there is a mixing between sea water mass and the river water [19]. Salinity is also affected by heat absorption, rainfall, the flow of the river, and patterns of current circulation [11]. A high or low salinity rate in the water will affect the presence of heavy metals. A high salinity rate will cause a decrease in concentration of heavy metals because of the high salinity there and an increase in the formation of chloride ions and heavy metals reacting to chloride ions [20].

3.1.4. Dissolved Oxygen (DO). Dissolved Oxygen (DO) are oxygen molecules that are completely dissolved in the water and oxygen that can enter the water through contact with the atmosphere [21]. Figure 5 below is the result of the DO measurement at the downstream of the Jagir River. Figure 5 indicates that the DO at the estuary of the Jagir River ranges from 2.6 mg L^{-1}-4.4 mg L^{-1} with an average DO of 3.2 mg L^{-1}. Compared to existing quality standards such as the Government Regulation No. 82/2001, then the whole station in the research location belongs to Class III, which is suitable for fish cultivation, farming, water for plants or others that having the same condition. Compared to the Minister of Environment Decree No. 51/2004 Annex III, then the DO condition at the research location was below the standard quality limit. Low DO value at the study sites could occur due to several factors such as: stirring, waste in the study site, or the substrate in the form of mud.

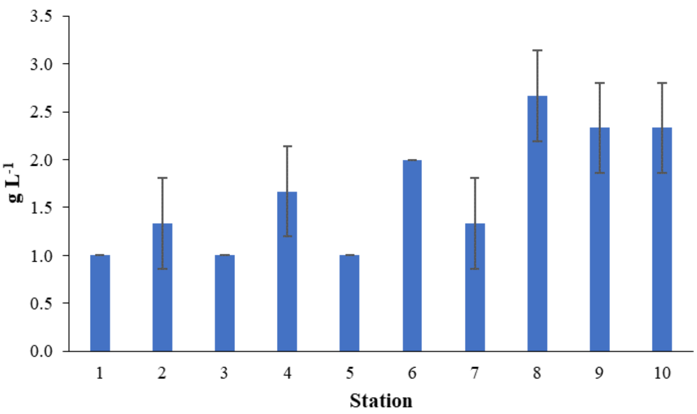

Figure 5. Average salinity distribution at the estuary of the Jagir River, Surabaya.

Several factors may cause high DO levels, which includes: the mixing of water masses, wastes in waters, respiration and photosynthesis [22] Mud substrate tends to have a lower DO value compared to other substrates [23]. Prior research in 2013 stated that DO at the estuary of the Jagir River was 4.55 mg L^{-1} [4], whereas at 2015 the DO value at the research locations was measured as much as 4 mg L^{-1} [9].

3.2. Concentration of Cu in water samples

The presence of the Cu metal in the waters will be harmful to the life of aquatic organisms due to the dissolved Cu metal which will easily enter aquatic organisms. The following is the result of analysis of Cu metal concentration at the Jagir River estuary, displayed in table 3.

Table 3. Cu metal concentrations in the water sampling station of the Jagir River estuary, Wonorejo Subdistrict.

Station	Concentration Cu (mg L^{-1})
1	<0.004
2	0.05
3	0.05

The table above illustrates that at station 1 the concentration of Cu metals was very small, meanwhile at stations 2 and 3 the concentration of Cu was 0.05 mg L^{-1}. Compared to Government Regulation Number 82/2001, the quality of the water at the estuary of the Jagir River was very bad to be used as drinking water, recreational facilities or water facilities, fish farming, livestock, and for irrigation. When compared with the quality standard of Decree of the Minister of Environment

Number 51/2004 Annex III, then stations 2 and 3 had also been classified as bad for aquatic organisms.

In previous research it was mentioned that by 2015 the concentration of Cu metal at the downstream area of the Jagir River ranges from 0.071 mg L^{-1}-0.091 mg L^{-1} [10]. Although concentrations of Cu at the research locations have decreased compared to previous research, concentrations of Cu were still relatively high and still exceeded the standard limits issued by the Indonesian Government and need further treatment of the concentrations of Cu in the research location. Waste disposal, waste treatment prior to entering waters, and seasons are some factors that affect changes in the concentrations of Cu in the environment [24]. Concentration of heavy metal in the estuary area influenced by several factors, such as: dilution and sedimentation which in the process is affected by current velocity and the depth of waters [25]. Other influencing factors are: pH, salinity, dissolved oxygen, hardness, TSS, TDS, BOD, and COD [2].

3.3. Concentration of Cu in sediment samples

Sediment is an indicator of pollution, because the sediment is a sink for contaminants produced by various activities on land and at sea [26]. Cu metal is a contaminant that belongs to a heavy metal category which is often found in water and sediment. The result of analysis of heavy metal concentration in estuary sediment of the Jagir River can be seen in figure 6. Figure 6 shows that the concentration of Cu metal in the sediment ranged from 35.65 mg Kg^{-1} to 49.08 mg Kg^{-1} with an average concentration of 44.73 mg Kg^{-1}. As seen from the environmental parameters found at the estuary of the River Jagir, the temperature, pH, and DO are environmental parameters that can help Cu metal settles to the deep waters of the the Jagir River estuary. Temperature at the estuary of the Jagir River at that time was 30.3ºC, it facilitated the Cu metal in the research site to settle because if the condition reaches a high water temperature or water temperature above normal, it will cause the Cu metal to be easily dissolved. Furthermore, the pH at the research locations that have alkaline properties also help the deposition of the Cu metal, while the low DO rate in the research location can also cause the Cu metal is not to be easily dissolved into the waters, or in other words the Cu metal will easily settle in the bottom surface of the water.

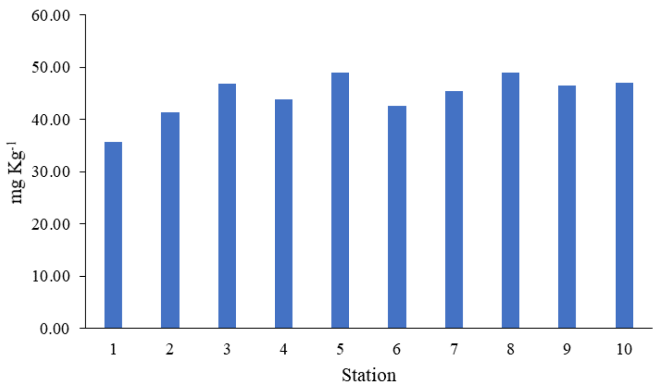

Figure 6. Cu metal concentrations in the sediment of the Jagir River estuary, Wonorejo Subdistrict.

Compared to the ANZECC quality standard, the concentration of Cu in the sediment in the research location was still low. The use of ANZECC as a quality standard because there is no standard quality for heavy metal concentration in sediment in Indonesia. However, the abundance of Cu concentrations in sediments ranges from 5 mg Kg^{-1} up to 80 mg Kg^{-1} [27]. Previous research mentioned that the concentration of Cu metal at the downstream area of the Jagir River was 3.19 mg Kg^{-1} [28], while a previous study in 2013 indicated that the concentration of the Cu was as high as 41.9 mg Kg^{-1} on sediments [4]. When compared with this study, the concentration of the Cu metal in sediment had increased. This happened because of the higher human activity in life using the Cu metal.

Concentrations of heavy metals present in sediments were higher at 3-5 times than those in the water [29], Its concentration in sediments were higher than in water because metals the weight present in the waters will be removed from the aquatic bodies through the process of precipitation, absorption, and adsorption [30]. The Cu metal also has affinity to settle in the sediment [31]. There are several things that may affect the presence of heavy metals in sediments such as the characteristics of heavy metals, organic matter content, sedimentary pH, sediment particle size, ion exchange ability, and temperature [1].

4. Conclusion and suggestion

We have concluded that the average aquatic temperature along the estuary of the Jagir River, Wonorejo Village was at 30.3ºC, the average aquatic pH was 7.6, the average aquatic salinity was 1.7 g L^{-1}, whereas the average DO was 3.2 mg L^{-1}. The concentration of Cu at the research location at station 1 was below than 0.004 mg L^{-1} while at the station 2 and 3 concentration of Cu were equal as much as 0.05 mg L^{-1}. When compared to the existing quality standards, the DO and Cu metals in the aquatic at stations 2 and 3 had exceeded the standard quality limits.

We suggest that handling the concentration of Cu in the water and the sediment in the Jagir River estuary, as positively the concentration of Cu increases. Mangrove forest ecosystem can be applied as natural biofilter to reduce the concentration of Cu in the sediment through phytoremediation process. Moreover, it is a cheaper way to rehabilitate the ecosystem. A continuous monitoring of environmental conditions at the research location should be conducted, avoiding biodiversity loss in that area.

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