Heavy metal toxicity and the influence of water quality in watershed for enhancing fisheries food security

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Abstract. This study investigated the toxicity of heavy metals such as Cu, Fe, Cr, Zn and Mn and the influence of water quality in Garang Watershed Semarang (Banjir Kanal Barat River), Central Java Indonesia for enhancing fisheries food security. The fish biomarker in this research is Nile Tilapia (Oreochromis niloticus). The range of Cu, Fe, Cr, Zn and Mn in aquatic environment were 0.15 mg/L; 0.82 mg/L; 0.025 mg/L; 0.562 mg/L and 0.01 mg/L. The range of Cu, Fe, Cr, Zn and Mn in Nile Tilapia were 2.547 mg/kg; 306.3 mg/kg; 0.36 mg/kg; 16.69 mg/kg and 35.6 mg/kg. Toxicity in fish is exceeded the limits of food security regulation in WHO and BPOM, and water quality regulation in Government Regulation of Indonesia No 82/2001 on Water Quality And Water Pollution Management. Management in water quality is and toxicity is important for enhancing fisheries food security. Maintaining food security in the fishery sector is very important for the stability of community nutrition because with good food public health will be guaranteed.

Keywords : food security, toxicity, fish, water quality, watershed

1. Introduction
Fish is one of the main food sources in Indonesia and has high nutritional value through its processed products. The fisheries sector is one of the sectors that support economic and regional development in Central Java [14]. The city of Semarang is the capital of the province of Central Java, which has many industries and directly borders the North Coast of the Laut Jawa and has a river that runs from upstream to downstream. This industrial area produces waste discharged into rivers and spreads to the estuary. As a result of industrial waste, pollution is high enough to result in a polluted water environment and contains heavy metals.

Heavy metal is one type of industrial waste that pollute the waters [11]. Heavy metals in relatively small waters will be very easily absorbed and accumulated biologically by aquatic plants or animals and will be involved in food web systems. The content of heavy metals in aquatic biota will usually increase over time because it is bioaccumulative [12]. Heavy metals are very dangerous for human life, for example when cases of heavy metal poisoning occurred in the Minamata Bay of Japan in the 1950s. Hundreds of lives lost as a result of consuming fish containing mercury [3]. The impact arising from the presence of heavy metals in the waters depends on the presence of metals in water and sediments, their toxicity and concentration in the environment. Heavy metals if pollute into the body
of living things will experience bioconcentration, bioaccumulation, and biomagnification [9]. This research should have been conducted to provide information to the public and industry owners regarding the heavy metals contained in fish in river waters, furthermore that risk factors could be minimized.

2. Methodology

2.1. Study Area
The Banjir Kanal Barat river is located on the coast of Semarang City, Central Java Province, Indonesia (Figure 1). The length of the Banjir Kanal Barat river is 5.4 km. On the left and right of the river is a resident's house. The main function of the Banjir Kanal Barat river as the main drainage channel of the city, but the occurrence of sedimentation causes the volume of water to be reduced. Furthermore, there was a flood around it due to the overflow of this river. The Semarang City Government and the Japanese Government through the Japan International Cooperation Agency (JICA) normalized of this river in 2010, furthermore that this normalization was able to restore the main function of the Kanal Banjir river as a flood control channel [51]. Determination of the sampling location using a purposive sampling method [52]. The source of heavy metal input becomes the basis for determining the sampling location. The sampling location is the entry point of heavy metals from the mainland to the sea (estuary) and is the final disposal site of all pollutants from the mainland area [53].

Figure 1. Study area: the map of the Indonesia (A), Central Java Province (B), Location of Banjir Kanal Barat River, Semarang, Central Java Province, Indonesia (C)
2.2. Sampling techniques
Fish collects in Banjir Kanal Barat River is downstream of Garang watershed, Semarang, Central Java, Indonesia. The downstream is used for estuary, settlement, port fishery and aquaculture. In this area, the waste comes from industry, domestic and thus affecting the water quality of the river [41]. This watershed is Garang river, the local name of the river is Banjir Kanal Barat / Kanal Banjir Barat, this river near settlements and downstream area, and this is the estuary zone of Laut Jawa.

2.3. Heavy Metals Analysis
Approximately 25 g (to nearest 0.1 g) of the test portion into a crucible. Dry at a temperature of 135°C to 150°C for 2h. Transfer to the furnace with temperature control. Increase the temperature to 500°C until overnight (16h). Set at room temperature, add 2 mL of HNO₃, and swirll it. Evaporation occurs on a hot plate and a steam bath. Transfer the sample to the furnace, raising the temperature to 500°C, for 1 hour. Afterward, the dish was removed and cooled down. To get clean, C-free ash, HNO₃ graying is repeated. Add 1M HCl, then heat it on the hot plate carefully to dissolve the ash. Transfer the sample to a 25 mL volumetric flask, 5 mL HCl 1M cooled, and diluted with 1M HCl. Set the optimal spectrophotometer conditions at a maximum signal of 283.3 nm. Using the airflow rate - the manufacturer recommends C₂H₂ is a standard condition for Pb. Read the results on a spectrophotometer. Calibrate the concentration mode with solutions containing 0.2 and 10.0 μg Pb / mL. Record the concentration directly after calibrating the instrument. For strip chart readings, adjust the amplification to give an absorption reading of %1% for a working solution of 0.2 μg Pb / mL and prepare a standard curve with μg Pb / mL [42].

3. Result and Discussion
3.1. Heavy Metals in Fish Tilapia (Oreochromis niloticus)
3.1.1 Arsenic
Arsenic is a metal that can be found in groundwater. The arsenic content in the study location ranges from <0.029 mg / kg - <0.030 mg / kg, the Maximum Limit of Contamination of Heavy Metals in Processed Food that is equal to 0.25 mg / kg [46]. Arsenic can be dangerous because it accelerates the development of cancer cells, infertility and miscarriage [27]. Source of manganese comes from pesticides, fungicides, metal smelters [16].

3.1.2 Iron (Fe)
Iron (Fe) concentration in Tilapia is 15.86 mg / kg; 256.2 mg / kg; 306.3 mg / kg [45]. The graph of Iron Concentration (Fe) in Tilapia is presented in Figure 1.

![Graph of Iron Concentration](image)

**Figure 2.** Concentration of Iron (Fe) (mg/kg) in Tilapia
Iron (Fe) concentrations at 3 stations exceed the threshold of heavy metal Fe determined by WHO (2003) [47] is 0.3 mg/kg. Fe is a silvery-white metal, clay and can be formed [24]. Industrial wastes containing Fe metal are toxic to plants, animals, and humans. Excessive amounts of Fe can cause poisoning, death, kidney disease, intestinal wall damage and hepatitis [30]. Tilapia fish (*Oreochromis niloticus*) liver which accumulated by Fe metal will experience pathological changes in the form of fatty cells and necrosis.

3.1.3 Chromium (Cr)
Cr at the study site is 0.29 mg/kg; 0.32 mg/kg and 0.36 mg/kg. Cr in these three locations exceeds the quality standards by BPOM Regulation 5/2018 [46]. The high Cr is thought to originate from the textile industry waste originating from upstream rivers. Another factor that causes high Cr concentrations at this station is the river mouth which is the point of mixing between freshwater and sea, furthermore that this sampling point contains higher of mud [20]. Source of manganese comes from mining, electroplating, textile, tannery industries [16]. The graph of Iron Concentration (Fe) in Tilapia is presented in Figure 2.

![Graph of Iron Concentration (Fe) in Tilapia](image)

**Figure 3.** Cr Concentration (mg / kg) in Tilapia

3.1.4 Lead (Pb)
Pb found in tilapia in the study location was <0.387 mg/kg; <0.389 mg/kg and 1.334 mg/kg. The Pb concentration at the BKB2 sampling point exceeds the quality standards set by WHO (2003) [47] is 0.01 mg/kg. Pb can pollute the fish through the body surface, gills, absorption through food, and osmoregulation mechanism. The increased Pb concentration in fish meat occurs due to accumulation. PB that accumulates over time will cause fish death because fish cannot adapt to lead exposure [4]. The accumulation of Pb in the body of the fish will interfere with the synthesis of Hb whose function is to bind oxygen. The inhibition of Hb synthesis causes the ability to bind oxygen to become smaller so that it affects its metabolism [10]. Source of manganese comes from paint, pesticides, batteries, automobile emission, mining, burning of coal [16].

3.1.5 Zinc (Zn)
Zn found in tilapia in the study location was 12.18 mg/kg; 13.09 mg/kg and 16.69 mg / kg. This Zn concentration exceeds the threshold set by WHO (2003) [47] which is 5 mg/kg. The graph of Zn heavy metal concentration is presented in Figure 3.
Zn in waters originating from effluent and run-off streams, this pollute the body of aquatic organisms [2]. Detecting heavy metals can be carried out in Zn contaminated fish livers [13]. Muscles are indicators of Zn at low levels [4]. Low Zn concentrations in muscles can be caused by low muscle ability in binding protein (metallothionein) [19]. Source of zinc comes from refineries, brass manufacture, and metal plating [16].

3.1.6 Cadmium (Cd)
The concentration of Cd contained in Tilapia Fish in the study location were: <0.097 mg / kg - <0.099 mg/kg. This concentration is still limit is 0.1 mg / kg (BPOM Regulation 5/2018) [46]. Cd is a dangerous metal sourced from the use of fuel, forest fires, industrial waste and the use of fertilizers and pesticides [1]. The accumulated CDs cause physiological damage to the body of the reproductive glands, bone fragility, sense of smell, kidneys, lungs, blood, and heart [23]. The low Cd content in waters is thought to be due to research time which is the dry season, furthermore that waters are at the lowest discharge so that Cd experiences dilution [17]. Source of cadmium comes from welding, electroplating, pesticides, fertilizer, batteries, nuclear fission plants [16].

3.1.7 Copper (Cu)
Cu concentration contained in Tilapia Fish in the study location was 1.369 mg/kg; 2.118 mg/kg and 2.547 mg/kg. Cu concentration contained in Tilapia Fish originating from BKB 2 sampling point exceeds the threshold of Cu concentration determined by WHO (2003) [47] is 2.25 mg/kg. Graph of Cu Concentration contained in Tilapia in the research location is presented in Figure 4.
water conditions. Influence factors the accumulation of heavy metals in aquatic organisms depend on the temperature of the aquatic environment, the state of the species, physiological activity and temperature of the water [6], the way the toxins enter the body, the duration and frequency of exposure, the toxicant concentration, shape, and the physical/chemical properties of metals the severity and susceptibility of various species to toxicity [43]. Cu is accumulated continuously in fish, if it will be consumed by humans and experiencing acute poisoning will cause symptoms of gastrointestinal and kidney disease [7]. Source of copper comes from electroplating, pesticides, and mining [16].

3.1.8 Manganese (Mn)
Mn concentrations contained in Tilapia Fish in the study site were 24.79 mg/kg; 34.29 mg/kg and 35.6 mg/kg, this concentration exceeds the threshold set by WHO (2003) [47] is 0.5 mg/kg. Manganese is an important component in metabolism that is the function of flavoprotein and the synthesis of mucopolysaccharides, cholesterol, and hemoglobin. The toxicity of manganese does not depend on the total concentration of manganese, but the concentration of oxidized manganese available. Mn concentrations exceeded the threshold, causing reddish, yellow and black waters, causing an unpleasant taste. The source of cadmium comes from welding, fuel addition, and ferromanganese production [16]. The Mn concentration of Mn in Tilapia Fish at the study site is presented in Figure 5.

![Figure 5. Graph of Manganese Concentration (mg/kg) in Tilapia](image)

3.1.9 Mercury (Hg)
The concentration of Hg contained in Tilapia Fish in the study site was <0.002 mg/kg. The limit is 0.5 mg/kg (BPOM Regulation 5/2018) [46], this concentration is under than the limit. Hg is a metal that is liquid at room temperature. Mercury (Hg) or mercury is a metal that is naturally present, is the only metal that is at room temperature in a liquid form. Hg metal in water and soil is mainly derived from industrial effluents, natural deposits, and volcanic activity. Hg that accumulates continuously can cause nervous system disorders, headaches, chromosomes, allergic damage to brain function, DNA, skin rashes, fatigue, sperm damage, disability in infants and miscarriages [1]. Hg contamination at the research location is suspected to be due to industrial waste contamination at the upstream location. environmentally friendly agricultural systems around rivers. Hg toxicity is influenced by environmental factors of these waters [18]. Source of mercury comes from pesticides, batteries, and paper industries [16].

3.1.10 Nickel (Ni)
The concentration of Ni contained in Tilapia Fish in the study location is <0.097 mg/kg - <0.099 mg/kg. This concentration is below the threshold set by the IAEA (International Atomic Energy Agency)-4017, is 0.6 mg/kg. Nickel can be absorbed by organisms through magnetized food in plants and the waters that become their habitat. Ni accumulates in sediments and aquatic organisms through the process of exposure, bioaccumulation, and biomagnification [39]. Ni is insoluble under anaerobic
conditions, and soluble under aerobic conditions [44], the level of Ni toxicity is influenced by the solubility level of Ni compounds [5]. Source of nickel comes from electroplating, zinc base casting and battery industries [16].

3.1.11 Fisheries Food Security
Heavy metals found in fish are very harmful. High heavy metals can reduce the level of food safety in fisheries. Wild tilapia fish have better omega-3 fatty acid content than cultivated tilapia [50], furthermore the habitat of wild tilapia (river) is important to maintain its water quality. Freshwater fish contain protein that is important for people and families in developing countries to maintain food security [48]. Characteristics of community who have good food security have adequate amounts of food and good nutrition for public health [49].

4. Conclusion
Heavy metals contained in rivers: As, Fe, Cr, Pb, Zn, Cd, Cu, Mn, Hg, and Ni. Heavy metal concentrations that exceed water quality standards: Fe, Cr, Zn, Cd, Cu, and Mn. The recommendation in this research are: harmonization of upstream and downstream sector policies in the long-term security of water, energy, and food security. Integration of planning and management of water, energy, land, forests, ecosystems, agriculture, and food security for the efficiency of natural resources and reducing environmental impacts. Synchronization between government agencies in terms of water use (for irrigation, energy, navigation, fisheries, and domestic) [54]. Management of disposal of industrial waste into the river, furthermore that the river are not polluted and the fish are not contaminated with heavy metals.

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