The chromium concentration downstream of the Opak River, Yogyakarta, Indonesia

[1]Djoko Rahardjo, [2]Djumanto, [1]Windu S. Manusiwa, [1]Aniek Prasetyaningsih

[1] Faculty of Biotechnology, Duta Wacana Christian University, Jl. Dr. Wahidin Sudirohusodo, Yogyakarta, Indonesia; [2] Department of Fisheries, Faculty of Agriculture, Gadjah Mada University, Yogyakarta, Indonesia. Corresponding author: Djumanto, lely4192@yahoo.com

Abstract. The ecological, biological and economical role of the Opak River's downstream is crucial for the people in the Bantul Regency area. Several home leather industries use the Opak River to dispose liquid waste, affecting water quality and aquatic biota. This study aimed to determine the concentration of chromium (Cr) in the Opak River ecosystem and fish. Sampling was carried out in February, April, and July 2020, in six locations, covering water, sediment and fish samples. The Cr concentration was measured for each sample using the atomic absorption spectrometer (AAS) method. The highest Cr concentration was found in *Osteochilus vittatus* (0.8489 mg kg^{-1}), followed by the sediment samples (0.7125 mg kg^{-1}), *Oreochromis niloticus* (0.3799 mg kg^{-1}) and the water samples (0.01889 mg kg^{-1}). The concentration of chromium in fish is still below the toxicity threshold for the biota and environmental health. The chromium concentration tends to increase according to the trophic level.
Key Words: home industry, heavy metals, liquid waste.

Introduction. Opak River is one of the rivers located in the east of the Yogyakarta Special Region, which has a flow length of approximately 65 km and a river basin area of 1,398.18 km^2. The upstream part of the Opak River is located on the slopes of Mount Merapi in Cangkringan District, Sleman Regency. The river's downstream side is located in the Srigading Village, Sanden District, Bantul Regency, where it joins the Indian Ocean. The Opak River has several tributaries of first and second order, such as the Oyo River, Winongo River, Code River, Gajahwong River, and the Tambakbayan River (Wardhana 2015). The Opak River plays a significant role as a habitat for fish, supporting the community life. The water quality needs to be considered for a viable ecosystem. According to the research results (Rahardjo & Prasetyaningsih 2017), the Opak River has been contaminated with heavy metal chromium (Cr) from the leather tanning industrial waste disposal.

Home industries that dispose heavy metal waste without treatment can cause environmental pollution. Chromium is a heavy metal which, in high concentrations, can affect the life of aquatic biota. Chromium can be present in various media, like water, sediment, or in aquatic biota, such as fish. Chromium that enters the river waters will accumulate through the food chain (Rahardjo & Prasetyaningsih 2017). Fish that live in contaminated waters can absorb chromium through semi-permeable membranes and digestive channels.

The concentration of chromium in various media can be an indicator of the environmental health level. Chromium concentration in fish is the most significant biomonitor for estimating the level of heavy metal pollution, providing information on habitat alterations (Rashed 2001; Lamas et al 2007; Authman 2008). When chromium is bound by plankton, it can accumulate at a higher trophic level. The higher the position of the fish in the food chain, the higher the concentration is. If contaminated fish is consumed, chromium will accumulate in the body, causing chronic disease (Al-Yousuf et al 2000). Therefore, chromium levels in the aquatic environment and fish bodies can indicate the health level of the waters (Rajeshkumar & Li 2018).

The chromium concentration in fish bodies indicates past exposure through the aquatic environment and food (Birungi et al 2007). In the short term, the contamination level is low and has no visible impact on fish. In the long term, these pollutants reduce fish's ability to reproduce, survival rates and thus accelerates the decline of the fish stocks (Ebrahimi & Taherianfard 2011; Krishnani et al 2003). Therefore, research on chromium concentration in the waters of the downstream Opak-Oyo River is fundamental. The present research can support riverine ecosystem conservation, liquid waste treatment and fisheries activities' sustainability and safety management.

Material and Method

Description of the study sites. The main economic activity in the area of Sitimulyo Village, in the Piyungan Sub-district, Bantul Regency, is the leathercraft home industry. The home industry discharges liquid waste into the river, becoming a major pollutant of the river ecosystem. The research was conducted in February, April, and July 2020, along the lower Opak River, where the volume of waste is considerable. There were six sampling stations, one station was located above the Sitimulyo village, and the rest of the stations were below the Sitimulyo village. The distance between stations was about 5 km (Figure 1).

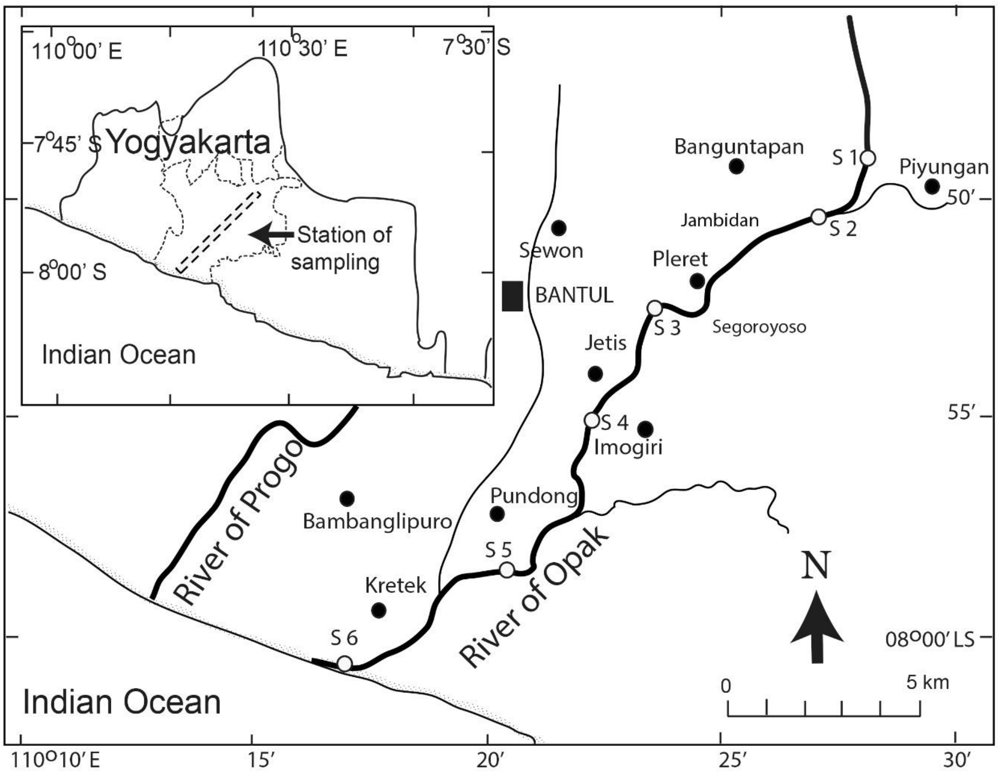

Figure 1. Sampling stations on the Opak River. The full circle is the sub-district, and the empty circle is the research station, S1-6 is the sampling station.

Collection of water, sediment, and fish samples. Water samples were taken at the water surface using a bucket, then put into a 1 L of plastic bottle HDPE (High-density polyethylene). 3 mL of 1% HNO_3 were added to the water sample, as a preservative, before storing it at 4°C. The sampling was carried out three times. Approximately ±100 g of riverbed sediment samples were taken using a shovel as a substitute for the sampler grab (EPA 2001). The sediment samples were put into clear plastic and stored at 4°C. Fish samples of tilapia (*Oreochromis niloticus*, Linnaeus, 1758) and bonylip barb (*Osteochilus vittatus*, Valenciennes, 1842) species were caught using cast nets with a mesh opening of 1 inch, then they were rinsed with tap water, put in a transparent plastic bag differentiated by species, and stored in the freezer at -20°C (Rajeshkumar & Li 2018).

Analysis of chromium concentration. Water samples were extracted using HNO_3, while solid samples were extracted using aqua regia. Fish and sediment samples were extracted by the acid method. Each sample of 2 g was put into an Erlenmeyer, then aqua regia was added, at a ratio of 1 part HNO_3 + 3 parts HCl, and then a volume of 10 mL was heated in the stove. This process was repeated twice. The extract obtained was transferred into a flask of 10 mL volume. If the volume was less than 10 mL, distilled water was added, and then filtered using filter paper. A measurement of extract chromium levels was carried out using atomic absorption spectrophotometry (AAS) based on the SNI 06-6989.17-2004 (National Standardization Agency for Indonesia 2004). Process analysis was carried out with a PerkinElmer PinAAcle 900T Atomic Absorption Spectrometer.

Bioconcentration factor. The calculations of the bioconcentration factor (BCF) and of the maximum tolerable intake (MTI) were performed according to the formula of Turkmen et al (2009):

$$\text{BCR Cr} = \frac{\text{the content of heavy metal Cr in fish meat}}{\text{the content of heavy metal Cr in water}}$$

$$\text{MTI} = \frac{\text{fish body weight x 23.3}}{\text{concentration of chromium in fish meat x 1000}}$$

Results. The chromium content in all samples, for each sample type (water, sediment, and fish), is presented in Table 1. Chromium concentrations found in water, sediment and fish samples had an average of 0.0004-0.0596 mg L^{-1}, 0.0736-1.4923 mg kg^{-1} and 0.0004-0.6570 mg kg^{-1} in *O. niloticus* and 0.5530-1.4850 mg kg^{-1} in *O. vittatus*, respectively. The highest concentration of chromium pollutants was found in *O. vittatus*, followed by sediment and *O. niloticus*, and the lowest was found in the water samples.

Table 1

Average chromium concentrations (mg L^{-1}) in water, sediment, and fish samples

Sample type	*n*	*S1*	*S2*	*S3*	*S4*	*S5*	*S6*	*Quality standard*
Water	2	0.0590	0.0521	0.0004	0.0004	0.0004	0.0004	0.05*
Sediment	2	0.8125	1.4923	0.7056	0.6070	0.5843	0.0736	80.00**
Oreochromis niloticus	2	0.6380	0.4920	0.0004	0.6570	0.0004	0.4920	1.00***
Osteochilus vittatus	2	0.7706	0.5530	1.1050	0.1780	1.4850	1.0020	2.50****

* Government Regulation 2008;** Australian and New Zealand Environment and Conservation Council 2000; *** Food and Agriculture Organization 1983; ***** Directorate General of Drug and Food Control 1989.

In *O. niloticus* and in *O. vittatus* there were found chromium concentrations of 0.0004-0.6570 mg kg^{-1} and of 0.1780-1.4850 mg kg^{-1}, respectively. Compared with the quality standards (Directorate General of Drug and Food Control 1989), all were still below the threshold of 2.5 mg kg^{-1}. However, if we refer to the FAO provisions (FAO 1983), which is 1 mg kg^{-1}, then the Cr concentrations in *O. vittatus* samples at stations 3, 4, 5, and 6 exceeded the threshold value.

The value of the bioconcentration factor (BCF) in *O. niloticus* and *O. vittatus* is presented in Table 2. The highest BCF value in *O. niloticus*, 1642.5 mg L^{-1}, was found at station 4, while the lowest, of 1 mg L^{-1}, was found at stations 2 and 4. The highest value of BCF in *O. vittatus*, 2762.5 mg L^{-1}, was found at station 2 and the lowest, 12.9 mg L^{-1}, at station 1.

Table 2

The bioconcentration factor (BCF) in *Oreochromis niloticus* and *Osteochilus vittatus*

Species	*S1*	*S2*	*S3*	*S4*	*S5*	*S6*	*Average*
Oreochromis niloticus	10.7	9.4	1.0	1642.5	1	1230	482.4
Osteochilus vittatus	12.9	10.6	2762.5	445.0	3712.5	2505	1574.8

Discussion. The leather tanning industry is one of the main contributors to the chromium pollution of the Opak River ecosystem, due to liquid waste discharges. At stations S1 and S2, which are the closest liquid waste disposals to the leather tanning industry locations, chromium concentrations exceed the allowable standard. At stations S3-S6, which are located farther from the wastewater disposal, chromium concentrations were still below the threshold of the quality standard (Government Regulation 2008), which is 0.05 mg L^{-1}. Higher concentrations of chromium at S1 and S2 are possibly due to the pollution source proximity. The concentration of chromium in the water decreases with the distance from the waste disposal site (Simanjuntak et al 2012).

The quantity of chromium concentration in water samples is influenced by the river morphometry, abiotic conditions, distance from the pollution sources and season. In the dry season, the volume of the river water is minimal and the flow is relatively slow or even stagnant, causing chromium accumulation. In the present study, sampling was carried out during the rainy season, when high rainfall causes river water volume to be very abundant, resulting in dilution (Ahmed et al 2013). The distance between sampling stations can affect the measured chromium concentrations (Yuniarto & Iqbal 2013). Water bodies also can carry out self-purification through physical and chemical processes such as flow dilution, deposition and adsorption (Tian et al 2011).

The average chromium concentration in *O. niloticus* and *O. vittatus* samples was 0.3799 mg kg^{-1} and 0.8489 mg kg^{-1}, respectively, much higher compared to 0.0188 mg L^{-1} in the water samples. The chromium concentration in fish meat is influenced by the trophic level and foraging activity of the fish. *O. vittatus* is an herbivorous fish (Rahmia 2012) that feeds on algae, moss, plankton and other organisms on the bottom of rivers (Vasconcelos et al 2018), while *O. niloticus* is an omnivorous fish foraging more in the water column (Kurnia 2017). Therefore, the chromium concentration in *O. vittatus* is higher than in *O. niloticus*.

The discharge of industrial effluents determine the increased chromium concentrations in the sediment samples, which are higher than in the water sample, due to the heavy metal fixation on the suspended particles or absorption and deposition. The chromium concentration in water samples is still very low, below the maximum thresholds, but in the long term it still has the potential to harm the life of aquatic biota and users of the Opak River ecosystem (Sfakianakis et al 2015; Pacheco et al 2013).

The chromium concentrations in *O. niloticus* and *O. vittatus* fluctuated between stations. Fish are aquatic biota that actively move upstream and downstream of rivers, so that the sampling location does not affect the chromium concentration of the two types of fish. Fish are nekton, actively moving from one place to another, according to the availability of food sources and to the environmental conditions, including pollutants. Aquatic organisms, such as fish, move faster and generally can avoid the effects of water pollution, but in narrow habitats, such as the Opak River, it is challenging to prevent pollutants' influence (Simanjuntak et al 2012). The chromium concentration in *O. vittatus* is higher than in *O. niloticus*, presumably due to the organisms' bioecological factors and to the river environment's physical condition. As an omnivorous fish, *O. niloticus* eats more phytoplankton and less zooplankton, which is washed away in the water column. Simultaneously, the *O. vittatus* is herbivorous, which likes algae, moss, detritus on the bottom of the waters so that the potential for exposure to chromium is higher than in *O. niloticus*. Another reason of the higher chromium accumulation in *O. vittatus* is the choice of habitats with lower debit flows and lots of organic matter or detritus (Rahardjo & Prasetyaningsih 2017). Riverbeds that are muddy or sandy and with calm currents generally have a high chromium deposit, so that the biota in these habitats has a relatively high concentration of chromium than the biota in fast-flowing habitats.

The BCF values between fish species and sampling locations were different, showing that the process of chromium absorption and accumulation in biota is influenced by many factors, such as: species, bio-ecology, chromium concentration in water and sediment, and environmental conditions. An organism is classified as high, medium or low accumulative if it has a BCF value of>1,000 mg L^{-1}, 100 to 1,000 mg L^{-1} or <100 mg L^{-1}, respectively (Amriani et al 2011). Based on these criteria, *O. niloticus* at stations S1, S2, and S5 and *O. vittatus* at stations S1 and S2 are classified as low accumulative. On the other hand, *O. vittatus* at station S3 is classified as medium accumulative. In comparison, *O. niloticus* at stations S4 and S6 and *O. vittatus* at stations S3, S5, and S6 are classified as highly accumulative. Based on the average BCF value, the *O. vittatus* is an organism that has a high accumulation ability, while *O. niloticus* is considered to have a moderate accumulation ability. Red tilapia can also accumulate chromium pollutants pollutants in muscle tissue at moderate levels (Handayani et al 2014).

The discovery of chromium accumulation in economically beneficial biota widely consumed by the community indicates the magnitude of the risk to the public health. Chromium pollutants can cause various disorders in humans, such as disintegration of muscle fibers, loosening and shrinkage of the surrounding perimysium, vacuolar degeneration and hemorrhagic damage in the liver (Sia Su et al 2013). Prolonged exposure to chromium pollutants can lead to behavior modification in fish, such as reduced appetite, slow and random swimming, changes in body color and accelerated operculum movement (Aslam & Yousafzai 2017).

The present study's results can be used as a source of information to analyze the health risks of consuming chromium-contaminated fish. Based on the provisional tolerable weekly intake (PTWI), the maximum threshold value for chromium is set to 23.3 μg kg^{-1} (FAO 1983), as the maximum weekly intake (MWI) value, assuming an adult's body weight is 50 kg. The chromium's maximum concentration value tolerable in fish meat is 1.15 mg Cr $week^{-1}$, for a safe consumption.

The tolerable maximum intake (MTI) value of chromium in *O. niloticus* is 3.0271 kg $week^{-1}$, and *O. vittatus* meat is 1.3546 kg $week^{-1}$. Fish biomass in the downstream Opak river area that fishers exploit is relatively small. The level of fish consumption in the Special Region of Yogyakarta is 36 kg $(capita\ year)^{-1}$ (Central Statistics Agency 2018). If it is assumed that 10% are fish from freshwater, the level of consumption of freshwater fish is 3.6 kg $(capita\ year)^{-1}$ or 0.069 kg $(capita\ week)^{-1}$. It shows that the consumption level of freshwater fish is still safe for public health.

Conclusions. The disposal of liquid waste from the leather industry in the Banyak area is a significant contributor to elevated chromium concentrations in river waters, sediments and fish along the Opak River. High concentrations of chromium pollutants were found in the meat samples of *O. vittatus*, in the sediment samples, in the meat samples of *O. niloticus* and lower Cr concentrations were also recorded in the water samples. *O. vittatus* has a higher chromium accumulation rate than *O. niloticus*. The discovery of chromium accumulation in fish indicates the magnitude of the risk it represents for the public health and for the surrounding environment.

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Authors:
Djoko Rahardjo, Kristen Duta Wacana University, Faculty of Biotechnology, Jl. Dr. Wahidin Sudirohusodo no. 5-25, 55224 Yogyakarta, Indonesia, e-mail: djoko@staff.ukdw.ac.id
Djumanto, Gadjah Mada University, Faculty of Agriculture, Department of Fisheries, 55281 Yogyakarta, Indonesia, e-mail: lely4192@yahoo.com
Windu Septriany Manusiwa, Kristen Duta Wacana University, Faculty of Biotechnology, Jl. Dr. Wahidin Sudirohusodo no. 5-25, 55224 Yogyakarta, Indonesia, e-mail: winduseptriany@gmail.com
Aniek Prasetyaningsih, Kristen Duta Wacana University, Faculty of Biotechnology, Jl. Dr. Wahidin Sudirohusodo no. 5-25, 55224 Yogyakarta, Indonesia, e-mail: aniek@staff.ukdw.ac.id

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