THE EFFECT OF BATIK INDUSTRY ON THE QUALITY OF WATER ENVIRONMENT AND ITS RISK ANALYSIS IN YOGYAKARTA, INDONESIA

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ABSTRACT

The use of synthetic dyes and other chemical by batik industry in Indonesia raises concern on its potential negative impact to the environment and eventually human health. The magnitude of the impact would be higher as most batik factories were home industries with limited capacity in term of occupational health and environmental management. This research discusses the effect of batik industry on the quality of water environment in Yogyakarta as one of the centers of batik industry in Indonesia. This research is divided into 8 major chapters as followed:

Chapter 1 Introduction

Chapter 1 briefly explained the overview of issues related to batik industry in study area as the background of this study followed by problem statements, research objectives, scopes of study, and outline of the thesis.

Chapter 2 Literature review

Chapter 2 covers information about batik industry and study area. In the beginning, it will discuss the cultural and economic importance of batik industry in Indonesia. Then, the general production process in batik industry will be introduced as well as environmental issues arising associated with its operation. It will then more focus on two groups of pollutant which will be the focus of the entire study. Those two groups are heavy metal and aromatic aryl amines. Reviews on previous studies regarding the toxic effect of those group of pollutants will also be presented. This chapter concludes with the description of demographic and physical condition of Yogyakarta Special Province and then focusing on Yogyakarta City and Bantul Regency as the study area.

Chapter 3 Profile of batik production and the potential generation of hazardous organic substances from the use of azo dyes in batik industry in study area

Chapter 3 presents the profile of batik industry in study area which covers production method and wastewater handling and to investigate whether the azo dyes used by batik industry in study area are those that can generate aromatic amines. Studies on 24 batik factories in Yogyakarta City and 53 factories in Bantul Regency showed that 92 % and 89% batik factories in each of these 2 areas used synthetic dyes in their production. Of this synthetic dyes, azo dyes especially naphthol have been used by more than 88% and 70 % of batik factories in Yogyakarta City and Bantul Regency, respectively. Regarding water consumption, average amount of water required for production of one sheet of batik product was 7.5 liter. Compared to other study, this amount is relatively low. Related to wastewater handling, 50 % factories in Yogyakarta City and 34 % factories in Bantul Regency did not have any kind of wastewater treatment plant. Hence, wastewater was just released into environment without prior treatment. One of the concerns was the implication of the widely used azo dyes. Laboratory analysis detected 11 toxic aromatic amines in varied concentration from reduced naphthol dye samples and 5 compounds in reduced wastewater samples. It is

confirmed that azo dyes widely used by batik factories in study area are those potentially release carcinogenic aromatic amines under reduction favorable environment.

Chapter 4 Metal and metalloid content in wastewater from batik industry in study area

Chapter 4 presents metal and metalloid characteristics of wastewater samples from batik factories in study area. The results shows that concentration of Al, Si, Fe, Zn, Cr, Co, Ni, Cu, As, Se, Cd, and Pb ranged from 0.11 to 300 mg/L, 25 to 280 mg/L, 0.56 to 12 mg/L, 0.11 to 180 mg/L, 11.7 to 100 µg/L, 0.6 to 17.7 µg/L, 7.2 to 82.8 µg/L, 20.9 to 1.9 10^3 µg/L, 1.5 to 21.2 µg/L, 7.6 to 2.6 10^3 µg/L, <0.05 to 220 µg/L, and 0.03 to 42.7 µg/L, respectively. No sample exceed relevant effluent standard in Indonesia as the only heavy metal parameter regulated is Cr. However, concentration of Cd, Se, Fe and Zn exceed relevant effluent standard in Japan and Malaysia. Compared to other studies, concentration of Cr, Pb and Si in this study were relatively lower. However, the concentration of Cu, Cd, Fe and especially Al and Zn were much higher than other studies. Hierarchical Cluster Analysis (HCA) produced dendrograms showing cluster of Ni, Cr and Co which indicates that the source of these metals is from dyes. Other clusters indicated various sources such as groundwater or another supporting chemical. HCA also indicates that factors other than the type of dye and production stage may affect heavy metal content in batik wastewater which represent the high variability of production process among batik factories.

Chapter 5 Effect of batik effluent seepage on groundwater quality

Chapter 5 focuses on analysis of various metals in groundwater samples taken from dug wells at and around batik factories in Winongo Watershed. Analysis on 32 groundwater samples taken from dug wells at and around batik factories revealed that the water quality is still within the acceptable level. Heavy Metal Contamination Index (HCI) confirmed this condition with very low HCI value. Numerical simulation using one dimensional contaminant transport equation showed very low concentration at groundwater table level which indicate that no groundwater contamination occurred from batik wastewater seepage. This is supported by the lithological and hydrogeological condition of alternating clay and sand layer that prevent the pollutant to seep into the groundwater.

Chapter 6 River water and sediment quality affected by effluent from batik industry

Chapter 6 focuses on analysis of heavy metals in water and sediment samples of Winongo River which is the receiving water body for discharged wastewater including from batik industries in Winongo Watershed. Distribution of various heavy metal in river water was following the order of Fe>Pb>Cd>Cu>Cr. Range of concentration were 42.8-121.4 µg/L for Fe, 7.6-54.9 µg/L for Pb, 8.9-14.4 µg/L for Cd, 3.0-6.8 µg/L for Cu, and <5.5 µg/L for Cr. For concentration in sediment samples following order occurred, Fe>Pb>Cu>Cr>Cd. Range concentration in sediment were 1473.4-3237.6 mg/kg for Fe, 16.3-49.0 mg/kg for Pb, 15.4-46.3 mg/kg for Cu, 0.5-12.6 mg/kg for Cr, and 1.7-3.3 mg/kg for Cd. Assessment by using Geo-accumulation index (Igeo) and Enrichment Factor (EF) suggested a serious contamination by Cd and Pb in river sediment. According to consensus-based sediment quality standard (Qm-PCA), all sediment samples were considered toxic. For water samples, assessment by using Heavy metal Pollution Index (HPI) and Nemerow Pollution Index (PN) agreed which area was among the mostly polluted. Statistical source identification revealed the heavy metal possible sources were agricultural activities and home industries. Monte Carlo simulation

showed the low probability of contribution of batik wastewater to cause the concentration of river water exceed stream standard for parameter Pb, Cd, Fe and Cu, but high probability for Zn.

Chapter 7 Risk analysis of heavy metal in edible fish from river receiving batik effluent

Chapter 7 presents risk analysis of the consumption of heavy metal contaminated edible fish from Winongo River which is affected by batik effluent. Ten fish samples were taken from Winongo River and analyzed for the concentration of Cr, Cr, Cu, Fe, and Cd in the flesh part of the fish. The distribution of heavy metal concentration is following the order of Fe>Cu>Cr>Cd>Pb with the range of 0.02-0.34 mg/kg for Pb, 0.03-0.51 mg/kg for Cr, 0.04-0.33 mg/kg for Cu, 0.05-0.17 mg/kg for Cd, and 0.62-6.68 mg/kg for Fe. Concentration of Cd and Pb exceed the relevant standard at some sampling points. The highest concentration occurred at the meeting point of main river and tributary from the direction of Yogyakarta City Center. Risk analysis on the consumption of this contaminated fish revealed the safe level for non-carcinogenic effect with Risk Quotients below 1 but not safe level for carcinogenic effect, since the ECR value for Cd and Cr are above 10^{-4}. This result is the indication of the urgency to conduct risk management program upon Winongo River and the various parties involved.

Chapter 8 Conclusion and Future Recommendation

Chapter 8 summarizes the conclusions of the previous chapters and their implication as well as recommendation for future research

Table of Contents

List of Figures

List of Tables

CHAPTER 1 INTRODUCTION

1.1 Research Background

Batik is a traditional Indonesian textile product. It serves as cultural asset as well as important economic and employment sector. Since 2009, the United Nations Education, Scientific, and Cultural Organization (UNESCO) has recognized batik as Indonesian heritage, and it has been put on the representative list of humanity's intangible cultural heritage (UNESCO 2009). This acknowledgement raises the popularity of this product and eventually increase its market demand (Pramugani, Soda, and Argo 2020).

In Indonesia, batik is mostly produced by small to middle scale industry or more commonly known as home or cottage industry (Sulthonuddin and Herdiansyah 2021; Kusumawati, Rahmadyanti, and Sianita 2021). One characteristics of home industry is their limited capacity in various aspects including environmental management. Most factories cannot afford a proper wastewater treatment plant, so that they just release their generated wastewater into environment without prior treatment. This will pose threat to environment and eventually human health. In addition, batik factories mostly located in vicinity to housing area or even in the backyard of the house of the business owner. This condition will magnify the risk as wider population were exposed to pollutant.

In their production, batik industry uses various chemicals including dye, fixing agent, and wax. Application of these chemicals produces wastewater characteristics of high pH, organic content (COD, BOD), total suspended solid and color intensity (Mukimin et al. 2018; Tangahu et al. 2019; Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011). The vivid colored nature of batik wastewater made it easy to recognize when improperly release of wastewater into for example river environment, occurred. On the other hand, batik industry has long been accused to be the source of various indication of environmental pollution (Syuhadah, Muslim, and Rohasliney 2015; Saraswati, Haeruddin, and Purwanti 2014; Naqsyabandi, Riani, and Suprihatin 2018; Budiyanto, Purnaweni, and Rya Sunoko 2018; Musfirah and Rangkuti 2019). Apart from these common parameters, the use of synthetic dyes since the beginning of 20th century raises another concern on the possible content of toxic organic substances and heavy metal in batik wastewater. The mostly used type of synthetic dye by batik industries is azo dye. Azo dyes may contain heavy metal as it is part of the building element of the dye usually to improve fastness of color into the fabric (Maria et al.

2014). Certain azo dyes are potentially hazardous on their own or when they are degraded under certain environmental condition to release carcinogenic aromatic amines (Chung 2016; Kapoor et al. 2021; Wei, Fung, and Men 2013). On the other hand, azo dyes are considered non-biodegradable (Selvaraj et al. 2021), that it would be persistent in environment posing long-term threat to environment and human health.

1.2 Problem Statements

Indonesia applies specific effluent standard for various type of industry. At national level, the most relevant effluent standard is Minister of Environment Regulation No.5/2014 on textile wastewater effluent standard. At local level, some provinces have specific effluent standard for batik industry. In Yogyakarta Special Province, it is stated in Local Regulation of Yogyakarta Special Region No.7/2016 on Effluent standard for batik sector in Yogyakarta Special Region. The parameters regulated in both standards are BOD, COD, TSS, TDS, phenol, total chromium, ammonium, sulfide and oil and grease. Hence, studies related to batik wastewater in Indonesia mostly focused on those parameters. The potential content of toxic heavy metal and organics had been addressed (Sulthonuddin and Herdiansyah 2021; Kusumawati, Rahmadyanti, and Sianita 2021; Harsini et al. 2017) but the specific studies on other potentially present hazardous metals and organics are still limited. Related to characteristic of generated wastewater and how it is handled is the material used for production and the availability of wastewater treatment plant. Therefore, the profile of batik production concerning the material used and wastewater handling is relevant to discuss. Finally, the released effluent will undergo physical, chemical, and biological transformation in its receiving environment compartment. The interaction between wastewater and environmental components would determine the fate of wastewater substances and eventually affecting environment quality. This study addresses the possibly present toxic heavy metal and carcinogenic aromatic amines in batik industry in relation to the general profile of batik production in Indonesia and followed by the analysis of its direct contribution to environmental pollution in Indonesia. The result of this study is expected to provide more information as the basis to improve the regulation related to batik industry. For example, on the possibility to ban azo dyes or to promote more seriously the use of natural dye in batik industry.

1.3 Research Objectives

The objectives of this study are:

1) To compile the profile of production process and wastewater handling in batik industry which will affect the characteristic of generated wastewater.

2) To assess the occurrence and level of toxic heavy metal and organics in dyes, wastewater, and various environmental media (groundwater, surface water, river sediment, edible fish)
3) To assess the direct effect of batik industry to groundwater and surface water pollution.

1.4 Scope of Study

This study focused on various metals and metalloid which have potential presence in batik wastewater (Al, Si, Fe, Zn, Cr, Co, Ni, Cu, As, Se, Cd and Pb) and aromatic amines compounds. For profiling of production process in batik industry, this study focused on batik industries located in Yogyakarta City and Bantul Regency. For analysis on environmental media, study focused in Winongo Watershed area of Yogyakarta City.

1.5 Thesis Outline

This thesis is divided into 8 chapters in which each chapter covers following part:

Chapter 1 Introduction

Chapter 1 briefly explained the overview of issues related to batik industry in study area as the background of this study followed by problem statements, research objectives, scopes of study, and outline of the thesis.

Chapter 2 Literature review

Chapter 2 covers information about batik industry and study area. In the beginning, it will discuss the cultural and economic importance of batik industry in Indonesia. Then, the general production process in batik industry will be introduced as well as environmental issues arising, associated with its operation. It will then more focus on heavy metal and aromatic amines as the focus of the entire study. Reviews on previous studies regarding the toxic effect of those group of pollutants will also be presented. This chapter concludes with the description of demographic and physical condition of Yogyakarta Special Province and then focusing on Yogyakarta City and Bantul Regency as the study area.

Chapter 3 Profile of batik production and the potential generation of hazardous organic substances from the use of azo dyes in batik industry in study area

Chapter 3 present the profile of batik industry in study area which covers production method and wastewater handling and to investigate whether the azo dyes used by batik industry in study area are those that can generate aromatic amines.

Chapter 4 Metal and metalloid content in wastewater from batik industry in study area

Chapter 4 presents metal and metalloid characteristics of wastewater samples from batik factories in study area and observe its possible origin through cluster analysis.

Chapter 5 Effect of batik effluent seepage on groundwater quality

Chapter 5 focuses on analysis of various metals in groundwater samples taken from dug wells at and around batik factories in Winongo Watershed and investigate the possibility of groundwater contamination from seepage of batik wastewater.

Chapter 6 River water and sediment quality affected by effluent from batik industry

Chapter 6 focuses on analysis of heavy metals in water and sediment samples of Winongo River which is the receiving water body for discharged wastewater including from batik industry in Winongo Watershed along with its risk assessment. Analysis on dilution ratio of batik effluent and river discharge was also conducted to quantitatively estimate the expected river quality.

Chapter 7 Risk analysis of heavy metal in edible fish from river affected by effluent from batik industry

Chapter 7 presents risk analysis of the consumption of heavy metal contaminated fish from Winongo River which is affected by batik effluent.

Chapter 8 Conclusion and Future Recommendation

Chapter 8 summarizes the conclusions of the previous chapters and their implication as well as recommendation for future research

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CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

This chapter covers information about batik industry and study area. In the beginning, it will discuss the cultural and economic importance of batik industry in Indonesia. Then, the general production process in batik industry will be introduced as well as environmental issues arising associated with its operation. It will then more focus on two groups of pollutant which will be the focus of the entire study. Those two groups are heavy metal and aromatic aryl amines. Data on the toxicological effect of those group of pollutants will also be presented. This chapter concludes with the description of demographic and physical condition of Yogyakarta Special Province and then focusing on Yogyakarta City and Bantul Regency as the study area.

2.2 Batik Production

2.2.1 Importance of batik industry in Indonesia

Batik is traditional Indonesian textile product, although it is also developed in Malaysia (Moradi et al. 2016; Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011; Khalik et al. 2015; Abu Bakar et al. 2019; Nuzul et al. 2020). Since 2009, United Nations Education, Scientific and Cultural Organization (UNESCO) has acknowledged batik as Indonesian heritage and was since included in the representative list of the intangible cultural heritage of humanity. Batik is mostly produced by small to medium scale industries which are categorized as home industry or cottage industry (Syuhadah, Muslim, and Rohasliney 2015; Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011; Sulthonuddin and Herdiansyah 2021). It is an important economic sector in Indonesia. In 2019, export of batik products from Indonesia reached US$ 52.4 million. It is a significant number as compared to US$ 442 billion of textile product global market value of the same year (Ekarina 2019). Batik industry also has provided workplace for around 200 thousand workers spread across 101 regional centers of Indonesia (IDN Finansials 2021).

Many regions in Indonesia especially in Java Island develop batik with their own unique motifs (Kusumawati, Rahmadyanti, and Sianita 2021). Some popular centers of batik industry are Cirebon in West Java, Pekalongan and Solo in Central Java, Lamongan, Ponorogo and Madura in East Java and in all 5 regions of Yogyakarta Special Province (Kusumawati, Rahmadyanti, and Sianita 2021; Sulthonuddin and Herdiansyah 2021). Developed and preserved since the Mataram Sultanate era, Yogyakarta becomes one of the biggest

and most important batik centers in Indonesia. It serves as cultural asset as well as important economic sector. In 2019, number of small to medium scaled batik industry in this area was 1,195 which absorbed 5,771 workers. Production value from this sector reached more than 300 billion rupiahs (Kementerian Perindustrian Republik Indonesia 2020). Originally, batik was introduced and developed by Mataram Sultanate or Yogyakarta Palace. It then spread to all the 5 regions in Yogyakarta Special Province. Presently, each region has their own centers for location of batik industries. They develop their own uniqueness especially regarding the motif.

2.2.2 Batik Production Process

Batik production method differs from common method used in textile industries that it involves the application of wax in its multiple coloring stages. A 2 (two) colored batik sheet will require two times coloring stages. A 3 (three) colored would require 3 times coloring stages, and so on. Part of the motive which is not intended to have the first color would be covered by wax to undergo the dyeing process of the first color. Afterwards, the wax is removed, and the process continues to the second coloring process with the same method.

In general, there are 2 (two) types of batik which are differentiated by the device used to apply wax on the cloth. Basically, both types are produced through the process described in Figure 2.1 (Mulyanto 2016; Susanto 2019). The first batik type is called '*batik tulis*" or hand painted batik in which a pen like device called "*canting*" is used during wax application as presented in Figure 2.2 left (Inibaru.id 2020). Another type is called "*batik cap*" or stamping batik in which a big stamp like device called "*cap*" is used during wax application as presented in Figure 2.2 right. *Cap* is made of copper with usually a 20 x 20 cm^2 in size.

Step 3-5 will be repeated according to the number of intended colors on each production. A "*canting*" is used in step 3 for hand painted type, while a "*cap*" is used in stamp batik making process. Chemical used during process consists of wax, coloring agent both natural or synthetic and fixation agent. Some mostly used chemicals are as presented in Table 2.1 (Mulyanto 2016).

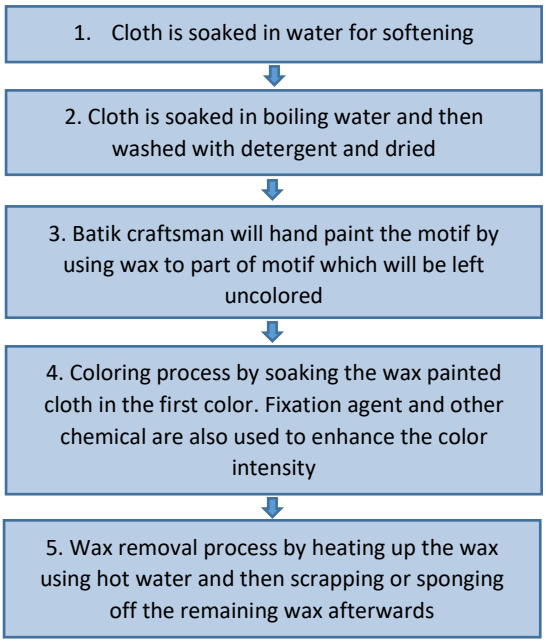

Figure 2.1 General batik production method

Figure 2.2 Hand painted batik (left) and stamping batik (right)

Table 2.1 Most common chemical used in batik industry

Dye	**Natural/Synthetic**	**Fixation agent**
Naphtol	Synthetic	Diazonium-salt
Remazol	Synthetic	Water glass ($Na_2(SiO_2)_nO$)
Indigosol	Synthetic	H_2SO_4, HCl
Indigofera	Natural	Air
Teger	Natural	Alum ($K_2(SO_4)_2$), tunjung ($FeSO_4$), Calcium hydroxide ($CaOH_2$)
Jambal	Natural	
Tingi	Natural	
Mahogany skin	Natural	

In recent years another technique called “colet” or direct coloring batik was introduced. Instead of soaking the cloth during coloring process, dye is directly applied onto cloth surface using a special brush. Remazol and indigosol type of dyes are used for the application of this technique (Supir et al. 2021).

2.2.3 Health and environmental issues on batik production

Batik is mostly produced by small to medium industry categorized as home or cottage industry. One characteristic of home industry is their limited capacity in various aspects including environmental management. Due to high cost and lack of awareness among related parties (Sulthonuddin and Herdiansyah 2021), wastewater from most batik factories are released to environment without prior treatment (Syuhadah, Muslim, and Rohasliney 2015; Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011).

Wastewater from batik industry is mostly generated after coloring or dying process. Due to water inefficiency, 95 % of water used during coloring process is released to environment as wastewater (Sulthonuddin and Herdiansyah 2021; Sutisna et al. 2017). The quality of the wastewater is of another concern. The application of wax and dye and also fixing agents in batik production results in wastewater characteristic of high pH, chemical oxygen demand (COD) and total suspended solids (TSS) (Moradi et al. 2016)**.**

Most batik industries use synthetic dyes for their coloring process. Synthetic dyes may contain carcinogenic substances and toxic heavy metal (Syuhadah, Muslim, and Rohasliney 2015; Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011). As dyes are usually non-biodegradable organic compounds, dye containing wastewater will be accumulated in environment (Putra, Annisa, and Budiarjo 2019) causing long-term environmental pollution. Natural dye is considered to be more environmentally friendly. However, most batik factories are reluctant to use natural dye as it is relatively more expensive, longer production time and more advance-skilled workers are needed (Martuti et al. 2020).

2.2.3.1 Hazardous organics over the use of azo dyes in batik production

One type of synthetic dye frequently used by batik industries in Indonesia is naphthol (Harsini et al. 2017). Naphthol belongs to the group of synthetic dye called azo dyes. Synthetic dyes can be classified according to the groups of atoms in their chemical structures which is called chromophores and auxochromes that decides the color of the dye. Example of chromophores are azo (-N=N-), carbonyl (-C=O), nitro ($-NO_2$), methine (-CH=) and quinoid groups. Meanwhile, the common auxochromes are amine ($-NH_3$), hydroxyl (-OH), carboxyl (-COOH) and sulfonate ($-SO_3H$) (C. Zhang et al. 2021). According to this classification, azo dyes

are compound identified by at least one nitrogen-nitrogen double bond (-N=N) (Ventura-camargo and Marin-morales 2013; Gürses et al. 2016). This azo group connects two groups of usually aromatics (Gürses et al. 2016).

Azo dyes are the most widely used dyes in the world, accounting for around 60-70% of all dyes used by industry (C. Zhang et al. 2021; Gürses et al. 2016; Benkhaya, M'rabet, and El Harfi 2020). This compounds are synthesized by diazotization of a primary aromatic amine and then coupling the resulting diazonium salt with an electron-rich nucleophile (Gürses et al. 2016). Figure 2.3 presents coupling reaction to synthesize C.I. Acid Red 21 (DyStar 2000).

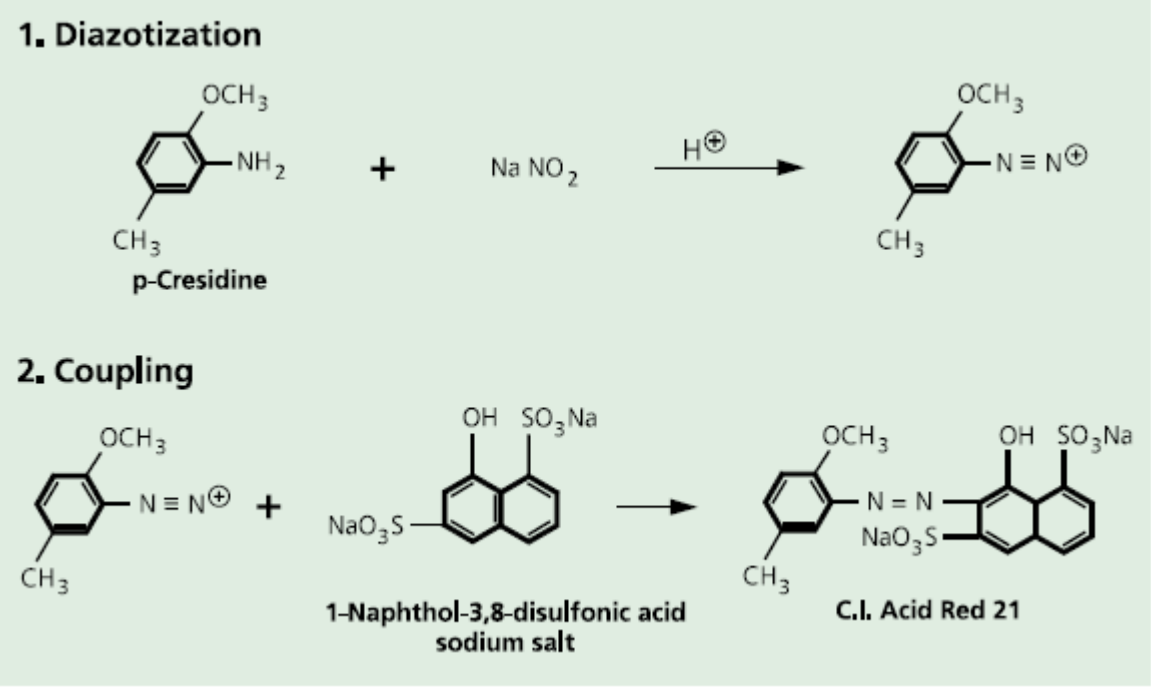

Figure 2.3 Coupling reaction of C.I. Acid Red 21

The massive use of azo dyes by textile industries potentially cause pollution especially to water environment with high organic parameter of TOC, BOD and COD (Tangahu et al. 2019). Numerous azo dyes were designed to be resistant to light, oxidizing agents, sweat, or soap that decrease their biodegradability (C. Zhang et al. 2021). Some azo dyes were reported to demonstrate toxicity on their own. Basic red 9 showed carcinogenicity in animals (Foguel et al. 2015). Toxicity through DNA penetration demonstrated by Azure-B (AB) dye (Haq, Raj, and Markandeya 2018). In addition, degradation of azo dye leads to dye decolorization which eventually produces aromatic amine. Many aromatic amines from azo dyes reduction were

considered or even proven to be carcinogenic through some studies (C. Zhang et al. 2021; Rawat et al. 2018; Özkan et al. 2019).

Several countries have regulation related to the use of azo dyes. In Germany, some azo dyes are considered allergenic (e.g., Disperse Yellow 1/3, Disperse Orange 3/37/76, Disperse Red 1), and some other are considered carcinogenic (e.g., Acid Red 26, Basic Red 9, Basic Violet 14) thus their use are prohibited (Ventura-camargo and Marin-morales 2013). On the other hand, European Union has banned the use of azo dyes that potentially release 22 carcinogenic aromatic amines as stated in the Regulation (EC) No. 1907/2006. Some of those 22 aromatic amines are presented in Tabel 2.2 along with their toxicity to health and environment according to Regulation by European Union (EU), Japan Government and WHO - International Agency for Research on Cancer (IARC). EU regulation as stated in Regulation (EC) No 1272/2008 on the classification, labelling and packaging of substances and mixtures (CLP Regulation). Meanwhile, Japan Regulation is based on 3 (three) reference laws/acts, Pollutant Release and Transfer Register (PRTR) Law, the Industrial Safety and Health Act, and the Poisonous and Deleterious Substances Control Act. Summary of classification of various chemicals by available related regulation in the world can be easily accessed through National Institute of Technology and Evaluation (NITE) Chemical Risk Information Platform (CRIP) website (National Institute of Technology and Evaluation 2016). The complete classification for all 22 aromatic amines and the criteria for each class are available in the appendix.

2.2.3.2 Metals in batik industry

Some reports present data of metal concentration in batik wastewater (Moradi et al. 2016; Syuhadah, Muslim, and Rohasliney 2015; Dewi et al. 2019; Putra, Annisa, and Budiarjo 2019; Suprihatin 2014). Metals are part of organic-based coloring dyes to enhance its absorption to fabrics or at least present as impurities of dyes (Syuhadah, Muslim, and Rohasliney 2015). Metals such as antimony, copper and chromium are used as catalyst in the synthesis of some intermediates (Sungur and Gülmez 2015). Chromium, iron, copper, cobalt and nickel are also use widely in the production of certain dyes or complexed metal dyes for dye characteristic of higher resistance (Rawat, Mishra, and Sharma 2016)(Lellis et al. 2019). When metal-dyes containing wastewater released to water environment, it will bioaccumulate through aquatic organism and eventually reach human via the food chain. Some essential metals are needed to support development and metabolism of living organism (Andreini et al. 2008; Y. Zhang and Zheng 2020). Some metals acts as cofactor for different enzyme, while other exchange electron in various redox reactions (Y. Zhang and Zheng 2020). However, they are needed only in small quantity. Lack or excess of these elements may cause adverse health

effects. Some heavy metal elements associated to textile industry whether they are essential or not and their possible health effect is presented in Table 2.3.

Table 2.2 Toxicity of several aromatic amines according to EU, Japan Regulation and IARC

No	CAS No	Substances	Health/Environment Hazard	EU	Japan	IARC
1	92-67-1	4-aminobiphenyl	Acute Toxicity	Oral 4	Oral 4	
			Mutagenicity		2	
			Carcinogenicity	1A	1A	1
2	92-87-5	benzidine	Acute toxicity	Oral 4	Oral 4	
			Mutagenicity		2	
			Carcinogenicity		1A	1
			STOT		RE 1 (liver, brain) RE 2 ((bone marrow, spleen, ovary, urinary, bladder)	
			Hazard to aquatic environment	Acute 1 Chronic 1	Chronic 2	
3	95-69-2	4-chloro-o-toluidine	Acute toxicity	Oral 3 Dermal 3 Inhalation 3	Oral 4 Dermal 4	
			Mutagenicity	2	2	
			Carcinogenicity	1B	1B	2A
			STOT		SE 1 (urinary, bladder, blood) RE 1 (urinary, bladder, blood system)	
			Hazard to aquatic environment	Acute 1 Chronic 1		

STOT : Target Organ Systemic Toxicity
RE : Repeated Exposure
SE : Single Exposure

Table 2.3 Health effects of some metals on human

No.	Metal Elements	Essential (E)/ Non-essensial (NE)	Health effect to human
1	Aluminum (Al)	NE	Decreasing intellectual function, hallucination, epileptic seizure, depression, dementia, osteomalacia fractures, bone marrow depression, microcytic anemia (Crisponi et al. 2013)
2	Arsenic (As)	NE	Liver cancer, nasal cavity, hyperkeratosis, Blackfoot disease, prostate cancer (Nkwunonwo, Odika, and Nneka 2020)
3	Chromium (Cr)	E (for trivalent)	Cr (VI) is carcinogenic, ulcer formation (commonly on the nasal septum), inducing DNA damage (Jaishankar et al. 2014)
4	Manganese (Mn)	E	Parkinsonian syndrome, altering cardiovascular function (O'Neal and Zheng 2015)
5	Iron (Fe)	E	Gastrointestinal bleeding, vomiting, diarrhea, shocks, hypotension, lethargy, tachycardia, hepatic necrosis, metabolic acidosis, gastrointestinal ulceration and strictures development (Jaishankar et al. 2014)
6	Cobalt (Co)	E	Neurological (e.g. hearing and visual impairment), cardiovascular and endocrine deficit (Leyssens et al. 2017)

No.	Metal Elements	Essential (E)/ Non-essensial (NE)	Health effect to human
7	Nickel (Ni)	Possible E	Fibrosis, chronic bronchitis, impaired pulmonary function, emphysema, allergic contact dermatitis (Nkwunonwo, Odika, and Nneka 2020)
8	Copper (Cu)	E	Nausea, abdominal pain, vomiting, diarrhea (Taylor et al. 2020)
9	Zincum (Zn)	E	Depression, skin irritations, cramps, anemia, lethargy (Velusamy et al. 2021)
10	Selenium (Se)	E	Diarrhea, fatigue, hair loss, joint pain, nail discoloration or brittleness, nausea (MacFarquhar et al. 2010)
11	Cadmium (Cd)	NE	Human carcinogenic, gastrointestinal disease, respiratory disease, skeletal disease, kidney disorder, anemia, emphysema, cardiovascular disease, renal problems, hypertension, itai-itai disease (Velusamy et al. 2021)
12	Barium (Ba)	NE	Hypokalemia (Tao et al. 2016)
13	Lead (Pb)	NE	Impaired cognitive function, behavioral disorder, stunted growth, impaired hearing, interfering calcium metabolism, interfering normal maturation of erythroid element in the bone marrow, toxic for nervous system, intelligent quotient deficit in children, headache, irritability, constipation, weight loss, fatigue, hypertension, miscarriages, stillbirth, and renal tumors, damage of bone tissue (Witkowska, Słowik, and Chilicka 2021)

2.3 Study Area

2.3.1 Administrative and demographic data

Study area is located in Yogyakarta Special Province, one of provincial administrative area of Indonesia. Yogyakarta Special Province lies between 7.33-8.12 South Latitude and 110.00-110.50 East Longitude (Badan Pusat Statistik Provinsi Daerah Istimewa Yogyakarta 2021). It is located in Java Island, bordered by the Indian Ocean in the south and sharing land border with Central Java Province. It consists of 4 (four) regencies, Bantul, Sleman, Kulonprogo and Gunungkidul, and 1 (one) city, Yogyakarta City as the capital (Figure 2.4). Yogyakarta City is well known as Education City as many high rank education institutions both public and private located in this city. This city is also known for its rich Javanese cultural heritage which attracts tourists from other areas in Indonesia as well as from foreign countries.

According to the data from National Land Agency, Yogyakarta Special Province has an area of 3,133.15 km^2 and population of 3,668,719 people. The area of Yogyakarta City only covers 1.04 % of the total area of the province. With population of 373,589 people, Yogyakarta City was among the highest population density

in Indonesia with 11,495 persons/km^2. The area and population of each regency/city is presented in Table 2.4 (Badan Pusat Statistik Provinsi Daerah Istimewa Yogyakarta 2021).

For the early part of this study on profiling of production process in batik industry, study area was focused on batik factories located in Yogyakarta City and Bantul Regency area as presented in Figure 2.5.

2.3.2 Climate

Special Region of Yogyakarta is located in tropical climate region. The average temperature, humidity, and other basic climate data of this region within 2018-2020 is presented in Table 2.5 (Badan Pusat Statistik Provinsi Daerah Istimewa Yogyakarta 2021).

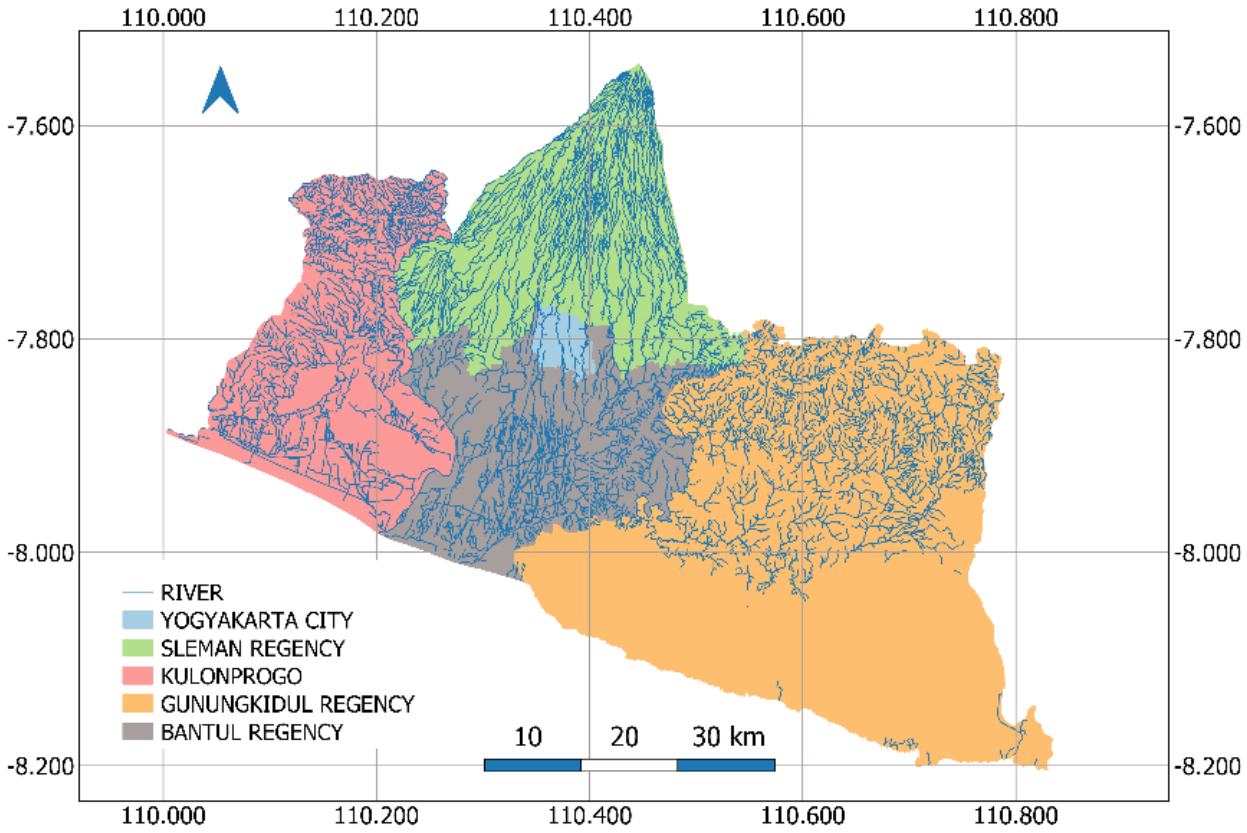

Figure 2.4 Yogyakarta Special Province

Table 2.4 Area and population of Yogyakarta Special Province

Regency/City	Area (km^2)	%	Population*	Population Density per km^2
Kulonprogo	587.27	18.71	436,395	744
Bantul	508.13	16.22	985,770	1,940
Gunungkidul	1,431.42	45.69	747,161	522
Sleman	574.82	18.35	1,125,804	1,959
Yogyakarta	32.50	1.04	373,589	11,495
Total	3,133.15		3,668,719	1,171

*According to census in 2020

Table 2.5 Climate data of study area

Climate elements	2018	2019	2020
Temperature (°C)			
Minimum	17.00	18.00	17.30
Average	27.68	25.94	28.00
Maximum	34.80	36.40	35.50
Humidity (%)			
Minimum	30.50	68.00	45.00
Average	73.50	81.46	78.00
Maximum	100.00	93.30	100.00
Precipitation (mm)	2488.30	2121.40	3057.80
Number of rainy days (day)	116	130	181

2.3.3 DIY waters and watershed

The area of Yogyakarta Special Province is part of 3 (three) large watersheds: Progo, Opak and Oyo Rivers. In case of Yogyakarta City, its area belongs mostly to Opak Watershed (97.5%), while the rest (2.5%) is part of Progo Watershed (Ministry of Public Work 2010). Opak Watershed covers an area of 737.68 km^2. The main river in this watershed is the 65 km long - Opak River. The largest tributary to Opak River is Oyo River, as such that this river usually obtained its separate resource development study and management. The other main and important tributaries of Opak River are Gajahwong, Code, Winongo, Kuning, Belik, Tambakbayan and Gendol River. Average monthly discharge of Opak River was 12.35 m^3/s, with maximum and minimum discharge are 83.2 and 1.89 m^3/s, respectively (Kementerian PUPR Ditjen SDA BBWS Serayu Opak 2016).

For the later part of this study on analysis on various environmental media including groundwater, river water and sediment, and edible fish, study was focused in Winongo Watershed area of Yogyakarta City, as presented in Figure 2.5. Winongo Watershed covers an area of 11,029.28 ha with 67.23 km circumference (Kementerian PUPR Ditjen SDA BBWS Serayu Opak 2016). More to the downstream direction of the river, the quantity and variation of human activities is rising giving increasing load to the watershed. The main

river of this watershed is Winongo River. It is a 49.12 km long river with maximum and minimum discharge were 4.61 m^3/sec. and 0.04 m^3/sec respectively (Dinas Lingkungan Hidup dan Kehutanan Daerah Istimewa Yogyakarta 2021). The upstream of this river is from two small streams originates from Mount Merapi flows across three administrative areas of Sleman Regency, Yogyakarta City, and Bantul Regency and eventually empties into Opak River.

2.3.4 Hydrogeology condition

According to environmental geological map issued by Indonesian Directorate of Environmental Geology, study area is a fluvio-volcanic plain with 8% slope to the south. Lithologically, the area is composed of volcanic debris from Merapi which consists of sand, gravel, silt, and clay. Its rock and surficial material has characteristics of loose to soft, semi consolidated and partly porous. Topsoil consists of tuffaceous clay with soft, low plasticity, sandy and high to moderate permeability (Directorat Geologi Tata Lingkungan 1993).

Study area is located in the central part of Yogyakarta-Sleman Groundwater Basin. This groundwater basin formed by the Merapi Volcano's Quaternary deposits which made up two formations, the Sleman and Yogyakarta Formation. The Sleman Formation lays from the north to the south with increasing thickness from 38 m to 120 m. This formation is composed of volcanic silt to gravel. Deposited on the top of Sleman Formation is Yogyakarta Formation with gradual thickness up to 45 m to the south. Yogyakarta Formation is composed of material sequences containing grains of gravel, silt, and clay. The clay layer thickened to the south overlayed by gravel layers. In general, grain size of the Yogyakarta Formation is coarser the that of the Sleman Formation. The Sleman and Yogyakarta Formation together form Merapi aquifer system which lays from north to south across 3 sub-regions of Sleman Regency, Yogyakarta City, and Bantul Regency. Aquifer in this area is generally unconfined, with exception in some areas with semiconfined aquifers. The Sleman Formation is deep aquifer. The Yogyakarta Formation on the other hand is a shallow and multilayer aquifer. The aquifer characteristics of hydraulic conductivity in this upper formation is 7.8 m/day, with storativity ranges from 0.03 to 0.20 and specific yield of 20% (Souvannachith, Eka Putra, and Hendrayana 2017). Geological map of this area is presented in Figure 2.6.

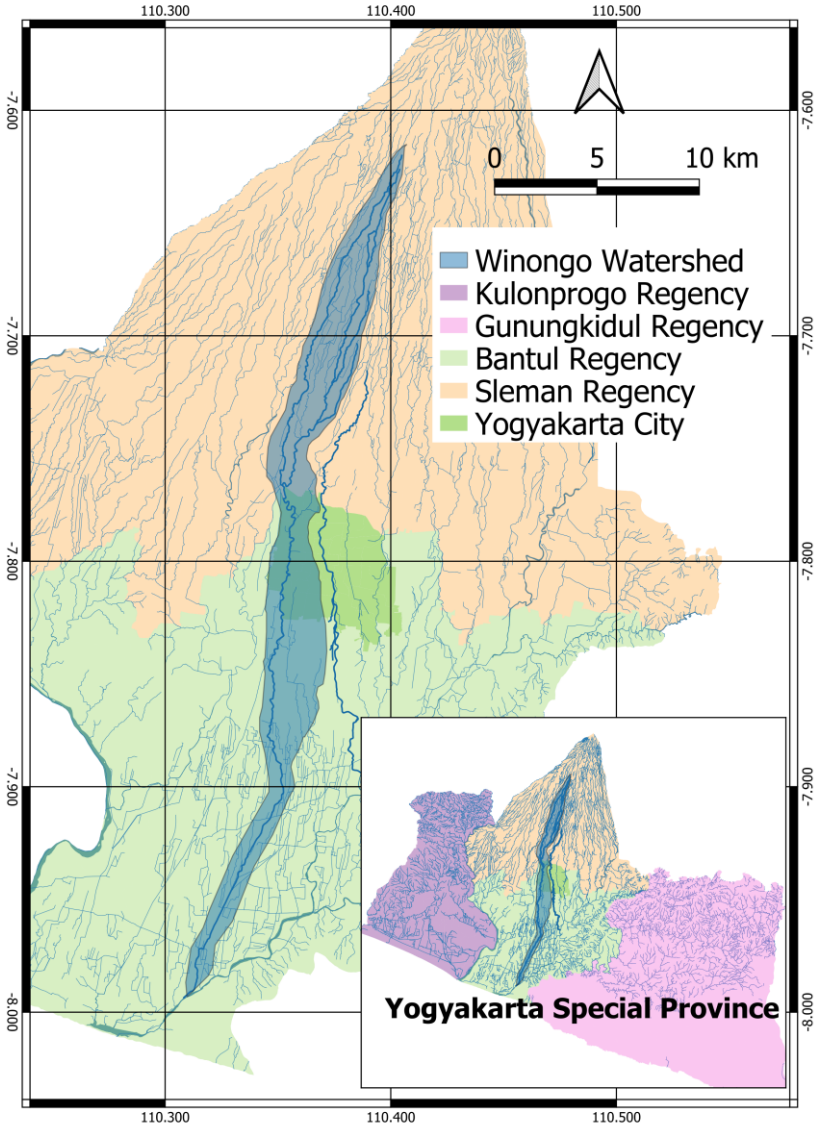

Figure 2.5 Study area

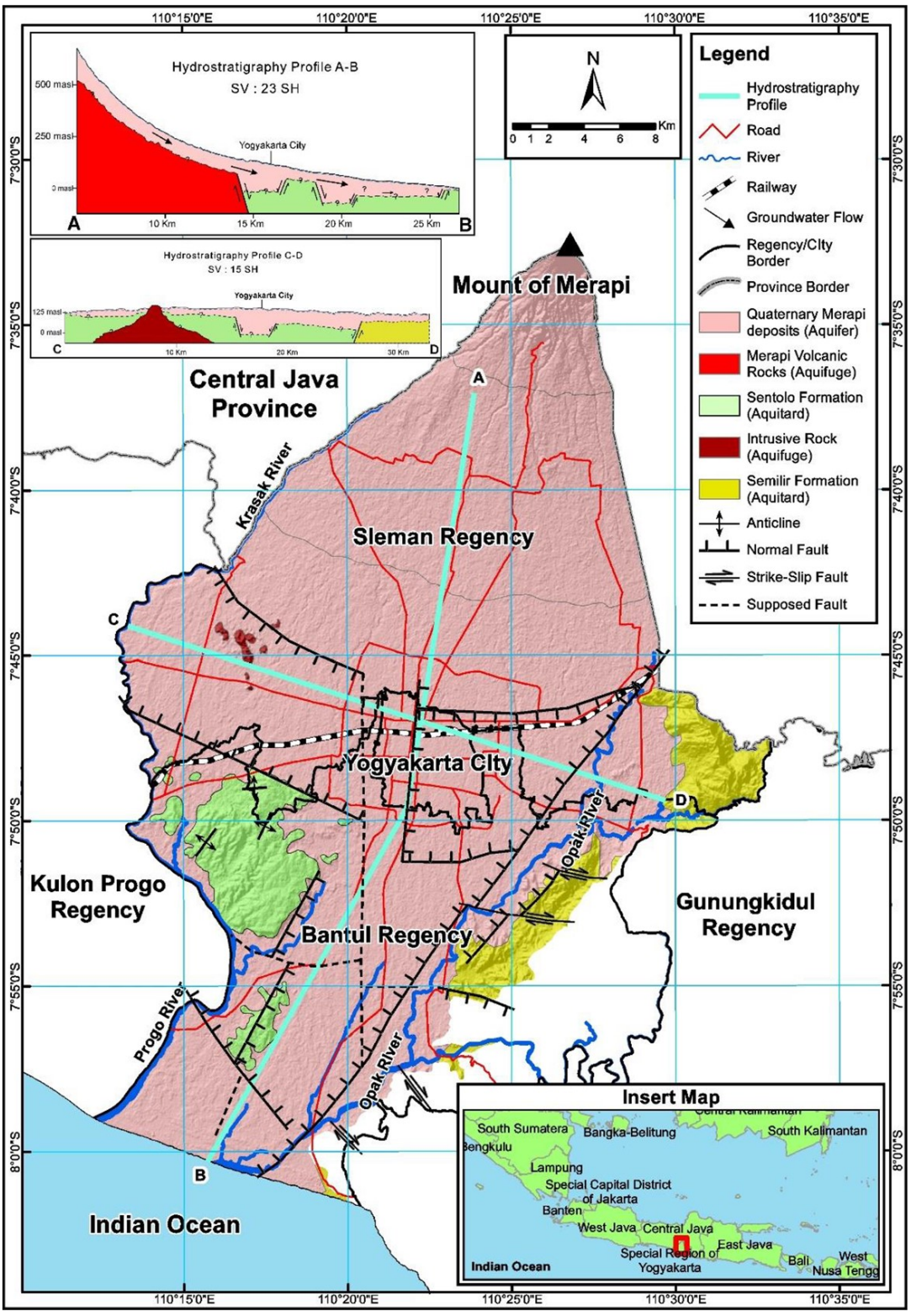

Figure 2.6 Geological map of study area (Wilopo, Putra, and Hendrayana 2021)

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CHAPTER 3 : PROFILE OF BATIK PRODUCTION AND THE POTENTIAL OF HAZARDOUS ORGANIC SUBSTANCES FROM THE USE OF AZO DYES IN BATIK INDUSTRY IN STUDY AREA

Abstract

Batik is mostly produced by home industries with high variation in production capacity and production method. This variation affects the material used for production and eventually the quality and quantity of wastewater generated by each factory. One essential material in batik production is dye. Since the beginning of the 20th century, natural dyes have been slowly replaced by synthetic dyes due to many superior qualities it offered. The use of synthetic dyes raised concern on its potential harm to environment and human health. One of the commonly used types of synthetic dyes is azo dyes. Some azo dyes are potentially toxic on their own or through generation of their breaking-down product of aromatic amines. Many aromatic amines are considered toxic by many studies and regulations. To date, studies related to wastewater generated by batik industry especially in Indonesia focused on parameters such as BOD, COD, TSS, TDS, phenol, chromium, ammonium, sulfide or oil and grease that stated in national or local regulation. The potential toxicity of azo dyes has been mentioned by many studies but a further or specific study on its carcinogenic reduction product has never been reported. This chapter is aimed to present the profile of batik industry in study area which covers production method and wastewater handling and to investigate whether the azo dyes used by batik industry in study area are those that can generate aromatic amines. Studies on 24 batik factories in Yogyakarta City and 53 factories in Bantul Regency showed that 92 % and 89% batik factories in each of these 2 areas used synthetic dyes in their production. Of this synthetic dyes, azo dyes especially naphthol have been used by more than 88% and 70 % of batik factories in Yogyakarta City and Bantul Regency, respectively. Regarding water consumption, average amount of water required for production of one sheet of batik product was 7.5 liter. Compared to other study, this amount is relatively low. Apart from different dyeing technique used, the practice of reusing dye solution multiple times can be another reason. It is usually practiced in producing lower quality batik product. Related to wastewater handling, 50 % factories in Yogyakarta City and 34 % factories in Bantul Regency did not have any kind of wastewater treatment plant. Hence, wastewater was just released into environment without prior treatment. This would lead to serious environmental pollution as well as direct and long-term threat to human health. One of the concerns was the implication of the widely used azo dyes. Laboratory analysis detected 11 toxic aromatic amines in varied concentration from reduced naphthol dye samples and 5 compounds in reduced wastewater samples. It is confirmed that azo dyes widely used by batik factories in study area are those potentially release carcinogenic aromatic amines under reduction favorable environment.

3.1 Introduction

Batik industry has played important role on cultural and economic sector in Indonesia. Yogyakarta Special Province is one of the centers of batik industry in Indonesia. This province has 5 administrative subregions

consists of 4 regencies and 1 city. The four regencies are Sleman Regency, Bantul Regency, Gunungkidul Regency and Kulonprogo Regency. The only city is Yogyakarta City which also serves as capital. Each of these subregions has developed their own batik industry with local uniqueness especially regarding the motif (Kusumawati, Rahmadyanti, and Sianita 2021). In addition, they also have their own center of batik production.

Batik is mostly produced by small to medium industry categorized as home or cottage industry (Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011; Syuhadah, Muslim, and Rohasliney 2015; Sulthonuddin and Herdiansyah 2021) with high variation of production capacity. Variation in production method among these factories were also high which depends mostly on dynamic market demand regarding motif or color. This variation affects the material used for production and eventually the quality and quantity of wastewater generated by each factory. About 95% of wastewater generated by batik industry comes from dyeing process (Sulthonuddin and Herdiansyah 2021). The use of synthetic dye by batik industry in Indonesia since the beginning of 20^{th} century raises concern on its potential harm to environment and human health. The use of synthetic dye along with other material such as wax, starch alum sulfate, starch (Mukimin et al. 2018) affect the general characteristic of batik wastewater which contain high pH and temperature (Syuhadah, Muslim, and Rohasliney 2015), high concentration of Chemical Oxygen Demand (COD), Total Suspended Solid (TSS) (Tangahu et al. 2019), Total Dissolved Solid (TDS) (Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011) and heavy metal (Syuhadah, Muslim, and Rohasliney 2015). In addition, synthetic dyes is complex molecular structure that is difficult to be biodegraded in environment (Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011). This generate threat to human health by potentially carcinogenic and mutagenic substances (Martuti et al. 2020; Harsini et al. 2017), soil and water pollution (Sulthonuddin and Herdiansyah 2021; Saraswati, Haeruddin, and Purwanti 2014; Syuhadah, Muslim, and Rohasliney 2015) and disturbance of ecological balance (Naqsyabandi, Riani, and Suprihatin 2018; Syauqiah, Nurandini, and Lestari 2020).

The type of synthetic dyes mostly used in batik industry is azo dyes. Some azo dyes are potentially carcinogenic and mutagenic (Harsini et al. 2017). Some azo dyes can be hazardous on their own (Wei, Fung, and Men 2013; Chung 2016; Kapoor et al. 2021). Some potentially toxic according to many studies such as Acid Red 26, Basic Red 9, Basic Violet 14 and Direct Black 38 have been banned in several countries (Ventura-camargo and Marin-morales 2013). In addition, azo dyes are considered recalcitrant, non-biodegradable and persistent (Selvaraj et al. 2021). Hence, the release of azo dyes containing wastewater to environment will pose a long-term human and environmental health problem. However, concern on the use of azo dyes

is more on the possibility of toxic aromatic amines formation from azo dyes reduction mechanism (Wei, Fung, and Men 2013; Chung 2016; Ventura-camargo and Marin-morales 2013; Zhang et al. 2021). Many aromatic amines are considered toxic by many studies and regulations (Chormey, Zaman, Maltepe, Büyükpınar, et al. 2020; Özkan et al. 2019; Brüschweiler and Merlot 2017). Some countries such as USA do not ban any specific azo dye but those which potentially generate aromatic amines under certain environmental condition.

To date, studies related to wastewater generated by batik industry especially in Indonesia focused on parameters such as BOD, COD, TSS, TDS, phenol, chromium, ammonium, sulfide or oil and grease that stated in national or local regulation. The potential toxicity of azo dyes has been mentioned (Sulthonuddin and Herdiansyah 2021; Kusumawati, Rahmadyanti, and Sianita 2021; Harsini et al. 2017) but a further or specific study on its carcinogenic reduction product has never been reported.

This chapter is aimed to present the profile of batik industry in study area which covers production method and wastewater handling and to investigate whether the azo dyes used by batik industry in study area are those that can generate aromatic amines.

3.2 Materials and Methods

3.2.1 Site description and sample collection

According to data from Center for Handicraft and Batik, Indonesian Ministry of Industry, in 2018, there were 218 batik shops and factories distributed over the 5 sub regions in Yogyakarta Special Province. This study focused only on batik factories where all risk generating activities were being occurred, hence batik shops were excluded. According to this database, the highest number of factories were in Bantul Regency and Yogyakarta City. Hence, these 2 areas were selected to be the focus of this study.

Among 218 batik shops and factories in Yogyakarta Special Province, 127 were listed as factories in which those located in Yogyakarta City and Bantul Regency were 41 and 49, respectively. However, after field survey to validate the data, some factories were no longer in operation or could not be found at the listed address. On the other hand, according to the information from the existing factories or communities, there were some factories which were not listed yet in the data from Center for Handicraft and Batik. After the survey, the number of batik factories to become sample for this study is 24 in Yogyakarta City and 53 in Bantul Regency. The location of those batik factories is plotted in map as presented in Figure 3.1.

Dye and wastewater samples were taken for the study of potential organic hazardous substances. Total of 25 (twenty-five) dye samples were acquired from 3 (three) local vendors in Yogyakarta City and Bantul area and then sent to Japan by post. On the other hand, 10 (ten) wastewater samples were collected from batik factories which use naphthol dye in their production.

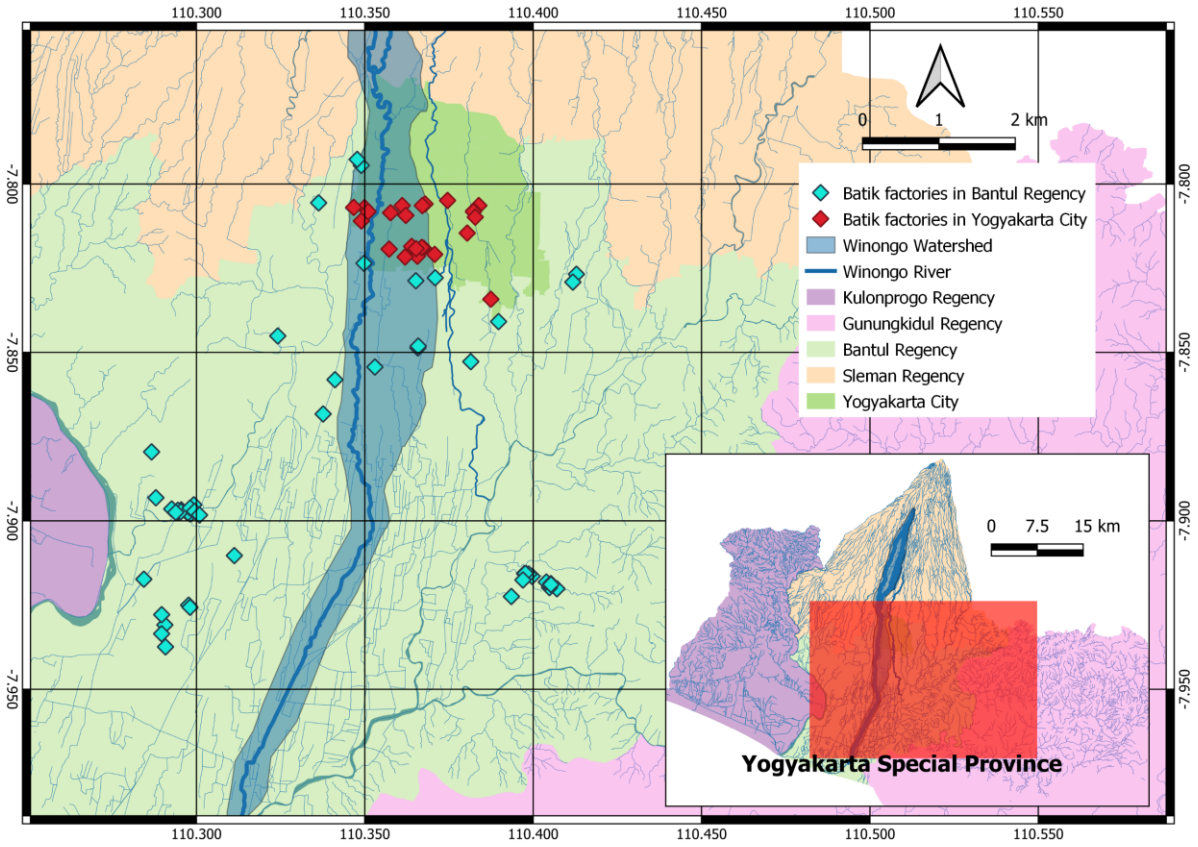

Figure 3.1 Location of batik factories in Yogyakarta City and Bantul Regency

3.2.2 Questionnaire data

A set of questions were asked to the owner or the staff of each batik factory to obtain data regarding the main material used for dyeing process, the quantity of water required for production and how they handle the generated wastewater.

3.2.3 Material, chemicals, and reagents

Mixed standard aromatic amines of target compounds and mixed internal standards were purchased from AccuStandard (New Haven, USA), whereas surrogate compounds p-Terphenyl-d14 and 2-Fluorobiphenyl were purchased from Sigma-Aldrich (Missouri, USA). Reagents used in this study; acetone, ethyl acetate,

methanol and n-hexane were purchased from Wako Chemical. Cartridge C18-500 mg (Sep Pak Vac 6 cc) used for Solid Phase Extraction (SPE) is product of Waters Corporation (Massachusetts, USA). Sodium dithionite EMSURE used for reduction of sample is product of Merck (Darmstadt, Germany). Membrane filter PTFE 0.45 µm DISMIC -13HP was purchased from Advantec (Tokyo, Japan). Deionized water used throughout the study was produced using Milli-Q by Merck.

3.2.4 Sample preparation

Dye samples acquired from vendor were in powder form prepared in sets of ingredients per color consists of naphthol, azo salt and caustic soda for coloring 1 m sheet of cloth. The commonly used ratio of naphthol, caustic soda and azo salt is 1: 1: 2, however each sample was prepared based on weight per item provided by vendor to imitate actual ratio practiced by industries.

To prepare dye sample, naphthol and caustic soda were diluted with boiling water, whereas azo salt was diluted with room temperature water. These 2 (two) solutions were then mixed to mimic the mixture of naphthol dye and azo salt solution after coloring process in batik production. Samples were then put in glass bottle and kept in 4°C until analysis.

3.2.5 Sample pretreatment

Direct analysis of azo colorant aromatic amines was not successful to detect their presence in samples. Analysis was then conducted by reduction process prior to extraction and instrument analysis. Reduction was conducted by addition of sodium dithionite in certain ratio and environmental condition as detailed below. This method is modification of that used by Chormey (Chormey, Zaman, Maltepe, Büyükpınar, et al. 2020).

3.2.5.1 Sample reduction by using sodium dithionite

Prior to target extraction, sample was reduced by adding 3 ml 200 mg/ml sodium dithionite solution into 17 ml sample in glass tube. The mixture was shaken vigorously and then put in water heater set at 70°C ± 2°C. After 30 minutes, sample was taken out from water heater and cool down until room temperature. Sample was then centrifuged for 15 minutes at 3500 rpm to separate suspended solids and ready for extraction. Summary of sample reduction method followed by Solid Phase Extraction is presented in Figure 3.2.

3.2.5.2 Sample extraction by using Solid Phase Extraction (SPE)

Extraction of target compound was conducted by using Solid Phase Extraction (SPE) method. Reverse phase extraction was employed by using C18 cartridge following modified EPA 3535A on Solid Phase Extraction.

Initially, cartridge was prewashed using 5 ml acetone and then 5 ml ethyl acetate. Prior to sample loading, 5 ml methanol was added for cartridge conditioning. Cartridge was allowed to soak for 1 minute during this step. Sample was then loaded onto the cartridge at a drop rate of 1 drop/second. At the end of sample loading, cartridge was washed with 5 ml methanol 20%. Drying with vacuum was following for 3 minutes. Target compounds were then eluted with 6 ml acetone, soak for 1 minute and continue eluted with 5 ml ethyl acetate. Elute solution was then evaporated under gentle stream of nitrogen to a volume less than 0.5 ml and then was reconstituted with n hexane until 1 ml volume and add internal standard. The eluant was then filtered by using PTFE filter and transferred to vial bottle, ready for GC-MS analysis. The summary of SPE method is presented in Figure 3.2.

3.2.6 Sample analysis

Analysis was conducted by using Gas Chromatography-Mass Spectrometry (GC-MS) Shimadzu QP2010SE. Chromatography column was Agilent J&W DB-5ms (60 m x 0.25 mm, 0.25 µm). Injection type was splitless and injection temperature was 240°C. Oven program was set initially at 50°C and hold for 1 minute, increase at 15°C/minute to 250°C and hold for 15 minutes. Then increased further at 25°C/minute to 300°C and kept for 15 minutes. Total running time was 46.33 minutes. The carrier gas was helium at constant flow of 1.37 ml/minute. For MS, temperature of ion source and interface were set at 240°C and 200°C respectively.

3.2.7 Statistical analysis and map works

Questionnaire data processing and statistical analysis were conducted by using Microsoft Excel 365 version 2111. Map works was produced by using QGIS open-source software version 3.16 Hannover (QGIS Development Team 2009). Basic maps were provided by Indonesia Geospatial Portal (BIG 2020).

3.3 Results and Discussion

3.3.1 Profile of batik production in study area

According to the survey as presented in Figure 3.3, synthetic dyes used by most of batik factories both in Yogyakarta City and Bantul Regency. In Yogyakarta City, about 92% factories used only synthetic dyes, while the remaining 8% used also natural dyes. In Bantul Regency, there are still 8% factories used only natural dyes, 11% used both, while the majority of 89% factories used only synthetic dyes.

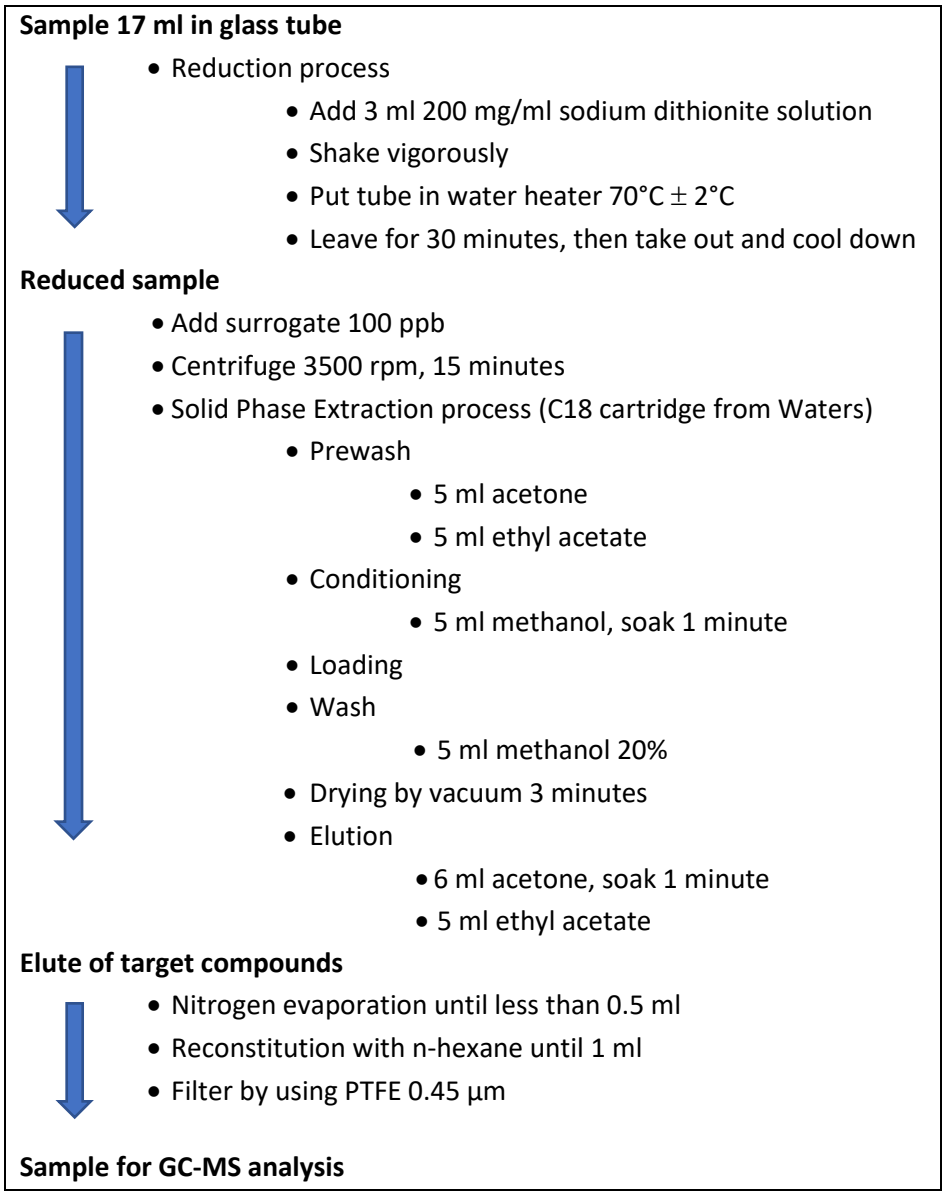

Figure 3.2 Sample reduction and extraction process

Batik factories in study area mostly used synthetic dyes in their production. Originally, batik industry used natural dyes which were derived from various plant organ (Martuti et al. 2020). Since the beginning of 20th century, natural dyes were slowly replaced by synthetic dyes from Britain and Germany (Shararuddin et al. 2021). Synthetic dyes offer many advantages over its natural counterpart. It can be applied on variety of textile material (Ventura-camargo and Marin-morales 2013), low cost (Rawat et al. 2018), have more diverse range of colors (Qisti, Utomo, and Rokhim 2021; Islam and Mostafa 2018), high resistance to commonly used oxidizing agents (Islam and Mostafa 2018; Ventura-camargo and Marin-morales 2013), strong photolytic stability (Islam and Mostafa 2018), have excellent fixative properties and easy to synthesize (Ventura-camargo and Marin-morales 2013). The use of synthetic dyes and the development of stamping

batik have significantly enhanced Indonesia batik production in the 1920s (Shararuddin et al. 2021). On the other hand, natural dye was considered unreliable in term of supply frequency as well as longer production time and the need of a more advanced skilled worker which eventually caused high production cost (Martuti et al. 2020). However, a small number of factories still use natural dyes. Usually, natural-dyed batik has much higher price as it offers exclusivity and uniqueness. In addition, the issue of the use of synthetic dye have made a decrease in the demand of batik in several export destination countries. Thus, the use of dyes back to natural dyes which is considered to be more environmentally friendly can be promoted.

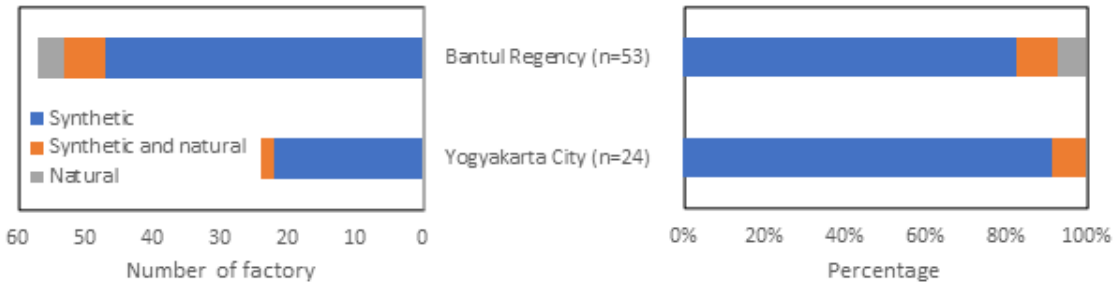

Figure 3.3 Synthetic or natural type dye used in study area

Regarding the type of dye used as presented in Figure 3.4, naphthol and indigosol were used by majority of batik industries in both Yogyakarta City and Bantul Regency. Both dyes used by 75% and 57% of batik factories in Yogyakarta City and Bantul Regency respectively. In Yogyakarta City, 13% factories used only naphthol dyes, 4% factories used only indigosol, 4% used napthol, indigosol and natural and the remaining 4% used remazol and natural dyes. In Bantul Regency, 13% factories used only naphthol dyes, 11% used naphthol, indigosol and natural dyes, 9% only used indigosol, 8 % only used natural dyes, and the remaining 2 % used indigosol and remazol dyes.

The type of dyes mostly used by batik factories in study area are naphthol and indigosol, followed by remazol and natural dyes. Naphthol, indigosol and remazol are synthetic dyes. Naphthol and remazol belong to the azo dye group, while indigosol belongs to other group called vat dyes. Naphthol dye can only be used for soaking dyeing technique in which the wax exposed cloth is soaked into desired color dye solution. Meanwhile, indigosol and remazol can also be used for direct dyeing/painting technique or “colet”. From this figure, azo dyes especially naphthol have been used by more than 88% and 70 % of batik factories in Yogyakarta City and Bantul Regency, respectively. This is also confirmed by studies on batik industry in other areas in Indonesia (Harsini et al. 2017; Munir et al. 2018; Qisti, Utomo, and Rokhim 2021).

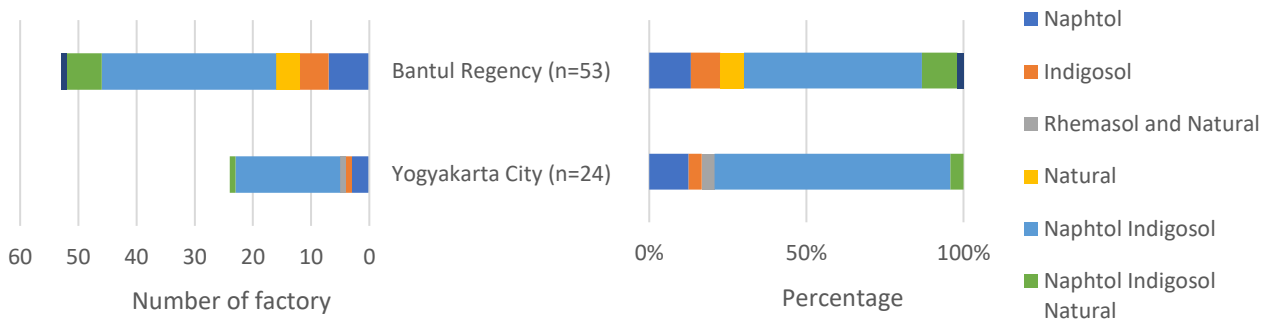

Figure 3.4 Type of dye used by batik industry in study area

Another concern regarding batik industry is water consumption. The batik industry is considered to consume a lot of water, especially during the dyeing process (Syuhadah, Muslim, and Rohasliney 2015). The figure of water consumption along with production quantity of batik factories in Yogyakarta City and Bantul Region is presented in Table 3.1 and Figure 3.5. The figure shows high variation in production quantity and water consumption. Batik factories in Bantul Regency produced more batik and consumed more water than those in Yogyakarta City. The ratio between production quantity and water consumption can be one criterion to measure water efficiency in batik production. Figure 3.6 presents the ratio of these two production parameters in batik industry.

There was high diversity on how much amount of water needed to produce one sheet of batik product in study area. Batik factories in Yogyakarta City consumed more water than Bantul Regency to produce one sheet of batik product. This high diversity caused by different production method. Soaking dyeing technique consume a lot more water than direct coloring method ("colet"). Practice in batik industry of using no precise measurement on material use during production (Handayani, Kristijanto, and Hunga 2018) may become another reason of this high diversity. For both areas in total, amount of water for production of one piece of batik product was 7.5 liter. As comparison, batik factory in Klaten, Central Java that used natural dyes requires 17.93 L water/sheet of batik product (Handayani, Kristijanto, and Hunga 2018). Other study on batik industry in 3 notable center of batik production shows different figure. Water consumption per piece of batik product are 26.0 liter, 6.3 liter, and 119,6 liter in Solo, Pekalongan and Yogyakarta, respectively (Susanty et al. 2015). The later study used 4 samples in Solo and 6 samples for each in Pekalongan and Yogyakarta. This study presents a much higher value of water requirement by factories in Yogyakarta, the same study area with the present study. It is probably due to a much lower number of 6 samples of batik factories compared to 77 samples in this study. Compared to other study, average amount of water to produce one sheet of batik product in study area is relatively low. High variation also showed by correlation

between water consumption and production quantity as presented in Figure 3.7. Spearman correlation give coefficient correlation of 0.64 represent a not strongly correlation association between water consumption and production quantity. Apart from different dyeing technique used as explained above, the practice of reusing dye solution multiple times can be another reason. It is usually practiced in producing lower quality batik product.

Table 3.1 Production quantity and water consumption of batik industries in study area

	Production Quantity (sheets/month)			**Water Consumption (Liter/month)**		
	Yogyakarta City (n=24)	Bantul Regency (n=53)	Total	Yogyakarta City (n=24)	Bantul Regency (n=53)	Total
Minimum	10	10	10	4	10	4
Maximum	250	1000	1000	1250	1000	1250
Average	59	179	144	413	497	471

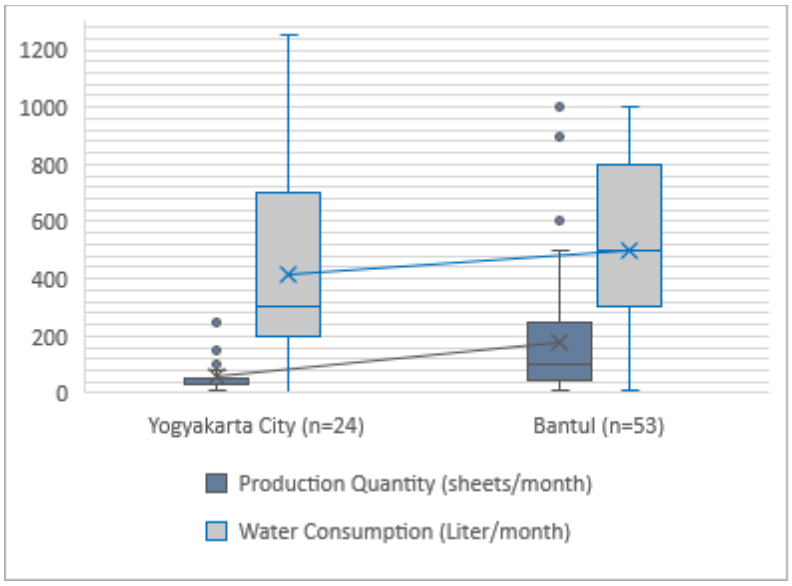

Figure 3.5 Production quantity and water consumption of batik industry in Yogyakarta City and Bantul Regency area

	Yogyakarta City	Bantul Regency	Total
Maximum	20.0	56.7	56.7
Minimum	4.0	0.8	0.8
Average	8.7	6.0	6.8
SD	5.0	8.2	7.5

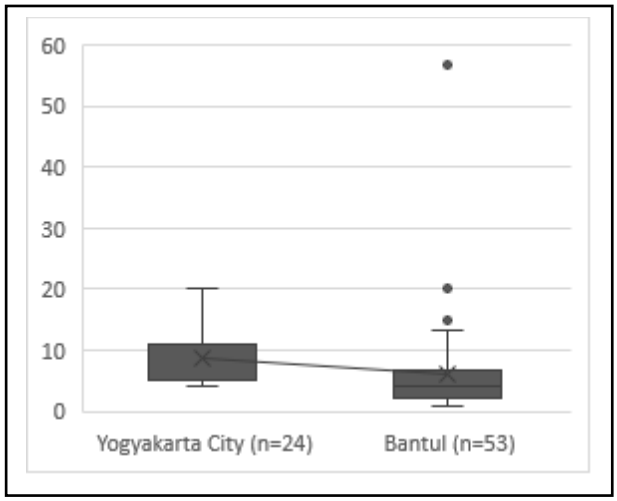

Figure 3.6 Water consumption (liter)/sheet of batik product

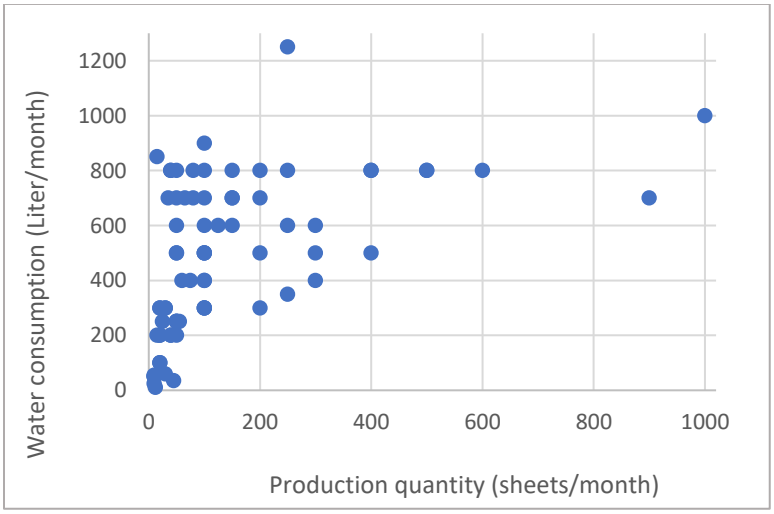

Figure 3.7 Water consumption Vs Production quantity of batik industry in study area

The biggest concern regarding batik industry is about wastewater in term of quality and management. The batik business generates a considerable amount of effluent with high pH, organics, and solids (Sulthonuddin and Herdiansyah 2021). Even for factory which use natural dyes, it may release wastewater with high pH up to 9.4 and low biodegradability with BOD and COD ratio of 0.05 (Handayani, Kristijanto, and Hunga 2018).

On the other hand, water inefficiency leading to large quantity of wastewater as 95% water used for dyeing released as wastewater into the environment (Sirait 2018). According to some studies, around 10 to 15% and even up to 50 % of the total dye used by the textile industries cannot be absorbed into fabric and are lost during the dyeing process, and are thus discharged into the environment (Ventura-camargo and Marin-morales 2013). For batik industry, this number would be higher due to limited capacity and low material efficiency. Figure 3.8 presents the profile of wastewater handling by batik industries in study area.

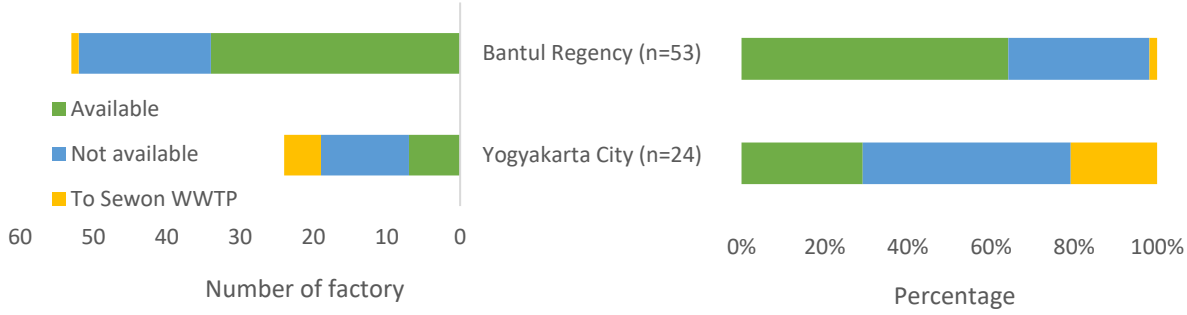

Figure 3.8 Wastewater handling of batik industry in study area

In Yogyakarta City, only around 29 % factories had their own wastewater treatment plant. About 21 % discharge their wastewater into sewerage system that goes to Sewon municipal wastewater treatment plant. However, the remaining 50 % just release their wastewater to environment without prior treatment. In Bantul area, the proportion of factories having their own wastewater treatment plant was higher with around 64 %. Because sewerage system did not cover all area of Bantul, only 2 % of factories can discharge their wastewater into sewerage system, those which were located near Yogyakarta City area. The remaining 34 % only throw their wastewater to nearby drainage channel or stream river. Even though in total there were 53 % factories in Yogyakarta City and Bantul having their own wastewater treatment facility, the plant was only simple sedimentation tank. Some factories had serial sedimentation tanks which from the last tank, the supernatant would eventually seep into the soil.

Most of batik factories are small to medium scale industries with their limited capacity in many aspects especially regarding occupational safety and environmental management. Poor handling of wastewater is example of this condition and it occurred also in other area in Indonesia. One batik industry area in East Java Province has been operating for around 350 years and discharge its wastewater to environment without prior treatment (Tangahu et al. 2019). It is also a common problem in Malaysia where batik is also developed. Batik industry in Kelantan state in Malaysia has the lowest level of compliance with regulation regarding wastewater handling (Subki Noor Syuhadah dan Rohasliney, Noor Syuhadah, and Rohasliney 2011).

3.3.2 Potential generation of aromatic amines from the use of azo dyes in batik industry in study area

As presented in the previous section, azo dyes are the type of dye that most widely used by batik industry in Yogyakarta City and Bantul Region. Several countries have regulation on the use of this type of dye, including some which are banned due to their toxic characteristics. In Indonesia, regulation regarding the use of azo dyes in textile industry is limited to textile product for babies. Azo dyes traces should not present in textile products for babies as stated in Regulation of Minister of Industry No. 07/M-IND/PER/2/2014 on the enforcement of Indonesian Nasional Standard on the Requirement of Concentration of Azo Dyes, Formaldehyde and Metal Extracted from Clothes Product for Babies, and in the revision of this regulation as stated in Regulation of Minister of Industry No. 97/M-IND/PER/11/2015. Other regulation on this issue is Regulation of Minister of Industry No. 13 Year 2019 on Standard of Green Industry for Dyeing, Printing, and Finishing Textile Industry. This later regulation suggests that azo dyes which generates amine compound after reduction should not be used.

Laboratory analysis was conducted to investigate whether the dyes widely used by batik factories in study area are those which potentially generate toxic aromatic amines. There were 23 aromatic amines (AAs) as the target in this study as presented in Table 3.2. Of these 23 targets, 19 compounds were accepted for qualitative and quantitative analysis by using GC-MS.

Table 3.2 Aromatic amines considered in this study

No	CAS Number	Name (IS)	Formula	Molecular Weight	Retention Time	Primary Ion
1	95-53-4	o-Toluidine [a)]	C_7H_9N	107.15	10.200	106
2	90-04-0	o-Anisidine [a)]	C_7H_9NO	123.15	11.485	108
3	106-47-8	4-Chloroaniline [a)]	C_6H_6ClN	127.57	11.895	127
4	120-71-8	p-Cresidine [a)]	$C_8H_{11}NO$	137.18	12.650	122
5	137-17-7	2,4,5-Trimethylaniline [a)]	$C_9H_{13}N$	135.21	12.905	120
6	95-69-2	4-Chloro-o-toluidine [a)]	C_7H_8ClN	141.60	13.040	106
7	95-80-7	2,4-Diaminotoluene [b)]	$C_7H_{10}N_2$	122.17	14.025	121
8	91-59-8	2-Naphthylamine [b)]	$C_{10}H_9N$	143.18	15.880	143
9	90-41-5	2-Aminobiphenyl [b)]	$C_{12}H_{11}N$	169.22	16.125	169
10	99-55-8	5-nitro-o-toluidine [b)]	$C_7H_8N_2O_2$	152.15	16.280	152
11	92-67-1	4-Aminobiphenyl [c)]	$C_{12}H_{11}N$	169.22	17.880	169
12	60-09-3	p-Aminoazobenzene [c)]	$C_{12}H_{11}N_3$	197.24	22.460	92
13	101-80-4	4,4'-Oxydianiline [c)]	$C_{12}H_{12}N_2O$	200.24	23.005	200
14	101-77-9	4,4'-Diaminophenylmethane [c)]	$C_{13}H_{14}N_2$	198.26	23.375	198
15	97-56-3	o-Aminoazotoluene [d)]	$C_{14}H_{15}N_3$	225.29	26.545	106
16	838-88-0	3,3'-Dimethyl-4,4'-diaminodiphenylmethane [d)]	$C_{15}H_{18}N_2$	226.32	27.385	226

No	CAS Number	Name (IS)	Formula	Molecular Weight	Retention Time	Primary Ion
17	119-93-7	3,3'-Dimethylbenzidine [d]	$C_{14}H_{16}N_2$	212.29	28.310	212
18	139-65-1	4,4'-Thiodianiline [d]	$C_{12}H_{12}N_2S$	216.30	30.230	216
19	101-14-4	4,4'-Methylenebis (2-chloraniline) [d]	$C_{13}H_{12}Cl_2N_2$	267.15	32.075	231
20	92-87-5	Benzidine *)	$C_{12}H_{12}N_2$	184.24		
21	119-90-4	3,3'-Dimethoxybenzidine *)	$C_{14}H_{16}N_2O_2$	244.29		
22	91-94-1	3,3'-Dichlorobenzidine *)	$C_{12}H_{10}Cl_2N_2$	253.13		
23	87-60-5	3-Chloro-o-toluidine *)	C_7H_8ClN	141.60		

*) not detected by the method

Internal standard employed during GC MS analysis:

[a] Naphthalene-d8
[b] Acenaphthene-d10
[c] Phenanthrene-d10
[d] Chrysene-d12

Laboratory analysis on naphthol dye samples obtained from common dye seller in Yogyakarta City and Bantul area is presented in Table 3.3. The table shows that 11 toxic AAs were detected in varied concentration from reduced naphthol dye samples. From 25 dye samples, 3.3'-dimethylbenzidine was detected in all samples. This compound also detected at the highest concentration of more than 5 mg/L, followed by 2-naphtylamine > o-toluidine > o-anisidine > 4-chloroaniline > 5-nitro-o-toluidine > 2-aminobiphenyl > 4-chloro-o-toluidine > 4-aminobiphenyl > p-cresidine > p-aminoazobenzene.

Table 3.3 Concentration of target compounds in dye samples

No	Compound	LoD (µg/L)*	Detected in	Concentration (µg/L)		
	Total samples		**25**	Max	Min	Average
1	o-toluidine	5	24	377.7	1.0	45.6
2	o-anisidine	20	13	307.0	0.6	29.4
3	4-chloroaniline	5	14	51.0	0.7	13.1
4	p-cresidine	5	2	1.7	1.1	1.4
5	4-chloro-o-toluidine	5	3	6.2	0.4	2.4
6	2-naphtylamine	10	17	510.8	0.6	36.3
7	2-aminobiphenyl	5	1	10.2	10.2	10.2
8	5-nitro-o-toluidine	20	1	15.6	15.6	15.6
9	4-aminobiphenyl	5	2	3.5	3.1	3.3
10	p-aminoazobenzene	20	2	1.6	1.5	1.5
11	3,3'-dimethylbenzidine	10	25	5,105.8	3.7	552.0

*LoD for quantitative analysis, end value in sample can be lower due to concentrated sample after extraction procedure

According to color, distribution of AAs in samples is presented in Table 3.4. Brown color generates 8 AA compounds followed by purple, yellow and red with 6 compounds. Black color generates 5 AA compounds while blue, orange, and green color produce 4 compounds. Yellow color dye generates the highest concentration of AAs followed by green > brown > red > purple > blue > orange and black.

Laboratory analysis on wastewater samples from batik factories which used naphthol dyes in study area is presented in Table 3.5. The result shows that o-toluidine was detected in 7 out of 8 samples while 3,3'-dimethylbenzidine only detected in 3 samples. However, the concentration of this compound was the highest.

Table 3.4 Concentration of target compounds in wastewater samples

No	Compound	LoD (µg/L)*	Detected in	Concentration (µg/L)		
	Total samples		**8**	Max	Min	Average
1	o-toluidine	5	7	4.3	0.8	1.6
2	o-anisidine	20	6	2.8	0.8	1.7
3	4-chloroaniline	5	5	22.6	0.6	7.3
4	2-naphtylamine	10	6	16.7	3.0	11.2
5	3,3'-dimethylbenzidine	10	3	366.8	4.8	133.5

*LoD for quantitative analysis, end value in sample can be lower due to concentrated sample after extraction procedure

This result shows that naphthol dyes used widely by batik factories in Yogyakarta City and Bantul Regency were those that would release toxic AAs under reduced condition. Azo dyes are reduced to aromatic amines at 70°C, under anaerobic conditions and in the presence of a trace amount of sodium dithionite (Chormey, Zaman, Maltepe, Bueyuekpmar, et al. 2020). The process of azo dyes reduction into colorless AAs can also be occurred biologically through degradation by anaerobic microbes (Chormey, Zaman, Maltepe, Bueyuekpmar, et al. 2020). Metabolism of azo dyes into AAs also occurs in human, catalyzed by gut microflora (Carvalho da Cruz Brambilla et al. 2019) or skin bacteria (Luongo et al. 2016).

Azo dyes are not easily degradable and are often not removed by standard wastewater treatment systems. In a study on 18 azo dyes that went through an activated sludge system, 11 remained virtually unaltered, four were absorbed by the sludge, and only three were biodegraded (Drumond Chequer, Junqueira, and de Oliveir 2011). Other study on the electrocoagulation of dyeing wastewater, the elimination of true color, TOC, and COD are 96.5%, 93.5%, and 85%, respectively. However, the treated wastewater is still harmful due to residual metal and recalcitrant byproducts formed during the treatment process (Lach et al. 2022).

Azo dyes are also persistent in environment. Zhou in Rehman discovered an average of 12.3-456.2 mg/kg of azo dyes in surface soils around dyeing and printing industry units (Rehman et al. 2018). According to other study, textile dye pollution stays in river sediments for years, even though the river water is no longer colored. The bacterial community in river sediment will gradually breakdown the dyes first, followed by AAs, which will take 2 years or longer, regardless of pollutant severity (Ito et al. 2016).

The broad variety of azo dyes is another issue. Even the small changes in the molecule can considerably change its hazardous quality, meanwhile studies on toxicity of these chemicals cover only small number of dyes (Carvalho da Cruz Brambilla et al. 2019). Different environmental condition or the presence of one specific type of microbe may transform the presumably non-toxic azo dyes into persistent and mutagenic byproduct (Rawat et al. 2018; Brüschweiler and Merlot 2017). This finding confirms that the issue on azo dyes is bigger than previously envisaged. The concern is not only for people wearing these dyed products, but also to workers in industries dealing with dyes in countries with low occupational safety and environment standards including batik industries in Indonesia.

3.4 Conclusion

Studies on 24 batik factories in Yogyakarta City and 53 factories in Bantul Regency showed that 92 % and 89% batik factories in each of these 2 areas used synthetic dyes in their production. Of this synthetic dyes, azo dyes especially naphthol have been used by more than 88% and 70 % of batik factories in Yogyakarta City and Bantul Regency, respectively. Regarding water consumption, average amount of water required for production of one sheet of batik product was 7.5 liter. Compared to other study, this amount is relatively low. Apart from different dyeing technique used, the practice of reusing dye solution multiple times can be another reason as usually practiced in producing lower quality batik product. Related to wastewater handling, 50 % factories in Yogyakarta City and 34 % factories in Bantul Regency did not have any kind of wastewater treatment plant. Hence, wastewater was just released into environment without prior treatment. This would lead to serious environmental pollution as well as direct and long-term threat to human health. One of the concerns was the implication of the widely used azo dyes. Laboratory analysis detected 11 toxic aromatic amines in varied concentration from reduced naphthol dye samples and 5 compounds in reduced wastewater samples. Thus, it is confirmed that azo dyes widely used by batik factories in study area are those potentially release carcinogenic aromatic amines.

Table 3.5 Distribution of detected aromatic amines (in µg/L) in dyes samples according to color

Color	Black	Blue	Brown	Orange	Green	Purple	Yellow	Red
Total number of samples	2	3	4	3	1	3	4	5
O-toluidine								
Detected *	2	3	4	2	1	3	4	5
Concentration range	3.0 - 34.8	1.1 – 144.8	1.0 – 18.0	10.6 - 51.5	20.4	5.9 – 152.3	7.8 - 23.8	1.3 – 377.7
O-Anisidine								
Detected *	2	2	1			3	2	3
Concentration range	0.6 - 8.2	12.8 - 17.4	3.2			3.6 – 307.0	0.7 - 1.9	1.6 - 3.8
4-Chloroaniline								
Detected *	2		3	1	1	2	1	4
Concentration range	32.1 - 37.7		1.4 - 5.0	51.0	1.5	2.1 - 15.9	0.7	3.3 - 16.1
p-Cresidine								
Detected *			2					
Concentration range			1.1 - 1.7					
4-Chloro-o-toluidine								
Detected *						1	2	
Concentration range						6.2	0.4 - 0.5	
2-Naphthylamine								
Detected *		2	2	2	1	3	4	3
Concentration range		0.9 - 9.8	1.8 - 3.3	6.1 - 7.4	2.8	1.2 - 12.5	0.6 - 19.4	1.0 – 510.8
2-Aminobiphenyl								
Detected *	1							
Concentration range	10.2							
5-nitro-o-toluidine								
Detected *			1					
Concentration range			15.6					
4-Aminobiphenyl								
Detected *			2					
Concentration range			3.1 - 3.5					
p-Aminoazobenzene								
Detected *								2
Concentration range								1.5 - 1.6
3.3'-dimethylbenzidine								
Detected *	2	3	4	3	1	3	4	5
Concentration range	7.2 - 14.3	6.3 - 29.5	5.4 – 905.1	4.8 - 23.8	1,427.8	27.8 - 203.9	1,587.0 - 5,105.8	3.7 - 61.1

*) in number of samples

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CHAPTER 4 : METAL AND METALLOID CONTENT IN WASTEWATER FROM BATIK INDUSTRY IN YOGYAKARTA AREA

Abstract

Batik in Indonesia is mostly produced by medium to small-scale industry with limited capacity in many aspects including its wastewater handling. Wastewater from most factories is discharged into environment without proper treatment. The increasing use of synthetic dyes in batik production raises concern on heavy metal content in its wastewater. The improper handling of wastewater would release pollutants including heavy metal and pose health risks to humans and the environment. However, data on heavy metal characteristics of wastewater from batik industry in Indonesia is very limited. This chapter is aimed to present the profile of heavy metal characteristic of 18 (eighteen) wastewater samples from batik factories in Yogyakarta Area, Indonesia. The total concentration of some heavy metal elements was measured by using inductively coupled plasma mass spectrophotometry (ICP-MS). The result was compared to other studies and relevant local and international effluent standards. Hierarchical Cluster Analysis (HCA) was then performed to observe group of samples or parameters with similar characteristics that represent similar production method which affects their wastewater characteristics. The results shows that concentration of Al, Si, Fe, Zn, Cr, Co, Ni, Cu, As, Se, Cd, and Pb ranged from 0.11 to 300 mg/L, 25 to 280 mg/L, 0.56 to 12 mg/L, 0.11 to 180 mg/L, 11.7 to 100 µg/L, 0.6 to 17.7 µg/L, 7.2 to 82.8 µg/L, 20.9 to 1.9 10^3 µg/L, 1.5 to 21.2 µg/L, 7.6 to 2.6 10^3 µg/L, and <0.05 to 220 µg/L, 0.03 to 42.7 µg/L, respectively. No sample exceed relevant effluent standard in Indonesia as the only heavy metal parameter regulated is Cr. However, concentration of Cd, Se, Fe and Zn exceed relevant effluent standard in Japan and Malaysia. Compared to other studies, concentration of Cr, Pb and Si in this study were relatively lower. However, the concentration of Cu, Cd, Fe and especially Al and Zn were much higher than other studies. Hierarchical Cluster Analysis (HCA) produced dendrograms showing cluster of strong similarity among parameters Ni, Cr and Co which indicates that the source of these metals is from dyes. Other clusters indicated various sources such as fixation agent, groundwater or another supporting chemical. HCA also indicates that factors other than the type of dye and production stage may affect heavy metal content in batik wastewater which represent the high variability of production process among batik factories.

4.1 Introduction

In Indonesia, Batik is mostly produced by medium to small-scale industry classified as home or cottage industries (Noor Syuhadah and Rohasliney 2011; Syuhadah, Muslim, and Rohasliney 2015; Sulthonuddin and Herdiansyah 2021). One characteristic of home industry is their poor capacity in a variety of areas, including its wastewater handling. Most batik factories discharge their wastewater into the environment without sufficient treatment. While many batik manufacturers are located near residential areas,

improper wastewater disposal may result in the release of pollutants into the soil and groundwater. Human health would be jeopardized because of direct usage and exposure to contaminated soil, water bodies, and groundwater.

Wastewater from batik industries has become a long-time concern. The application of wax, dye and other supporting chemicals results in wastewater characteristic of high color, pH, organic and solid. The use of azo dyes by most batik factories raises concern on the carcinogenic organic and toxic heavy metal release to environment (Syuhadah, Muslim, and Rohasliney 2015; Moradi et al. 2016). Some azo dyes are complexed with metal to improve fastness to fabric and the commonly employed metal for this purpose are chromium, cobalt and copper (Maria et al. 2014). The use of this metal complex dye could lead to the discharge of especially chromium which is potentially carcinogenic into the environment (Islam and Mostafa 2018).

Data on heavy metal concentrations in batik wastewater are presented in some papers. Several heavy metals, including Pb, Fe, Cu, Zn, Al, Mn, Mg, Ca, Cr, and Si, were discovered in batik wastewater samples from a Malaysian batik factory using a similar production method to that used in Indonesia (Moradi et al. 2016). In Indonesia, data on metal content in batik wastewater mostly focus on chromium as it is the only metal regulated for batik effluent standard.

This chapter is aimed to present the metal and metalloid characteristics of wastewater samples from batik factories in Yogyakarta City area, compared to other studies and relevant local and international effluent standard and perform cluster analysis to observe group of samples. This group of samples may provide information on the nature or origin of metal and metalloid content in batik wastewater.

4.2 Materials and Methods

4.2.1 Sample collection

A total of 18 samples were taken from batik factories located in Yogyakarta City area as presented in Figure 4.1. Samples were wastewater from two production stages, either after dyeing process (A) or wax removal process (B) as presented in Table 4.1. Samples were collected in polypropylene (PP) bottle. Parameter pH, temperature, TDS were measured on site by using Multiparameter Water Quality Checker Horiba U-50. For preservation, concentrated HNO_3 (grade for heavy metal analysis, 65%, Merck) were added until pH<2. Samples were then kept in 4°C until analysis.

Table 4.1 Origin of wastewater samples

Sample code	Source of	Type of dyes used	Sample	Source of	Type of dyes used
X1	**A**	Naphthol	**X10**	B	Naphthol, Indigosol
X2	B	Naphthol	**X11**	B	Naphthol, Indigosol
X3	A	Naphthol	**X12**	A	Remazol
X4	B	Naphthol	**X13**	A	Naphthol, Indigosol
X5	A	Naphthol, Indigosol	**X14**	A	Naphthol, Indigosol
X6	A	Naphthol, Indigosol	**X15**	B	Naphthol, Indigosol
X7	**A**	Naphthol, Indigosol	**X16**	B	Naphthol, Indigosol
X8	A	Naphthol, Indigosol	**X17**	A	Naphthol, Indigosol
X9	A	Naphthol, Indigosol	**X18**	A	Naphthol, Indigosol

4.2.2 Sample pretreatment

Samples were pretreated prior to instrumental analysis following modification of United States Environmental Protection Agency (USEPA) method 3015A for microwave assisted acid digestion. Concentrated HNO_3 (grade for heavy metal analysis, 61%, Wako Chemical) and HCl (35-37%, Wako Chemical) were added to sample following volume ratio of 0.8: 0.2: 9. Sample mixture was then digested in laboratory microwave oven (CEM type MARS 6 using Easy Prep Plus vessel type). Digestion was set under 800 psi pressure and 200 °C temperature held for 15 minutes and ramping time of also 15 minutes. After digestion, samples were filtered by using 0.45 µm cellulose acetate membrane filter and ready for instrument analysis.

4.2.3 Sample analysis and quality control

Prior to instrument analysis, filtered samples were diluted in 1 N HNO_3 solution as necessary based on range of expected concentration for each target element. Series of standard solution were prepared by dilution of standard stock of each element (Wako Chemical) in 1 N HNO_3 solution. To ensure stability during measurement, internal standard ^{89}Y and ^{115}In were added to both samples and standard. Two (2) instruments were used for concentration measurement as presented in detail below.

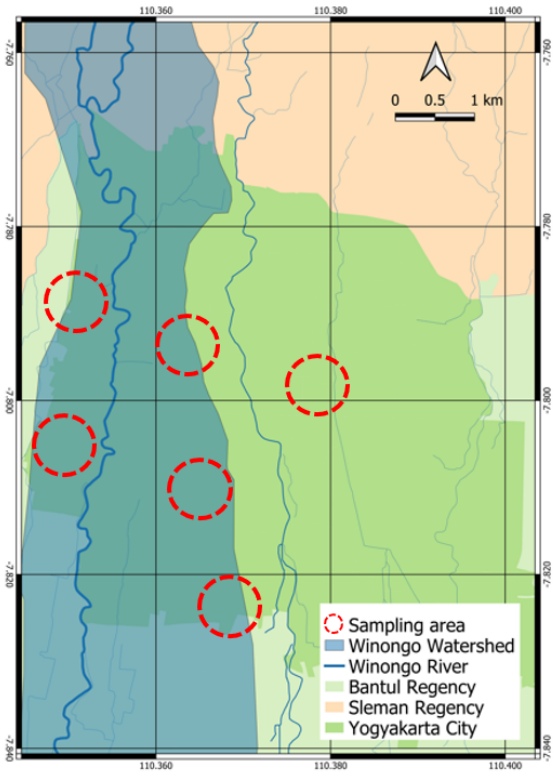

Figure 4.1 Wastewater sampling location

4.2.3.1 Analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS (XSERIES 2, Thermo Scientific) was used to measure concentration of metal Cr, Co, Ni, Cu, As, Se, Cd, Ba and Pb. Isotopes used for measurement were ^{52}Cr, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{75}As, ^{82}Se, ^{111}Cd and ^{208}Pb and limit of detection (LoD) for each element are 0.18, 0.05, 0.31, 0.05, 0.07, 0.19, 0.05, 0.06 µg/L respectively.

4.2.3.2 Analysis by Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

MP-AES (4200 MP-AES, Agilent Technology) was used to measure concentration of metals Al, Fe, Zn, and metalloid Si. Emission wavelength for measurement of each element were 394.401 nm for Al, 371.993 nm for Fe, 213.857 nm for Zn, and 250.690 nm for Si, with limit of detection (LoD) are 0.01, 0.05, 0.06, and 0.165 mg/L respectively.

4.2.4 Statistical analysis and Map Works

R software version 4.0.3. was used for statistical analysis in this study (R Core Team 2020). Basic R package "base" was used to present summary statistics (R Core Team 2020). Correlation among parameter along with correlation coefficient and its significance was measured by using "stats" Package (R Core Team 2020) and "Hmisc" package (Harrell, Dupont, et.al. 2020). Hierarchical Cluster Analysis (HCA) was conducted

using “Spearman” distance measure in “factoextra” Package (Kassambara and Mundt 2020) and “Average” clustering method available in “stats” package (R Core Team 2020). To ensure comparability among datasets, normalization or standardization was performed before clustering using “BBmisc” Package (Bischl et al. 2017). Dendrogram visualization of HCA was performed by using “factoextra” Package (Kassambara and Mundt 2020). There were 5 data on cadmium concentration below LoD. For correlation and clustering analysis, this data was substituted with half LoD. However, to get mean, median, and standard deviation, “NADA2” Package was used to process this non-detect data (Julian and Helsel 2021). Map works was produced by using QGIS open-source software version 3.16 Hannover (QGIS Development Team 2009). Basic maps were provided by Indonesia Geospatial Portal (BIG 2020).

4.3 Results and Discussion

4.3.1 Concentration of metal and metalloid in samples

Summary statistics of concentration of all analyzed elements are presented in Table 4.2. Based on their standard deviation (SD), Al had the highest variation among all measured metal elements followed by Si, Zn, Fe, Se, Cu, Cd, Cr, Ni, Pb, As and Co respectively. Based on their mean and median, Si has the highest concentration among all measured elements followed by Al>Zn>Fe>Se>Cu>Cr>Ni>Cd>Pb>As>Co. Compared to relevant standards, total chromium (Cr) is the only heavy metal parameter regulated in Minister of Environment Regulation No.5/2014 on Textile Wastewater Effluent Standard and Local Regulation of Yogyakarta Special Region No.7/2016 on Effluent Standard for Batik Sector in Yogyakarta Special Region. According to both standards, the maximum Cr concentration in batik effluent is 1 mg/L. No sample in this study exceeded the maximum Cr concentration when compared to both standards. In comparison to other countries' effluent standards, concentration of Cd and Se in few samples were above the Japan’ effluent standard for human health. Meanwhile, concentration of Fe and Zn exceed Japan’ standard for protection of living environment. Compared to effluent standard in Malaysia which also has batik industry, these concentrations except for Se, also exceed 2 types of effluent standards applied in Malaysia. The comparison of wastewater data to these effluent standards is presented in Table 4.3.

Table 4.2 Summary statistics for wastewater data (in µg/L)

Parameter	LoD	Min.	Max.	Mean	Median	SD
Al	10	$1.1\ 10^2$	$3.0\ 10^5$	$3.7\ 10^4$	$3.8\ 10^3$	$7.6\ 10^4$
Si	165	$2.5\ 10^4$	$2.8\ 10^5$	$6.6\ 10^4$	$5.4\ 10^4$	$5.5\ 10^4$
Fe	50	$5.6\ 10^2$	$1.2\ 10^4$	$3.9\ 10^3$	$2.1\ 10^3$	$3.9\ 10^3$
Zn	60	$1.1\ 10^2$	$1.8\ 10^5$	$2.5\ 10^4$	$1.7\ 10^3$	$5.3\ 10^4$
Cr	0.18	11.7	$1.0\ 10^2$	38.5	29.8	24.0
Co	0.05	0.6	17.7	3.0	1.8	3.8

Parameter	LoD	Min.	Max.	Mean	Median	SD
Ni	0.31	7.2	82.8	27.2	19.1	21.8
Cu	0.05	20.9	$1.9\ 10^3$	$2.3\ 10^2$	94.2	$4.3\ 10^2$
As	0.07	1.5	21.2	6.1	4.5	5.5
Se	0.19	7.6	$2.6\ 10^3$	$3.5\ 10^2$	21.7	$7.4\ 10^2$
Cd	0.05	< 0.05	$2.2\ 10^2$	16.1	1.5	51.6
Pb	0.06	0.03	42.7	15.6	13.5	13.5

Compared to other studies, concentration of Cr, Pb and Si in this study were relatively lower. However, the concentration of Cu, Cd, Fe and especially Al and Zn were much higher than other studies. Because only Cr is regulated for batik effluent standards in Indonesia, data on heavy metal content in batik wastewater in Indonesia was primarily focused to this parameter, as reported by (Dewi et al. 2019) and (Suprihatin 2014). The Cr concentration in batik wastewater samples collected from factory in Banyumas, Central Java Region, and Sidoarjo, East Java Region, was reported in these investigations. Putra, Annisa, and Budiarjo (Putra, Annisa, and Budiarjo 2019) reported Cr^{6+} and Pb concentrations in batik wastewater collected from a one factory in Yogyakarta, the same area as this study. Data on other heavy metal components in batik wastewater was obtained from Malaysian batik companies, as reported by (Moradi et al. 2016) and (Syuhadah, Muslim, and Rohasliney 2015). These studies reported heavy metal concentrations in samples taken from batik factories in Kelantan, Malaysia. Also compared to these studies, concentration of Al, Si, Fe, Zn and Cu were consistently among the highest. Data from other studies is presented in Table 4.3.

4.3.2 Source identification

Correlation analysis and cluster analysis were conducted to observe relationship among heavy metal elements and possible common source. Spearman rank was used for correlation analysis. Correlation coefficient for every pair of elements is presented in Table 4.4. Significant correlations (95% confident interval) are demonstrated by some pairs of heavy metals.

Al and Fe show strong correlation as well as Al and Zn. This may indicate that those heavy metals were from the common source. Strong correlation also shown between Pb-Zn, Cd-Zn, and Pb-Al. Moderate correlations are shown by other pairs; Co-Zn, Co-Fe, Co-Al, Co-Cr, Ni-Cr, As-Cu, Se-As, Pb-Fe, Pb-Co, Cd-Fe, Cd-Al, Cd-Co, and Cd-Pb.

Table 4.3 Comparison of maximum concentration in samples to effluent standards of Indonesia, Japan, and Malaysia and to other studies (in mg/L)

Effluent Standard	Cr	Cr^{6+}	Cr^{3+}	Cu	Ni	As	Cd	Co	Pb	Se	Al	Si	Fe	Zn
A. Indonesia														
Local [1)]	1.00	-	-	-	-	-	-	-	-	-	-	-	-	-
National [2)]	1.00	-	-	-	-	-	-	-	-	-	-	-	-	-
B. Japan														
B [1)]	-	0.50	-	-	-	0.10	0.03	-	0.10	0.10	-	-	-	-
B [2)]	2.00	-	-	3.00	-	-	-	-	-	-	-	-	10.00	2.00
C. Malaysia														
C [1)]	-	0.05	0.20	0.20	0.20	0.05	0.01	-	0.10	-	-	-	1.00	1.00
C [2)]	-	0.05	1.00	1.00	1.00	0.10	0.02	-	0.50	-	-	-	5.00	1.00
This study (max. conc.)	**0.10**	**-**	**-**	**1.89**	**0.08**	**0.02**	**0.22**	**0.02**	**0.04**	**2.59**	**$2.96\ 10^2$**	**$2.78\ 10^2$**	**12.4**	**$179\ 10^2$**
Banyumas, Indonesia[a]	1.10	-	-	-	-	-	-	-	-	-	-	-	-	-
Yogyakarta, Indonesia [b]	-	0.16	-	-	-	-	-	-	0.47	-	-	-	-	-
Sidoarjo, Indonesia[c]	0.06	-	-	-	-	-	-	-	-	-	-	-	-	-
Sidoarjo, Indonesia[d]	0.45													
Solo, Indonesia[e]				0.52										
Malang, Indonesia[f]	0.82													
Pekalongan, Indonesia[g]	0.76						0.07		0.79					
Kelantan, Malaysia[h]	0.08	-	-	0.29	-	-	-	-	0.04	-	12.00	$8.97\ 10^3$	3.00	0.29
Kelantan, Malaysia[i]	0.00	-	-	0.57	-	-	0.01	-	0.47	-	-	-	2.90	0.47

A 1) Indonesian Minister of Environment Regulation No.5/2014, A 2) Local Regulation of Yogyakarta Special Region No.7/2016

B 1) Japan Standard for the protection of human health, B 2) Japan Standard for the protection of living environment

C 1) Malaysia Standard A: if discharged to inland waters within catchment areas, C 2) Malaysia Standard B: if discharged into other inlands or Malaysian waters

a (Dewi et al. 2019)

b (Putra, Annisa, and Budiarjo 2019)

c (Suprihatin 2014)

d (Tangahu et al. 2019)

e (Kariada et al. 2020)

f (Qisti, Utomo, and Rokhim 2021)

g (Budiyanto, Purnaweni, and Rya Sunoko 2018)

h (Moradi et al. 2016)

I (Syuhadah, Muslim, and Rohasliney 2015)

Table 4.4 Correlation matrix among heavy metal parameter in wastewater samples

	Zn	Si	Fe	Al	Cr	Co	Ni	Cu	As	Se	Pb	Cd
Zn	1.00											
Si	-0.27	1.00										
Fe	*0.68	0.30	1.00									
Al	***0.84**	0.20	***0.93**	1.00								
Cr	-0.01	-0.17	0.06	-0.07	1.00							
Co	*0.59	-0.02	*0.57	*0.58	*0.53	1.00						
Ni	0.19	-0.32	0.15	0.07	*0.54	0.39	1.00					
Cu	0.06	0.32	0.11	0.18	0.11	0.08	-0.25	1.00				
As	0.17	0.28	0.19	0.25	-0.11	0.07	-0.25	*0.54	1.00			
Se	0.05	0.25	0.17	0.10	-0.01	0.02	0.15	0.30	*0.61	1.00		
Pb	***0.75**	0.04	*0.67	***0.74**	-0.08	*0.54	0.28	-0.02	0.05	0.06	1.00	
Cd	***0.78**	-0.27	*0.50	*0.65	0.02	*0.63	0.21	-0.26	-0.13	-0.23	*0.68	1.00

* Correlation is significant at 95% confident interval

These correlations are confirmed by cluster analysis. Hierarchical Cluster Analysis (HCA) was performed to group parameters into different clusters. Dendrogram of parameters clusters is presented in Figure 4.3. The first cluster with the lowest dissimilarity consists of Al, Fe, Pb, Cd, and Zn. Consistent with high correlation coefficient in correlation analysis, Al and Fe have the lowest dissimilarity indicating that these 2 metals were from one common source. With Pb, Cd and Zn, this cluster may be from mixed source. The source of Al and Fe may be from the use of $KAl(SO_4)_2 \cdot 12H_2O$ and $FeSO_4$ as fixation agent especially for natural dye (Martuti et al. 2020). With Pb, Cd and Zn, other possible source is from the dye itself. These metals are used in metal complex dyes (Yaseen, Scholz, and Yaseen 2019; Hunger 2003). Al and Fe were possibly come from groundwater as the main source of water for batik production especially in Yogyakarta Area. Both metals are among the most abundant in earth crust, thus become the natural component of soil particle and groundwater (Viaroli et al. 2016). The second cluster consists of Cr, Co, and Ni. These metals along with Cu are said to be predominant element for metal complex azo dyes (Maria et al. 2014; Chakraborty 2011) which are the type of dyes mostly used in batik production in study area. The third cluster consists of As, Cu and Se. Other than dyes and fixing agent, source of these metals may be from fibres or wax. Similar to textile wastewater, other source of heavy metals in batik wastewater can be from impurities of chemical used in different stages of production processes (Yaseen, Scholz, and Yaseen 2019). Among all metals analyzed in this study, Si does not belong to any cluster. It is also shown in correlation matrix that no significant correlation occurs between Si and other metals in the samples. This is an indication that Si was from different source than other metals. Si concentration in samples is also the highest among all analyzed metals. The source of this high concentration of Si is the use of sodium metasilicate (Na_2SiO_3) or also known as water glass in batik production as batik dye fixer (Dalimin and Hassan 2020). It functions as batik dye fixer to ensure color fastness into the fabric. The type of dye to use

water glass as fixer is remazol dyes. Other possible source of silica is groundwater. Silica is natural content of groundwater as a result of chemical weathering of silicate minerals in rocks (Pradeep et al. 2016). However, as it belongs to single cluster, meanwhile groundwater is used in all factories, Si is most probably from the former possibility.

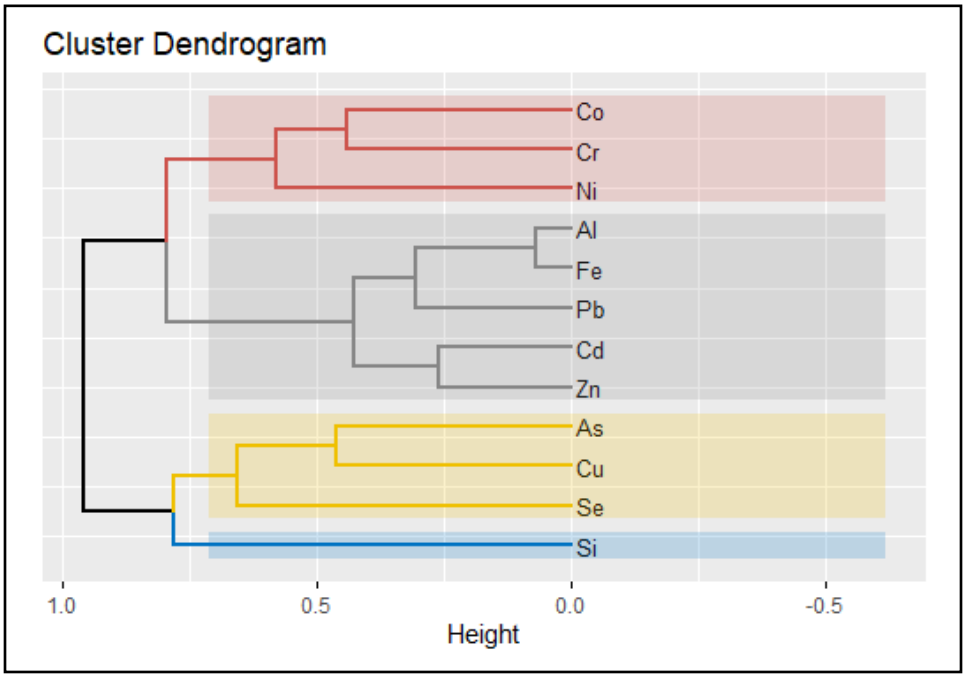

Figure 4.2 Dendrogram of HCA among parameters

Hierarchical Cluster Analysis was also conducted to observe similarity among samples. The 3 clusters generated consists of mixed of different type of dyes and production stages. This indicates factors other than the type of dye and production stage that affect wastewater characteristic. Also similar to textile wastewater, composition of batik wastewater may vary among factories due to variation of type of fabric, chemicals other than dyes, quality of water and equipment used for production (Yaseen, Scholz, and Yaseen 2019). However, further observation on the member of each cluster shows the following pattern:

- the first cluster (marked in pink color) is associated with low concentrations of Fe, Mn, Al, Cr, Co, and Ni
- the second cluster (marked in grey color) is associated with high concentrations of Se
- the third cluster (marked in yellow color) is associated with high concentrations of Zn, Al, Cd and Pb
- the fourth cluster (marked in blue color) is associated with high concentrations of Si, Cr, and Cu

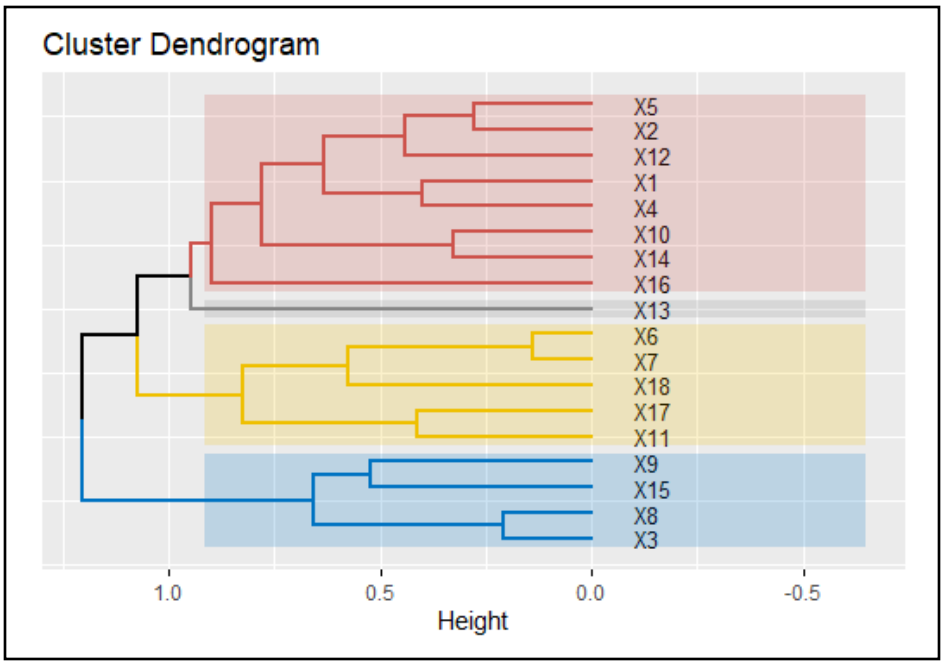

Figure 4.3 Dendrogram of HCA among samples

4.4 Conclusion

Analysis on 18 (seventeen) wastewater samples from batik factories in Yogyakarta Region showed variation among elements and samples. The concentration of Al, Si, Fe, Zn, Cr, Co, Ni, Cu, As, Se, Cd, and Pb ranged from 0.11 to 300 mg/L, 25 to 280 mg/L, 0.56 to 12 mg/L, 0.11 to 180 mg/L, 11.7 to 100 µg/L, 0.6 to 17.7 µg/L, 7.2 to 82.8 µg/L, 20.9 to 1.9 10^3 µg/L, 1.5 to 21.2 µg/L, 7.6 to 2.6 10^3 µg/L, and <0.05 to 220 µg/L respectively. No sample exceed relevant effluent standard in Indonesia as the only heavy metal parameter regulated is Cr. However, concentration of Cd, Se, Fe and Zn exceed relevant effluent standard in Japan and Malaysia. Compared to other studies, concentration of Cr, Pb and Si in this study were relatively lower. However, the concentration of Cu, Cd, Fe and especially Al and Zn were much higher than other studies.

Hierarchical Cluster Analysis (HCA) produced dendrograms showing cluster of strong similarity among parameters Ni, Cr and Co which indicates that the source of these metals is from dyes. Other clusters indicated various sources such as fixation agent, groundwater or another supporting chemical. HCA also indicates that factors other than the type of dye and production stage may affect heavy metal content in batik wastewater which represent the high variability of production process among batik factories.

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CHAPTER 5 : EFFECT OF BATIK EFFLUENT SEEPAGE ON GROUNDWATER QUALITY

Abstract

Small to medium scale batik industry in Indonesia have limited capacity in term of environmental management. Most of batik factories released their wastewater without proper treatment. One possible negative effect of this condition is groundwater contamination. This chapter is aimed to present the of heavy metal in groundwater samples taken from dug wells at and around batik factories located in Winongo Watershed and investigate the effect of wastewater seepage on groundwater quality in study area. Analysis on 32 groundwater samples taken from dug wells at and around batik factories revealed that the water quality is still within the acceptable level. Heavy Metal Contamination Index (HCI) confirmed this condition with very low HCI value. Numerical simulation using one dimensional contaminant transport equation showed very low concentration at groundwater table level which indicate that no groundwater contamination occurred from batik wastewater seepage. This is supported by the lithological and hydrogeological condition of alternating clay and sand layer that prevent the pollutant to seep into the groundwater.

5.1 Introduction

The use of synthetic dyes and various chemicals in batik industry raises concern on its potential negative effect to environment and human health (Martuti et al. 2020; Sulthonuddin and Herdiansyah 2021; Saraswati, Haeruddin, and Purwanti 2014; Naqsyabandi, Riani, and Suprihatin 2018; Syauqiah, Nurandini, and Lestari 2020). The possible risk is higher since most batik industries are small to medium scale industry with limited capacity in many aspects, including environmental management (Syuhadah, Muslim, and Rohasliney 2015). Most factories do not have proper wastewater treatment plant and just released their wastewater into environment. Some factories have simple treatment plant by using serial sedimentation tank which eventually seep into the soil. One possible negative effect of this condition is groundwater contamination. Pollutants from the wastewater which may contain heavy metal can get into groundwater which is the main source of drinking water for the people. Long term exposure to heavy metal contaminated groundwater will increase the risk of getting health problem (Velusamy et al. 2021). This chapter is aimed to present the distribution of heavy metal in groundwater samples taken from dug wells at and around batik factories located in Winongo Watershed and investigate the effect of wastewater seepage on groundwater quality in study area.

5.2 Materials and Methods

5.2.1 Site description and sampling points

Groundwater samples were taken in area part of Winongo Watershed. Winongo Watershed covers an area of 11,029.28 ha with 67.23 km circumference (Kementerian Pekerjaan Umum dan Perumahan Rakyat 2016). More to the downstream direction of the river, the quantity and variation of human activities is rising giving increasing load to the watershed. The main river of this watershed is Winongo River. It is a 49.12 km long river with maximum and minimum discharge were 4.61 m^3/sec. and 0.04 m^3/sec respectively (Dinas Lingkungan Hidup dan Kehutanan Daerah Istimewa Yogyakarta 2021). The upstream of this river is from two small streams originates from Mount Merapi flows across three administrative areas of Sleman Regency, Yogyakarta City, and Bantul Regency and eventually empties into Opak River. Groundwater sampling points for this study were located along the middle section of Winongo Watershed. A total of 32 (thirty-two) samples were taken from dug wells at and around batik factories in Winongo Watershed. Coordinate of groundwater sampling points is presented in Table 5.1. Location of groundwater sampling points is presented in Figure 5.1.

Table 5.1 Coordinate of groundwater sampling points

No.	Sample ID	Coordinate		No.	Sample ID	Coordinate	
		S	E			S	E
1	AT1	07°48'24.92"	110°20'48.19"	17	AT17	07°48'24.73"	110°21'9.47"
2	AT2	07°48'25.20"	110°20'59.71"	18	AT18	07°49'30.06"	110°21'9.66"
3	AT3	07°48'34.02"	110°21'38.00"	19	AT19	07°49'32.78"	110°21'13.58"
4	AT4	07°48'33.99"	110°21'36.73"	20	AT20	07°49'31.79"	110°21'12.63"
5	AT5	07°48'33.20"	110°21'34.84"	21	AT21	07°49'30.76"	110°21'13.01"
6	AT6	07°48'33.36"	110°21'32.61"	22	AT22	07°49'32.88"	110°21'13.15"
7	AT7	07°48'34.82"	110°21'25.92"	23	AT23	07°49'30.13"	110°21'11.25"
8	AT8	07°48'34.36"	110°21'22.71"	24	AT24	07°49'22.94"	110°21'35.42"
9	AT9	07°48'32.75"	110°21'19.79"	25	AT25	07°49'22.86"	110°21'32.54"
10	AT10	07°48'32.63"	110°21'19.83"	26	AT26	07°49'22.84"	110°21'29.13"
11	AT11	07°48'33.14"	110°21'19.23"	27	AT27	07°49'22.56"	110°21'25.75"
12	AT12	07°48'23.77"	110°20'59.98"	28	AT28	07°49'22.11"	110°21'27.24"
13	AT13	07°48'24.39"	110°21'11.33"	29	AT29	07°49'22.38"	110°21'27.41"
14	AT14	07°48'22.32"	110°21'11.42"	30	AT30	07°48'23.03"	110°21'40.01"
15	AT15	07°48'24.56"	110°21'6.05"	31	AT31	07°49'40.19"	110°22'15.35"
16	AT16	07°48'23.77"	110°20'59.51"	32	AT32	07°47'39.93"	110°20'52.69"

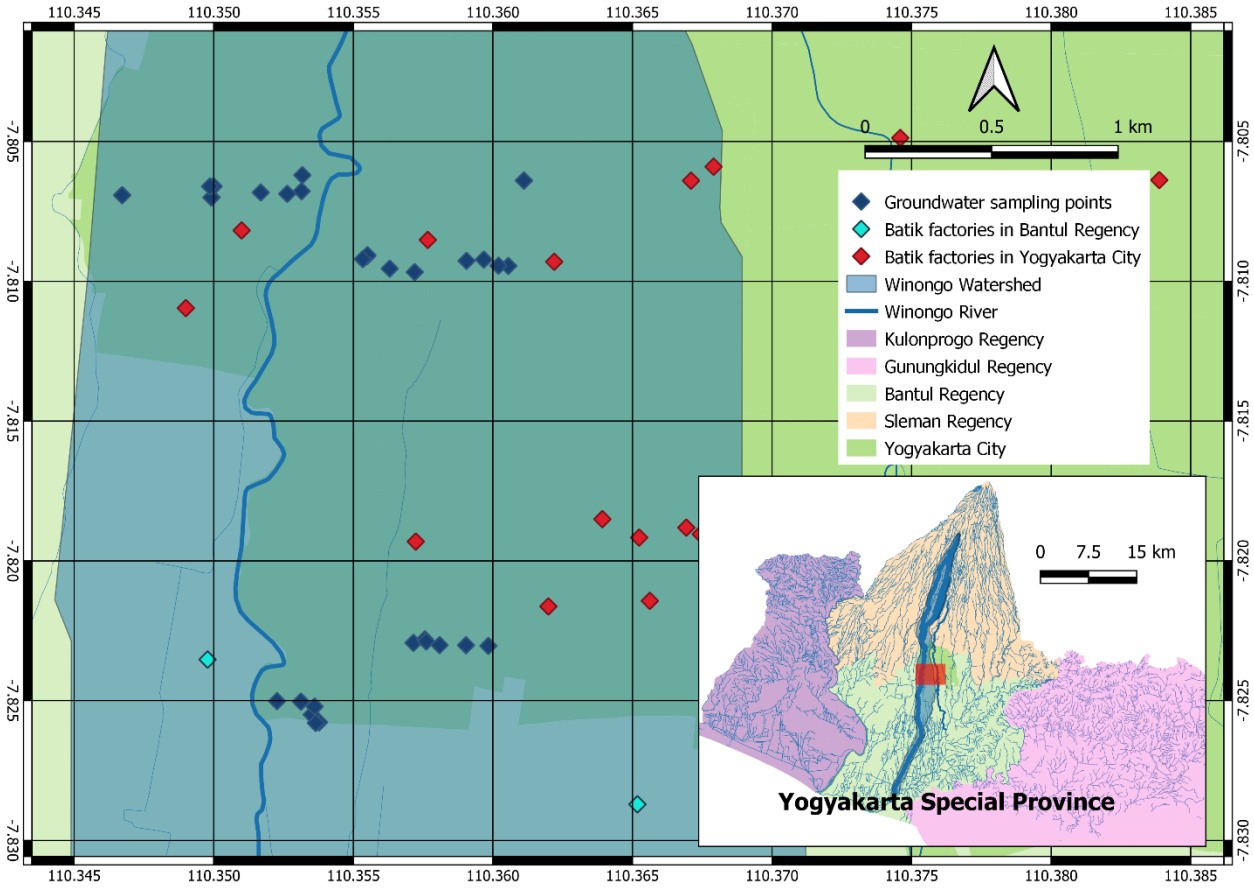

Figure 5.1 Location of groundwater sampling points

5.2.2 Chemical and reagents

Standard stock for each element to be analyzed and internal standards were purchased from Wako Chemical. Concentrated HNO_3 used for sample preservation was from Merck (grade for heavy metal analysis, 65%). For standard solution and sample dilution, concentrated HNO_3 (1.38) used was from Wako Chemical (for analysis of poisonous metal). Cellulose acetate membrane filter 0.45 µm from Advantec was used for sample filtration.

5.2.3 Sample collection

Groundwater sampling was conducted in August during dry season. Temperature, pH, Electric Conductivity (EC), Oxygen Reduction Potential (ORP) were measured on site by using Multiparameter Water Quality Checker Horiba U-50. Samples were collected in polypropylene (PP) bottles. Concentrated nitric was added to sample as necessary until pH < 2 to preserve sample. All samples were then kept in 4°C until analysis.

5.2.4 Sample analysis

Prior to instrument analysis, samples were filtered by using 0.45 µm cellulose acetate membrane filter. Dilution with 1 N HNO_3 solution was conducted to the expected concentration range for each target element. A series of standard solutions was generated by diluting each element's standard stock in 1 N HNO_3 solution. Internal standards 89Y and 115In were applied to both samples and standard to ensure stability during measurement. Two (2) instruments were used to determine concentrations, as detailed below.

5.2.4.1 Analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The concentration of metals Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Ba, and Pb in samples was determined using ICP-MS (XSERIES 2, Thermo Scientific). ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{111}Cd, ^{138}Ba and ^{208}Pb were utilized as isotopes. Limit of detection (LoD) for each element are 0.18, 0.04, 0.65, 0.05, 0.31, 0.05, 0.20, 0.07, 0.19, 0.05, 0.06, and 0.06 µg/L, respectively.

5.2.4.2 Analysis by Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

The MP-AES (4200 MP-AES, Agilent Technology) was used to determine the concentrations of metals Al, in samples. The emission wavelengths used to measure this element was 394.401 nm with limits of detection (LoD) of 0.01 mg/L.

5.2.5 Heavy Metal Contamination Index (HCI)

Heavy Metal Contamination Index (HCI) was introduced by (Rajkumar, Naik, and Rishi 2020) to overcome limitation of other earlier available indexing method to assess heavy metal pollution in groundwater. HCI assessment consists of four stages as described below:

a. The first stage is the selection of heavy metal parameters to be assessed based on various considerations regarding toxicity or any local conditions
b. Weightage assignment for the selected parameter ranges from 1 to 4 with the maximum weight is given to the most toxic parameter
c. Calculation of HCI by using the following formula:

$$Wi = \frac{Awi}{\sum_{i=1}^{n} Awi} \qquad (5.1)$$

$$qi = \frac{Ci}{Si}\ x\ 100 \qquad (5.2)$$

$$MIi = Wi\ x\ qi \qquad (5.3)$$

$$HCI = \sum_{i=1}^{n} MIi \qquad (5.4)$$

Where Wi = relative weight of the input parameter, Awi = assigned weight of the input parameter, n = number of parameters, qi = quality rating of the selected parameter, Si = standard limit, MI = metal sub-index.

d. Evaluation of HCI value

HCI value was used to determine water quality classes as presented in Table 5.2.

Table 5.2 HCI value, water quality class and description

HCI ranges	Class	Water Classes	Reasons
0 < HCI < 20	A	Excellent	All parameters are below standard limit
21 <HCI < 40	B	Good	Majority of parameters are below standard limit
41 < HCI < 60	C	Marginal	Rarely the parameters exceed standard limit
61 < HCI < 80	D	Poor	Often the parameters exceed standard limit
81 < HCI < 100	E	Very Poor	Usually the parameters exceed standard limit
HCI > 100	F	Unfit	Majority of parameters exceed standard limit

(Rajkumar, Naik, and Rishi 2020)

5.2.6 Effect of batik wastewater seepage into groundwater

Direct effect of batik wastewater seepage into groundwater was examined using the following one-dimensional groundwater material transport equation:

$$Rd\ \frac{\partial C}{\partial t} = D\ \frac{\partial^2 C}{dx^2} - V\frac{\partial C}{\partial x} \qquad (5.5)$$ (Dong et al. 2020; Genuchten and Alves 1982)

In which, $Rd = 1 + \frac{(1-n)\rho\ Kd}{n}$, and $V = \frac{K\ i}{n}$

C = pollutant concentration
D = diffusion coefficient
Rd = retardation factor
V = groundwater flow velocity
K = groundwater hydraulic conductivity
i = hydraulic gradient of groundwater flow
n = soil porosity
ρ = soil density

Equation (5.5) was used to simulate the transport of heavy metal in batik wastewater to groundwater for the possibility of contamination from batik wastewater seepage. Finite-difference numerical method was used to solve partial differential equation as that of equation (5.5) above. The second-order derivative is solved using the central differentiation method, which requires three points, whereas the first-order

derivative is solved using the forward Euler differentiation method, which requires just two points (Dong et al. 2020).

$$\frac{\partial^2 C}{\partial x^2} = \frac{Cj+1-2Cj+Cj-1}{\Delta x^2} + O(\Delta x^2) \qquad (5.6)$$

$$\frac{\partial C}{\partial x} = \frac{Cj+1-Cj-1}{\Delta x} + O(\Delta x) \qquad (5.7)$$

Using equation (5.6) and (5.7), explicit solution at time t_{k+1} for equation (5.5) is as follows:

$$C_{k+1,\,j} = (\gamma + \alpha)C_{k,j-1} + (1 - 2\gamma - \alpha)C_{k,\,j} + \gamma C_{k,\,j+1} \qquad (5.8)$$

where, $\gamma = \frac{\Delta t}{R\Delta x^2}$, and $\alpha = \frac{V\Delta t}{R\Delta x}$

The simulation was conducted upon 3 (three) batik factories (CB, LL, and CM) with the assumption that concentration at the source (wastewater tank) was constant along simulation and that concentration at other points were 0. These assumptions were set as initial and boundary condition to run the simulation. Cu and Zn were used for this simulation as both elements showed distinctive distribution among all heavy metal elements in groundwater samples. Table 5.3 and Table 5.4 present all the input value for all variables in the equation. Simulation was conducted by using Microsoft Excel 365 version 2111.

Table 5.3 Input parameter for numerical simulation

Parameter	Unit	Value	Source
D	m^2/day	$14.3\ 10^{-4}$	(Jayanudin and Fakhrurozi 2016)
Kd Cu	L/kg	$5.0\ 10^2$	(Allison and Allison 2005)
Kd Zn	L/kg	$1.3\ 10^3$	(Allison and Allison 2005)
K	m/day	7.8	(Manny, Atmaja, and Eka Putra 2017)
ρ	kg/L	1.8	(Manek, Putra, and Hendrayana 2021)
n	%	40	(Xaixongdeth et al. 2015)

Table 5.4 Factory data for simulation

Parameter/ Factory	Concentration at source/Co *		Concentration in groundwater		Groundwater table depth (m) **
	Cu (mg/L)	Zn (mg/L)	Cu (µg/L)	Zn (µg/L)	
CB	0.13	0.22	0.9	26.0	3.2
LL	1.89	0.33	1.0	11.5	5.8
CM	0.08	179.2	2.8	4.5	8.2

*Batik wastewater data (chapter 4)

**From groundwater flow interpolation map

5.2.7 Statistical analysis and map works

Descriptive statistical analysis was conducted by using Microsoft Excel 365 version 2111 and R program version 4.0.0 (R Core Team 2020) to obtain the mean, median and standard deviation for non-detect variables using "NADA2" Package (Julian and Helsel 2021). Map works was produced by using QGIS open-

source software version 3.16 Hannover (QGIS Development Team 2009). Groundwater flow map was developed to obtain hydraulic conductivity data for the simulation of wastewater seepage into groundwater. This map was developed with ArcGIS version 10.8.1 by interpolation of data of groundwater table from (Nurroh, Gunawan, and Kurniawan 2020). Basic maps as well as topography map to develop groundwater flow map were provided by Indonesia Geospatial Portal (BIG 2020).

5.3 Results and Discussion

5.3.1 Physicochemical parameters of groundwater samples

Physicochemical parameter of groundwater samples compared with Indonesian standard for drinking water and clean water is presented in table 5.5. Temperature of groundwater sample varied from 27.3 – 31.9°C. For pH value, 3 sampling points had pH under the standard and 1 sampling point had pH value above the standard. Low or high pH may become an indication of contamination. The point where the pH value is high (9.7) is located within the area of batik factory. One of the characteristic of batik wastewater is high pH due to the application of caustic soda during dyeing process (Khalik et al. 2015). Electric Conductivity (EC) values ranged from 0.2 – 0.7 mS/cm. EC is an indicator of amount of dissolved solid or salinity in water. It may also become indicator of water pollution (Rezaei et al. 2019). This parameter is important to determine suitability for irrigation (Rawat et al. 2019). According to WHO, maximum allowable limit for EC is 1.5 mS/cm (World Health Organisation (WHO) 2011). No samples in this study exceed this value. Total Organic Carbon (TOC) value in samples varied within the range 0.33-3.20 mg/L. TOC represents the total concentration of organic carbon in groundwater. According to a study in 2019 by Kaempfner in (Manek, Putra, and Hendrayana 2021), baseline TOC for Yogyakarta area is 3.7 mg/L. This means that the value above this number is considered contaminated. Refer to this study, TOC value in samples in this study are considered to be not contaminated.

Table 5.5 Summary statistics of physicochemical parameters of groundwater samples

Parameter	Max	Min	Mean	Median	SD	Std.1	Std.2
T (°C)	31.9	27.3	29.4	29.4	1.2	± 3°C	± 3°C
pH	9.7	6.3	7.1	7.0	0.6	6.5-8.5	6.5-8.5
EC (mS/cm)	0.7	0.2	0.4	0.4	0.1	-	-
TOC (mg/L)	3.2	0.3	1.1	0.9	0.7	-	-

5.3.2 Distribution of metal and metalloid in groundwater samples and Heavy Metal Contamination Index (HC) determination

Summary statistics of metal and metalloid concentration in groundwater samples and comparison with Indonesian standard for drinking water and clean water is presented in Table 5.6. Compared to Indonesian

standard for drinking water and clean water, no samples in this study exceed the maximum allowable concentration. It means that groundwater in this area was relatively safe for daily consumption in terms of metal and metalloid content.

Concentration of various heavy metal at each groundwater sampling location is presented in Figure 5.3 and 5.4. Figure 5.3 presents group of heavy metal with lower concentration, while Figure 5.4 presents group with higher concentration. From these two figure, Cu and Zn show dominance and distinctive pattern.

Table 5.6 Summary statistics of metal and metalloid concentration in groundwater samples (µg/L)

Parameter	Max	Min	Mean	Median	SD	LoD	Std.1	Std.2
Al	60.0	<10	30.0	20.0	10.0	10.0	200	-
Cr	1.4	<0.18	0.1	-	0.1	0.18	50	-
Mn	283.6	0.1	16.5	3.3	50.0	0.04	400	500
Fe	71.4	1.6	17.8	10.4	18.6	0.65	300	1,000
Co	0.2	<0.05	0.1	0.1	0.02	0.05	-	-
Ni	4.6	<0.31	0.9	-	0.8	0.31	70	-
Cu	9.9	0.9	3.3	2.9	2.0	0.05	2,000	-
Zn	235.0	2.7	51.4	17.7	71.8	0.2	3,000	15,000
As	3.3	0.8	1.9	1.9	0.7	0.07	10	50
Se	7.6	0.9	2.0	1.7	1.2	0.19	10	10
Cd	Only detected in 1 sampling point for 0.05 µg/L					0.05	3	5
Ba	36.8	9.1	21.9	23.2	7.6	0.06	700	-
Pb	3.2	0.2	0.6	0.4	0.6	0.06	10	50

Std.1: Indonesia drinking water standard Regulation of Ministry of Health No. 492/2010
Std.2: Indonesia clean water standard Regulation of Ministry of Health No. 32/2017

Heavy Metal Contamination Index (HCI) is used to assess the effect of various metal simultaneously to help in the determination of the focus for environmental management effort. In this study HCI calculation is also used to observe the possible relationship between the state of heavy metal contamination in sampling point and batik industry. The first stage of the calculation of HCI is the selection of heavy metal parameters to be assessed. From thirteen parameters measured in the laboratory, four parameters include Fe, Cr, Cu, Zn, and Se were selected based upon various considerations. Apart from their toxicity, these parameters were selected because of their association with batik industry. For Fe, even though this metal is soil particle component, but it is also associated with batik production for the application of fixation agent (Martuti et al. 2020). For the other four metals, their association with batik industry is related to metal complex azo dyes (Yaseen, Scholz, and Yaseen 2019; Maria et al. 2014; Chakraborty 2011). The variable used for HCI calculation is presented in Table 5.7.

Table 5.7 AWi and Si value for HCI calculation

	Cr	Cu	Se	Fe	Zn
AWi [a)]	4	3	4	1	2
Si [b)]	50	2000	10	300	300

[a)] (Rajkumar, Naik, and Rishi 2020)

[b)] Indonesia drinking water standard Regulation of Ministry of Health No. 492/2010

HCI value for every sampling point is presented in Figure 5.2. Only 1 sampling point exceed the limit value of 20. The other sampling points were put into class A which means that water quality in those areas is excellent based on the concentration of Cr, Cu, Se, Fe, and Zn. Because all parameters are below standard limit, HCI value are also low. However, the overall effect of multiple heavy metals can be compared to assess each sampling point. In this case, sampling point 6 has the highest HCI value. Sampling point 6 is situated in one of the tourism centers in Yogyakarta City. Many hotels, marketplaces and home industries were located in this area. It is also one of the centers of batik industry in Yogyakarta City area. Even though the HCI value is relatively higher than other sampling points, it is still categorized as in good condition.

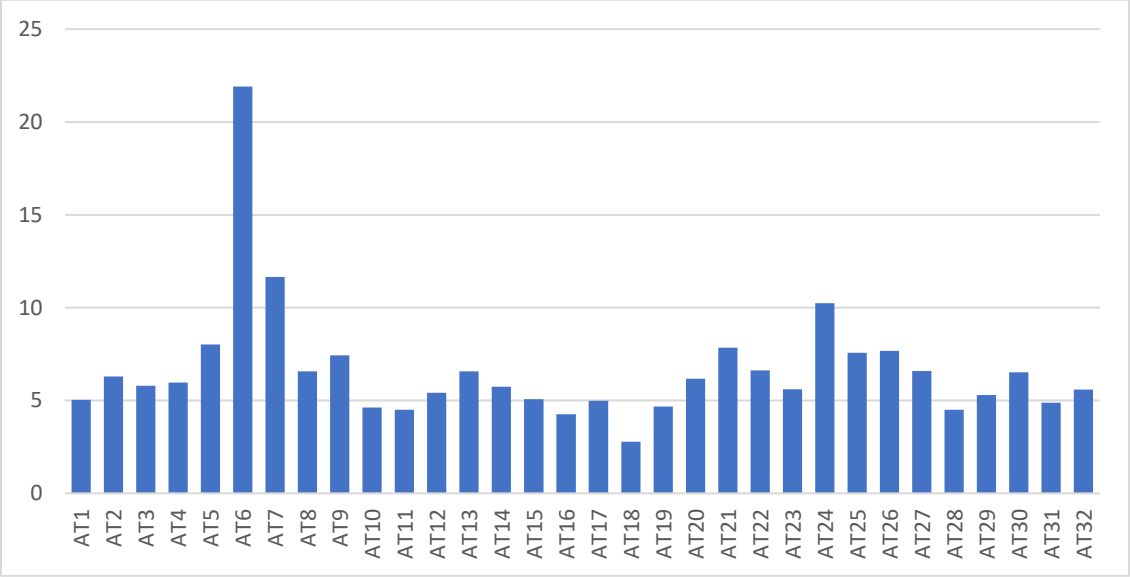

Figure 5.2 HCI value at every sampling point

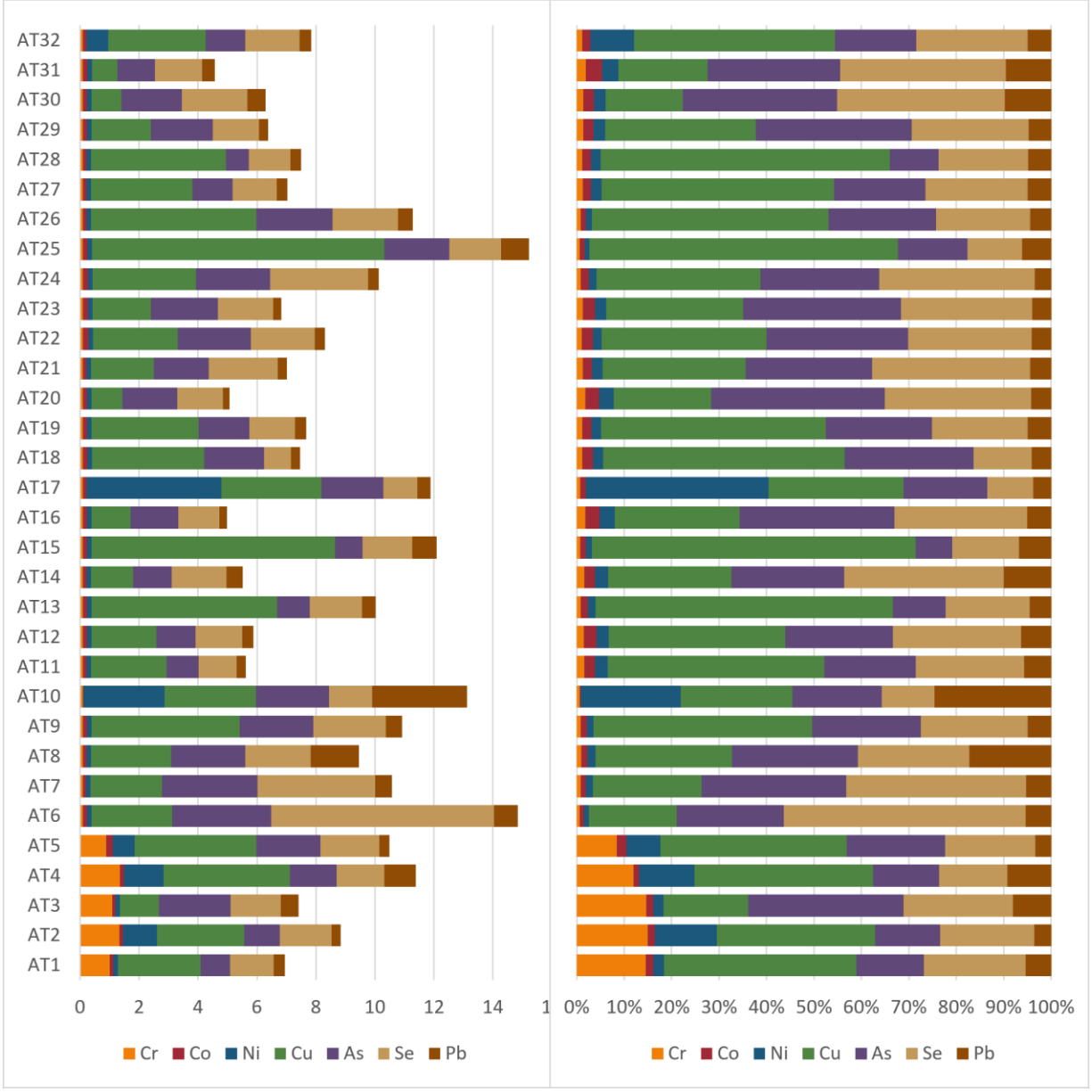

Figure 5.3 Concentration of Cr, Co, Ni, Cu, As, Se and Pb di groundwater (in µg/L)

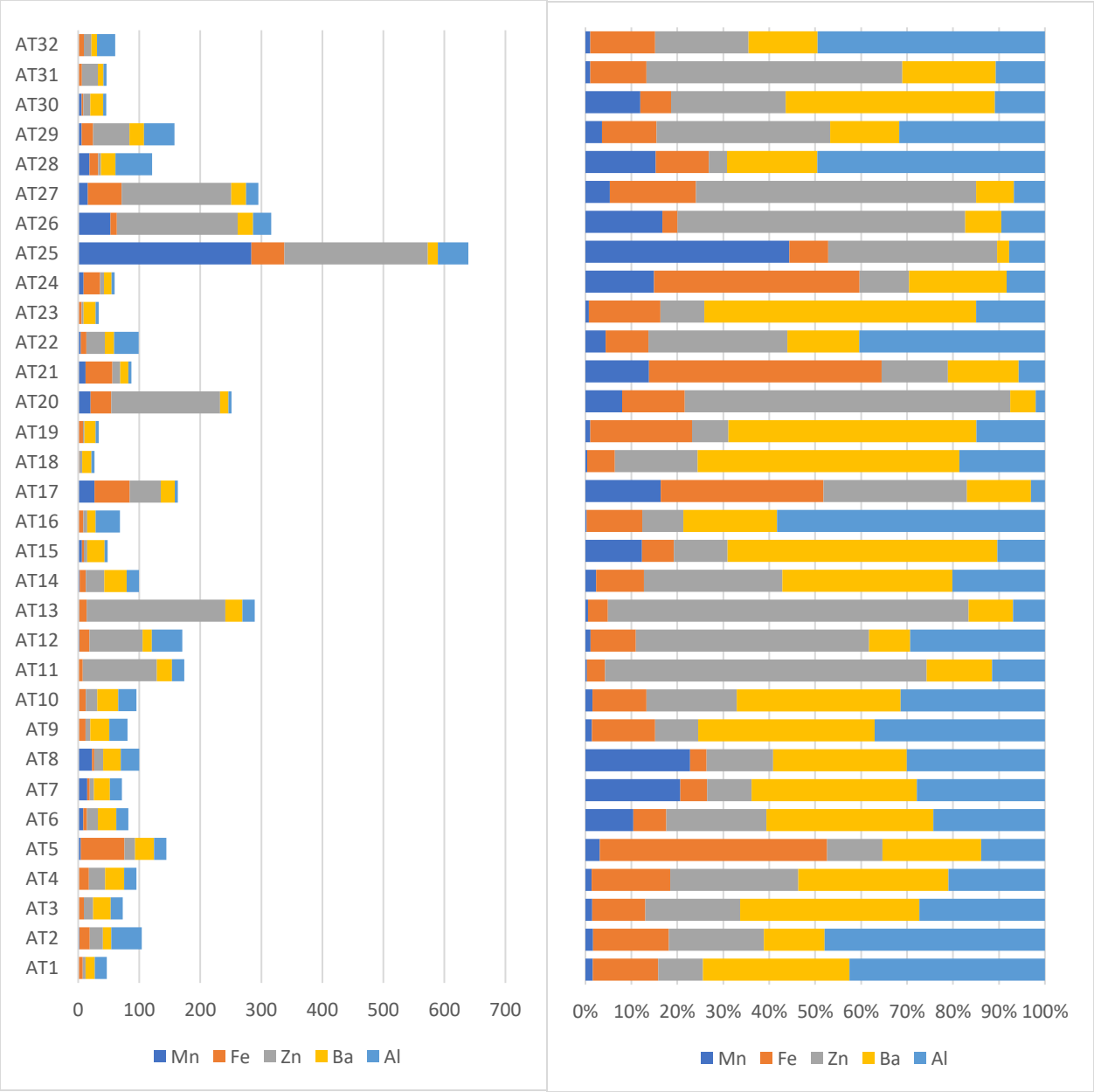

Figure 5.4 Concentration of Mn, Fe, Zn, Ba, and Al in groundwater (in µg/L)

5.3.3 Effect of batik wastewater seepage into groundwater

The current practice of wastewater handling in batik industry raising concern on its possible contribution to groundwater contamination. However, analysis of heavy metal concentration in the groundwater around batik shows concentration below the standard. The transport of heavy metal through the soil into the groundwater depends on many factors, including heavy metal adsorption by soil particle, concentration of pollutant, lithology of the area, and characteristic of aquifer. The possibility of

groundwater contamination by batik wastewater seepage was examined using equation (5.5) upon 3 (three) batik factories. Area location of these 3 factories is presented in Figure 5.5. The concentration of Cu and Zn at groundwater table was simulated and then compared to field data for each factory location. Simulation result is presented in Figure 5.6 until 5.8 for each factory.

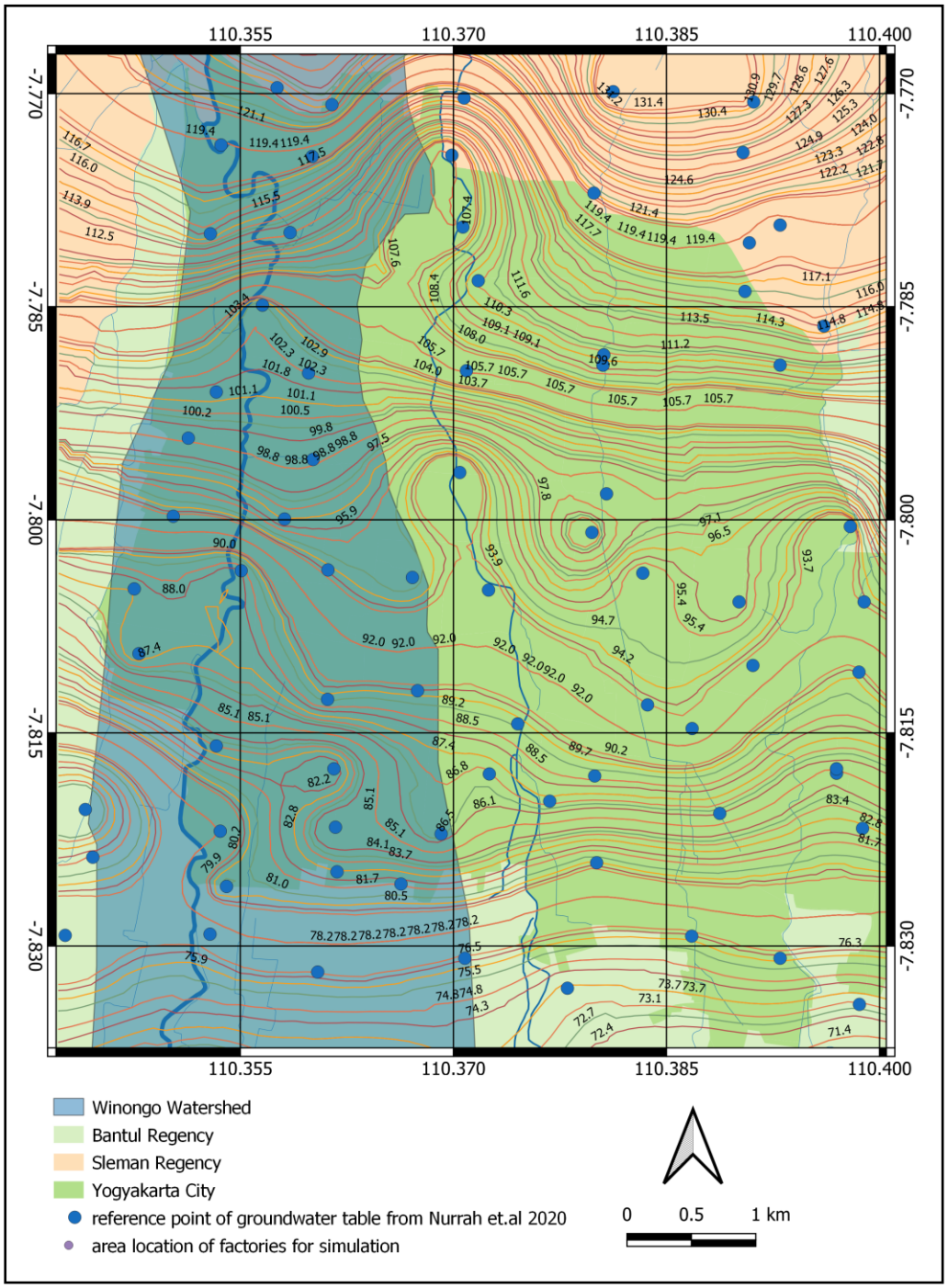

Figure 5.5 Groundwater flow map and area location of factories for simulation

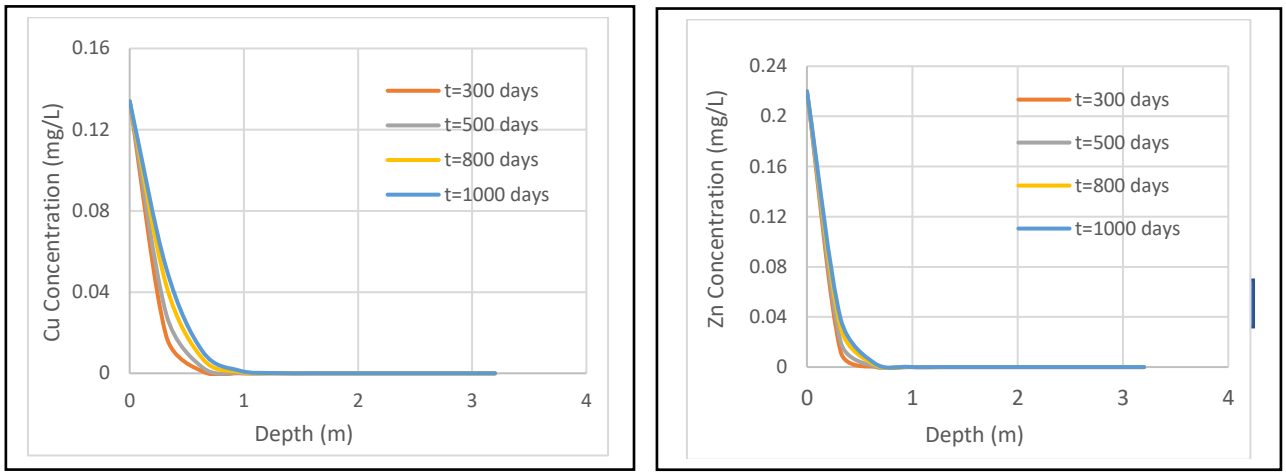

Figure 5.6 Simulation result for Cu (left) and Zn (right) at Factory CB

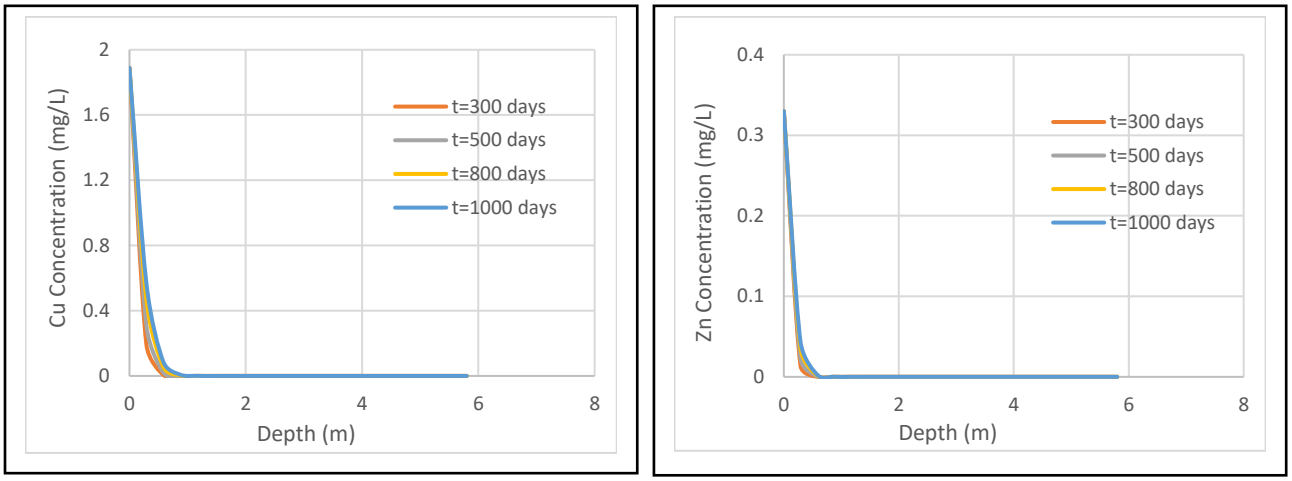

Figure 5.7 Simulation result for Cu (left) and Zn (right) at Factory LL

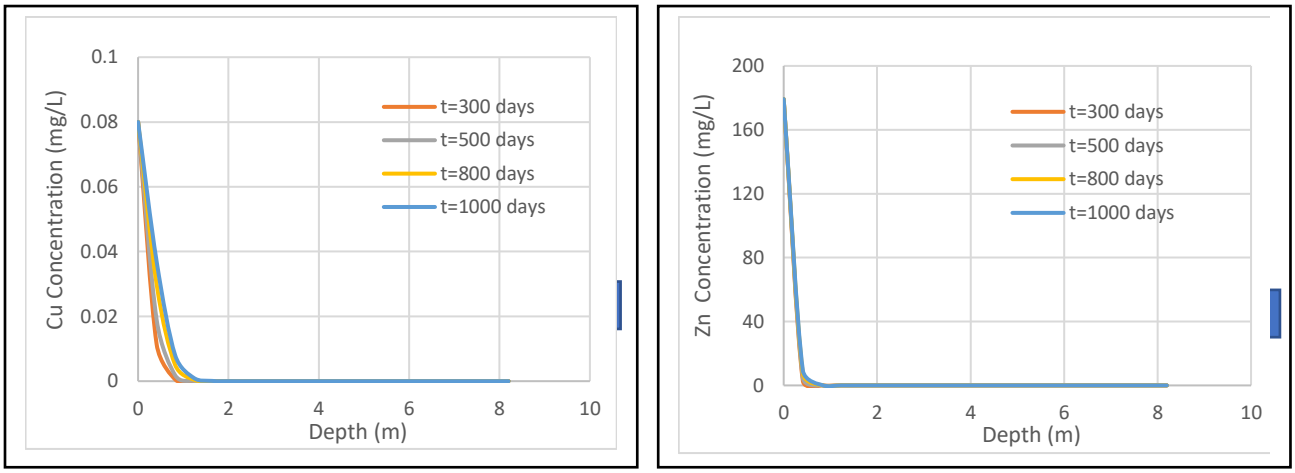

Figure 5.8 Simulation result for Cu (left) and Zn (right) at Factory CM

Simulation result from all the three factories shows that concentration of Cu and Zn at level of groundwater table are very low. The study area composed of volcanic debris which consists of fine sand, coarse sand, gravel, silt, and clay. The characteristic of rock and surface material are loose to soft, semi consolidated and partly porous. Topsoil consist of tuffaceous clay with soft, low plasticity, sandy and high to moderate permeability (Directorat Geologi Tata Lingkungan 1993). According to (Manek, Putra, and Hendrayana 2021), lithology or study area consists of alternating layers of sandstone with loam-clay sand and alternating clay sandstone with clay as presented in Figure 5.9. Clay and silt fraction of soil have tendency to accumulate trace metals (Agbaji and Gimba 2015; Bairwa et al. 2018) which prevented the contaminant from batik wastewater to go into groundwater. The contaminant is most probably adsorbed by soil particle at the surface of the soil. The simulation result, lithological and hydrogeological condition of study area indicate that the possibility of groundwater contamination by heavy metal from batik factory in study area is very low. It should be noted, however, that in the infiltration of metal ions into the subsurface, the permeability is not necessarily homogeneous, so that the metal ions may infiltrate faster than expected through water courses that are connected by areas of high permeability.

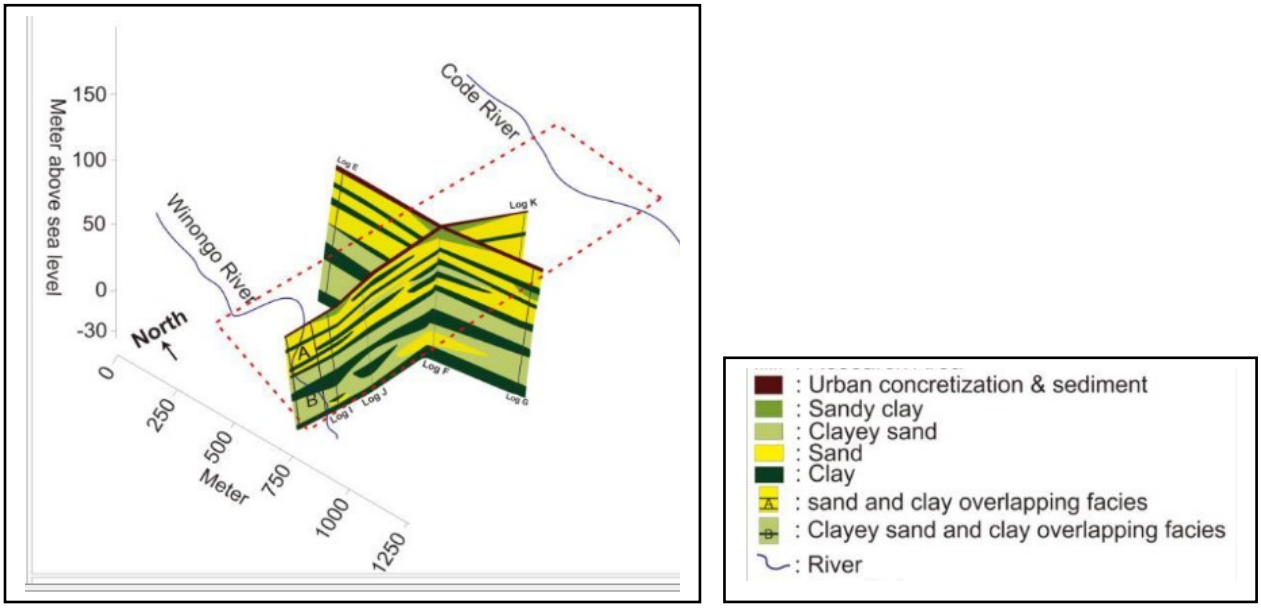

Figure 5.9 Lithology and hydrogeological condition of study area (Manek, Putra, and Hendrayana 2021)

5.3.4 Distribution of Cu and Zn in groundwater

Figures 5.3 and 5.4 show distinctive distribution of Cu and Zn in groundwater samples. Spatial distribution of these 2 elements are presented in Figure 5.10 and 5.11. Range concentration of Cu in groundwater sample is between 0.9 – 9.9 µg/L. As the possibility that the source of this heavy metal content is from the

seepage from above the ground activities is low, other possible source is from the river. The physical, chemical and biological processes in the streambeds controls the river-groundwater interaction (Brunner et al. 2017) which may result in groundwater quality affected by river quality. For this possibility, the concentration of Cu in Winongo River water was observed which ranged from 3.0 – 6.8 µg/L as presented in Chapter 6. This range is even lower than that in groundwater that it may not affect the Cu concentration in groundwater. The variation of Cu concentration in groundwater then can be assumed to be of natural cause. However, as it is only one time measurement data, it may not represent the true profile of Cu concentration in Winongo River. So, that the more frequent monitoring data is required to conduct analysis.

Distinctive distribution also shown by Zn with the range of concentration from 2.7 – 235 µg/L. Compared to Cu, this range is wider which may indicate possible non-natural source. Possible source from Winongo River cannot be directly examined as no data of Zn concentration in Winongo River is available. However, from the analysis of wastewater dilution as discharged to Winongo River as presented in Chapter 6, Zn is potential to be in high concentration in Winongo River. This may affect the concentration of Zn in groundwater as well. Other possible source of Zn in groundwater is probably due to local variation of soil permeability in study area. This variation allows wastewater seepage to reach groundwater table in some spots. So, even though the general lithological and hydrogeological condition of the study area which is supported by simulation result at the previous section suggests the very low possibility of wastewater seepage into groundwater, some local variation may present to allow this seepage to occur. In Figure 5.11, it is also shown that the high Zn concentration spots are randomly distributed. On the other hand, at points closer to the river, Zn concentration is both high and very low, whereas points with high concentration also located further from the riverbank.

5.4 Conclusion

Analysis on 32 groundwater samples taken from dug wells at and around batik factories revealed that the water quality is still within the acceptable level. Heavy Metal Contamination Index (HCI) confirmed this condition with very low HCI value. Numerical simulation using one dimensional contaminant transport equation showed very low concentration at groundwater table level which indicate that no groundwater contamination occurred from batik wastewater seepage. This is supported by the lithological and hydrogeological condition of alternating clay and sand layer that prevent the pollutant to seep into the groundwater. Concentration of Zn is high at some spots probably because of the effect

of Winongo River or the variation of soil permeability to allow wastewater seepage reaching groundwater table.

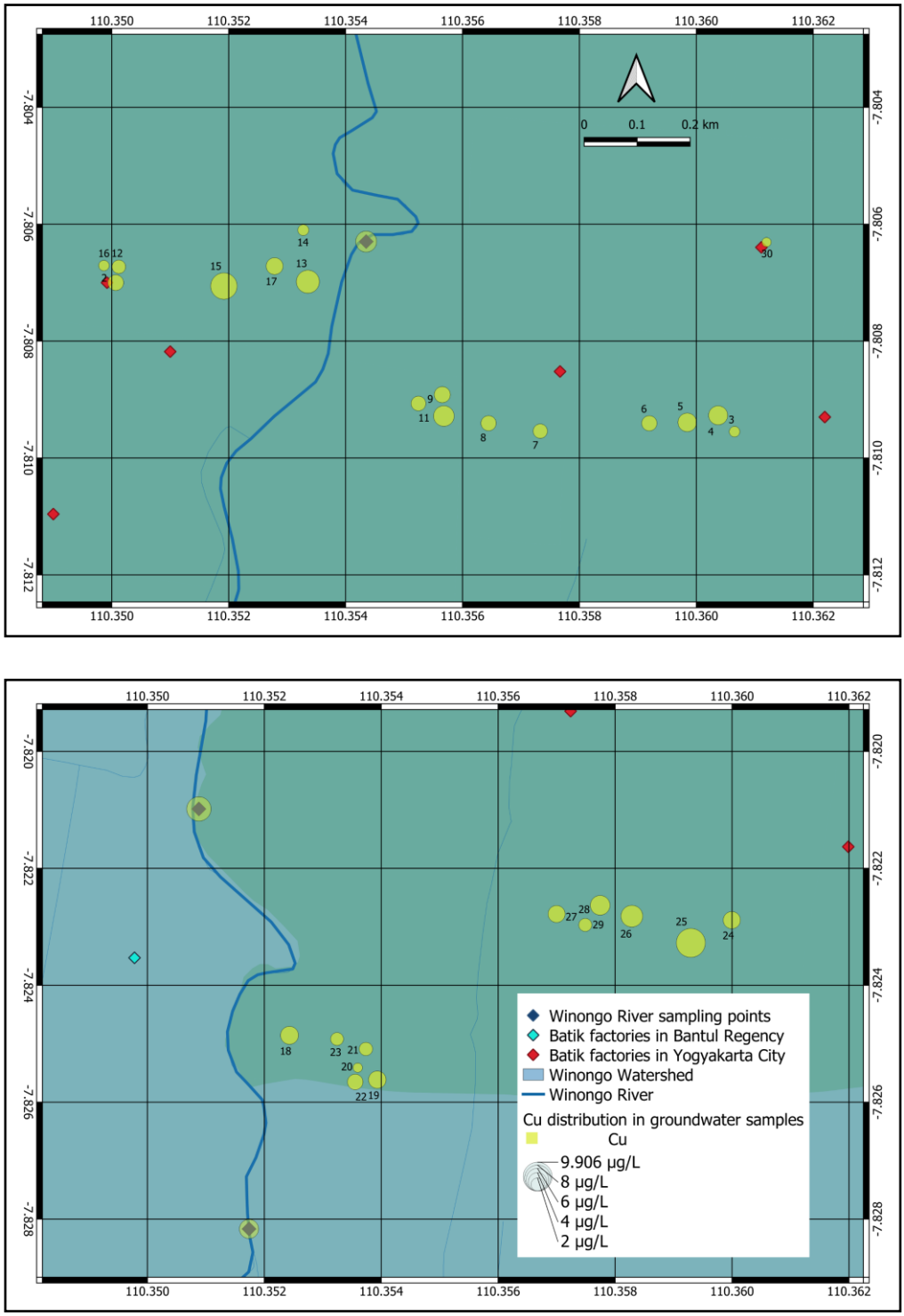

Figure 5.10 Spatial distribution of Cu in groundwater samples

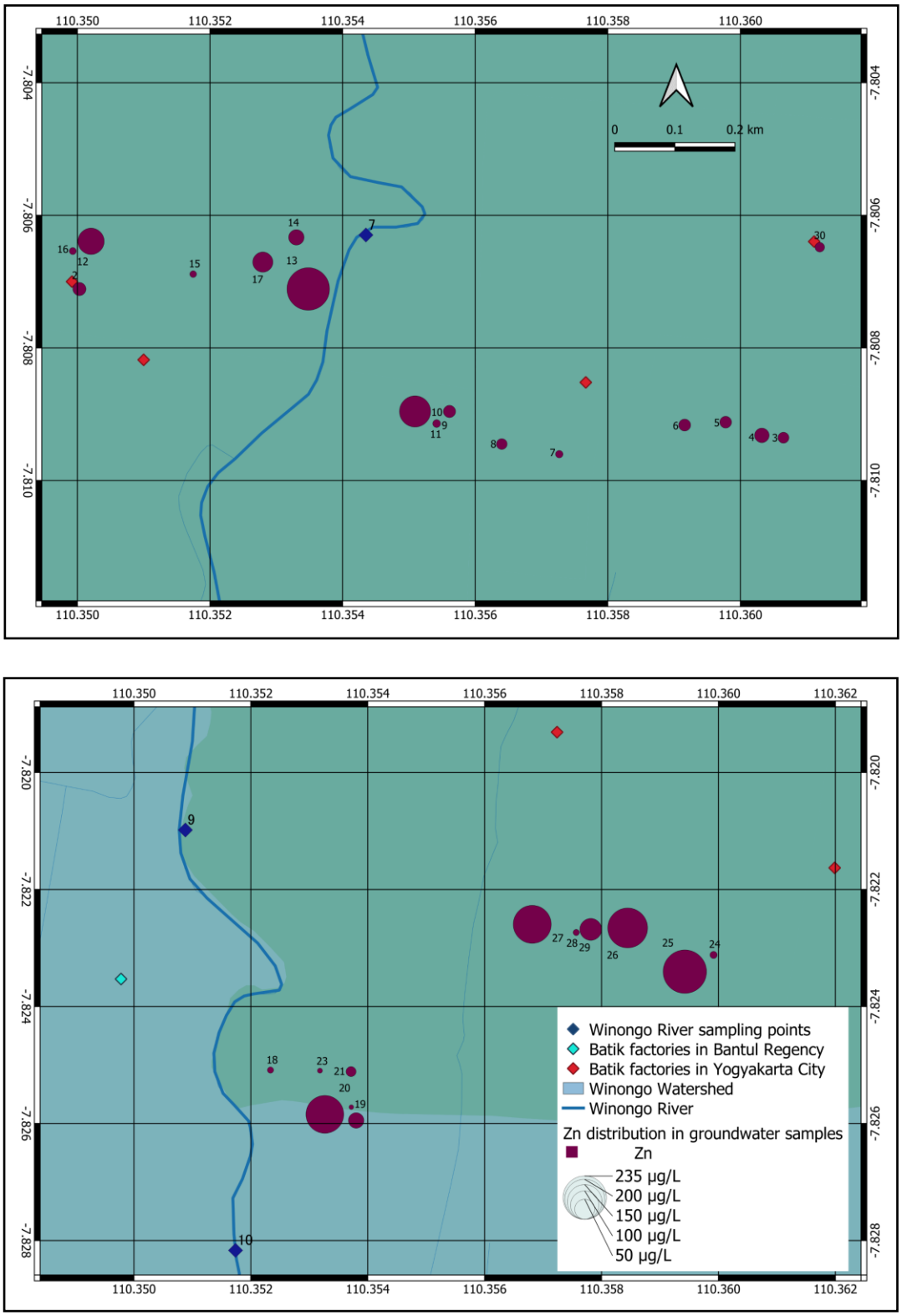

Figure 5.11 Spatial distribution of Zn in groundwater samples

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CHAPTER 6 : RIVER WATER AND SEDIMENT QUALITY AFFECTED BY WASTEWATER EFFLUENT FROM BATIK INDUSTRY

Abstract

The use of synthetic dye and various chemicals in batik industry raises concern on the possibility of heavy metal content in its wastewater. As most batik industries in Indonesia just released their wastewater to environment without prior treatment, heavy metal contamination is expected to occur. One of the most affected environmental compartments is river environment including Winongo River. Winongo River is one of three main rivers flowing in Yogyakarta City area. This river plays important role as the source of water, irrigation, fishery, and tourism. Apart from domestic houses, small-scale industries including batik industries are situated along the river. Hence, this river became one of the receiving water bodies for the discharge of untreated batik wastewater. This chapter is aimed to present the distribution of heavy metals in water and sediment samples of Winongo River and assess the degree of contamination and its ecological risk accordingly. The possible source of these heavy metal in Winongo River is investigated through statistical source identification. On the other hand, the contribution of batik industry effluent to river water quality is also examined through Monte Carlo method to simulate dilution process. Distribution of various heavy metal in river water was following the order of Fe>Pb>Cd>Cu>Cr. Range of concentration were 42.8-121.4 µg/L for Fe, 7.6-54.9 µg/L for Pb, 8.9-14.4 µg/L for Cd, 3.0-6.8 µg/L for Cu, and <5.5 µg/L for Cr. For concentration in sediment samples following order occurred, Fe>Pb>Cu>Cr>Cd. Range concentration in sediment were 1473.4-3237.6 mg/kg for Fe, 16.3-49.0 mg/kg for Pb, 15.4-46.3 mg/kg for Cu, 0.5-12.6 mg/kg for Cr, and 1.7-3.3 mg/kg for Cd. Assessment of the degree of contamination by using Geo-accumulation index (I_{geo}) and Enrichment Factor (EF) suggested a serious contamination by Cd and Pb in river sediment. In addition, ecological risk index by using consensus-based sediment quality standard (Q_{m-PCA}) categorized sediment sample from all sampling points were toxic to sediment dwelling organisms. For water samples, Heavy metal Pollution Index (HPI) suggested a highly polluted state for all sampling points but according to Nemerow Pollution Index (PN) only 4 sampling points were categorized as polluted. Both indexes agreed upon which sampling points were the mostly polluted which includes sampling points in the area where many home industries including batik factories were located. In general, for all assessment index employed in this study, Cd consistently become the biggest contributor to high contamination degree or high ecological risk suggestion the prioritization of Cd monitoring. Source identification by using Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA) and Correlation Analysis (CA) revealed the heavy metal possible sources were agricultural activities from the using of fertilizer, pesticides, and metal-enriched cattle fodder and also from home industries along the river including batik industries. Monte Carlo simulation showed the low probability of contribution of batik wastewater to cause the concentration of river water exceed stream standard for parameter Pb, Cd, Fe and Cu, but high probability for Zn.

6.1 Introduction

The use of synthetic dyes and other chemicals in batik industry raises concern about their potential negative impact on the environment and ultimately on human health. The degree of the impact would be greater because the majority of batik factories were small to medium scaled industry with limited capacity for occupational health and environmental management. Most batik factories do not have sufficient wastewater treatment system, so that wastewater discharge directly into drainage system or nearby river without prior treatment. Direct discharge of this untreated wastewater to water body become source of serious pollution to river environment. Furthermore, it will threaten human health as well, as the river water is used for different purposes for people living in the close vicinity. Especially in developing countries, river water is still used for bathing, washing, aquaculture, source of food (fish) and even as raw water for local drinking water company.

The common characteristics of batik wastewater are aggregate organics, color, odor and solid which made it noticeable when it is released to water body without proper treatment. However, the use of synthetic dyes, fixing agent and other chemicals during batik production may generate other pollutants as well including heavy metals. Heavy metals are found in dyes as impurities or are incorporated into the dye molecule (Syuhadah, Muslim, and Rohasliney 2015). Certain azo dyes are complexed with metals to improve their fastness to fabric and the most often used metals are chromium, cobalt, and copper (Maria et al. 2014).

Heavy metal from untreated wastewater discharged into the river system would undergo physical, chemical and biological transformation (Liao et al. 2017). Only less than 1% of pollutant are dissolved in water in aquatic environment, over 99 percent are stored in sediments, which serve as the primary sink and carrier for toxins (Rodríguez-Espinosa et al. 2018). Sediments are long-term reservoir for contaminants including heavy metals (Rajeshkumar et al. 2018). This would pose health risk to human once it enters food web via benthic organisms living in sediment. A certain chemical condition in aquatic environment may release heavy metal in the sediment to the water (Liao et al. 2017; Vu et al. 2017; Rajeshkumar et al. 2018). This occurs more frequently in surface sediments due to the rapid changes in environmental variables such as pH, temperature, and bioturbation (or resuspension) (Vu et al. 2017). In addition, heavy metals from anthropogenic origin are highly mobile and bioavailable, making them more likely to cause a detrimental effect on aquatic species (Vu et al. 2017). If the contaminated water body is important to support daily lives, people would be highly exposed to heavy metal as well.

Winongo River is one of three main rivers flowing in Yogyakarta City area. This river plays important role as the source of water, irrigation, fishery, and tourism (Dinas Lingkungan Hidup Kabupaten Bantul 2020). Apart from domestic houses, small-scale industries including batik industries are situated along the river. Hence, this river became one of the receiving water bodies for the discharge of untreated batik wastewater. This chapter is aimed to present the distribution of heavy metals in water and sediment samples of Winongo River and assess the degree of contamination and its ecological risk accordingly. The contribution of batik wastewater in heavy metal content of Winongo River will also be investigated through statistical source identification.

6.2 Materials and Methods

6.2.1 Site description and sampling points

River water and sediment samples were taken in area part of Winongo Watershed. Winongo Watershed covers an area of 11,029.28 ha with 67.23 km circumference (Kementerian Pekerjaan Umum dan Perumahan Rakyat 2016). More to the downstream direction of the river, the quantity and variation of human activities is rising giving increasing load to the watershed. The main river of this watershed is Winongo River. It is a 49.12 km long river with maximum and minimum discharge were 4.61 m^3/sec. and 0.04 m^3/sec respectively (Dinas Lingkungan Hidup dan Kehutanan Daerah Istimewa Yogyakarta 2021). The upstream of this river is from two small streams originates from Mount Merapi flows across three administrative areas of Sleman Regency, Yogyakarta City, and Bantul Regency and eventually empties into Opak River. For this study, sampling points were located along the middle section of Winongo Watershed. A total of 12 sampling points in Winongo River were selected for this study. Coordinate of sampling points is presented in Table 6.1, while their location is presented in Figure 6.1.

Table 6.1 Coordinate of river sampling points

Sampling point	Location		Coordinate	
1	Jambon Bridge	Main river	7°45'58.11"S	110°21'6.50"E
2	Panggungan	Tributary	7°46'16.61"S	110°21'7.06"E
3	Jatimulyo Bridge	Main river	7°46'27.02"S	110°21'17.41"E
4	Bumijo, Jetis	Tributary	7°46'50.80"S	110°21'29.14"E
5	Kyai Mojo	Main river	7°46'58.38"S	110°21'25.44"E
6	Merah Bridge	Main river	7°47'52.53"S	110°21'18.20"E
7	Ngampilan	Main river	7°48'22.67"S	110°21'15.67"E
8	Mantrijeron 1	Main river	7°48'52.33"S	110°21'4.70" E
9	Mantrijeron 2	Main river	7°49'15.54"S	110°21'3.17"E
10	Jogonalan Lor,	Main river	7°49'41.41"S	110°21'6.26"E
11	Jogonalan Kidul	Main river	7°50'1.67"S	110°21'5.84"E
12	Winongo Bridge	Main river	7°50'15.07"S	110°20'59.72"E

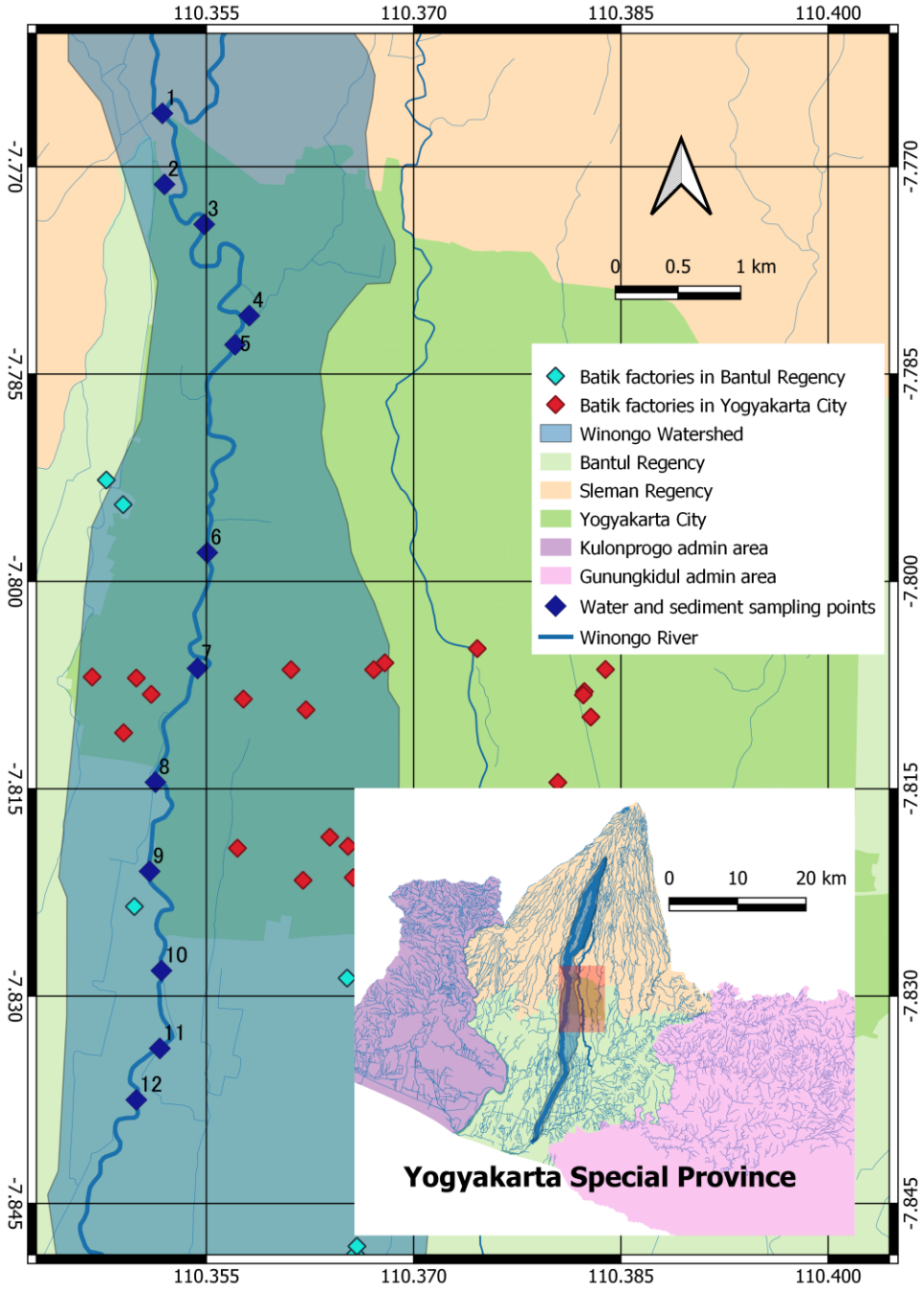

Figure 6.1 Water and sediment sampling points

Sampling point 1 is located in Sleman Regency. Land-use around this point mostly were agriculture area and domestic housing. There were also some workshops and food home industry. Sampling point 2 is part of Yogyakarta City surrounded by domestic housing and agricultural area in the northern part which is part of Sleman Regency. Sampling points 1 and 2 were expected to be background points as those were

located at the upstream area with less anthropogenic activities especially batik industries. Sampling point 3 until 7 are located in Yogyakarta City area. Land-use type along these points were mostly domestic housing. Some workshop, hotel, laundry shops, and during the time of sampling there was still one manufacture industry near sampling point 4. Sampling point 4 is located in one of the tributaries of Winongo River to the eastern part in the direction to the center of Yogyakarta City. It means that the intensity of anthropogenic activities affecting this point is high. Sampling point 8 is located between two areas, Yogyakarta City in the east and Bantul Regency in the west. Apart from housing area, there was also home food industry and gas station in the vicinity of this point. It was also observed some minor scale sand mining activities by people living near this location. Sampling point 9 to 12 are part of Bantul Regency. Land-use along these points were dominated by housing and agriculture area especially in the western part of the watershed apart from few workshops, laundry shops, and home industries. Batik industries were located mostly around sampling point 7 to 10.

6.2.2 Chemical and reagents

Standard stock for each element to be analyzed were the product of Supelco - Merck Chemical. Concentrated HNO_3 used for sample preservation, standard and sample dilution was from Merck (grade for heavy metal analysis, 65%). Filter paper 0.45 µm from Whatman was used for sample filtration.

6.2.3 Sample collection

Sampling campaign was conducted during rainy season at the beginning of January 2021. Temperature, pH, Electric Conductivity (EC), Oxygen Reduction Potential (ORP) of river water were measured on site by using Multiparameter Water Quality Checker Horiba U-50.

From each sampling point, 2 kinds of samples were taken: river water and sediment sample. River water sample was taken at 30 cm depth of the river directly using polypropylene (PP) container that has been previously washed 3 times with sample water. Concentrated nitric acid was added to sample as necessary until pH < 2 to preserve sample. All samples were then kept in 4°C until analysis. Sediment sample was taken from 5 to 10 cm depth of the riverbank using plastic shovel. The sample was then put into plastic bag with an identification label.

6.2.4 Sample pretreatment

Prior to instrument analysis, river water and sediment samples were pretreated following Indonesian Standard Method (SNI) for analysis by using Atomic Absorption Spectrometer (AAS) for each target element. In general pretreatment was conducted using open acid digestion method.

For river water sample, 5 ml concentrated HNO_3 was added to 50 ml sample filtrate using Whatman paper 42. Flask was covered and then heated over hot plate until the remaining 15 – 20 ml. The process of HNO_3 addition and heating over hot plate should be repeated until a clear solution was obtained.

Sediment sample was oven dried at 105°C to constant mass (Memmert UN series) to constant mass. The sample were ground in a mortar and then sieved through 200 mesh shaker to obtain homogeneous sample. Acid digestion was then conducted by addition of 25 ml distilled water and 5 ml concentrated HNO_3 into 3 grams homogenous sediment sample. The mixture then heated over 105 – 120°C hot plate until the remaining 10 ml. Another 5 ml of concentrated HNO_3 and 2 ml $HClO_4$ were then added. Heating using hot plate was continued until white smoke appear and clear solution was obtained. Sample was allowed to cool until room temperature and then filtered using Whatman paper 40. Filtered sample was then transferred into 100 ml volumetric flask. Distilled water was added until 100 ml mark.

Reference method for each type of sample and element is presented in Table 6.2.

Table 6.2 Reference method for river water and sediment analysis

Element	Method for water sample	Method for sediment sample
Cr	SNI 6989.17:2004	SNI 06-6992.6-2004
Fe	SNI 6989.4 :2009	USEPA
Cu	SNI 6989.6: 2009	SNI 06-6992.5-2004
Cd	SNI 6989.16:2009	SNI 06-6992.4-2004
Pb	SNI 6989.8:2009	SNI 06-6992.5-2004

6.2.5 Sample analysis

Prior to instrument analysis, a series of standard solutions was generated by diluting each element's standard stock in HNO_3 solution. The concentration of Al, Cr, Fe, Ni, Cu, Cd, and Pb and was determined by using Atomic Absorption Spectrometry/AAS (series GBC Sigma Avanta A 6840). Wavelength used for each element is 309.3 nm for Al, 357.9 nm for Cr, 248.3 nm for Fe, 232 nm for Ni, 324.7 nm for Cu, 228.8 for Cd, and 283.3 for Pb.

6.2.6 Contamination and risk assessment

a. Geoaccumulation index (I_{geo})

Geoaccumulation index (I_{geo}) developed by (Müller 1979) has been widely used by many researchers to estimate the degree of contamination in sample compared to background or baseline concentration. The following equation is used to calculate I_{geo}:

$I_{geo} = (\log_2 Cn/1.5Bn)$ (6.1)

Where Cn is the concentration of element "n" in the sample and Bn is the background/baseline concentration for element "n". The multipliers 1.5 is employed to accommodate lithogenic variation among different sites. I_{geo} suggests seven classes of the degree of contamination and their evaluation criteria is presented in Table X. As no background concentration available in the study area, global average shale value presented by (Turekian and Wedepohl 1961) was adopted for this study. The evaluation criteria for the derived I_{geo} value are presented in Table 6.3.

b. Enrichment Factor (EF)

Enrichment Factor (EF) was used to determine whether the heavy metal content in one sediment is from anthropogenic origin or not. The element of concern is normalized with conservative element such as Fe, Al, and Li. Conservative element is assumed to be geogenic and not affected by weathering (Duodu, Goonetilleke, and Ayoko 2016). EF value is derived by comparing the normalized element in sample and that in background data as presented in following equation:

$$EF = \frac{\left(\frac{Ci}{Cref}\right)sample}{\left(\frac{Ci}{Cref}\right)background} \quad (6.2)$$

Where Ci is the concentration of element of interest and Cref is the concentration of the normalization element. Normalization element used in this study is Fe. Same as Igeo, background concentration for calculation of this index refer to global average shale value (Turekian and Wedepohl 1961). The evaluation criteria for the derived EF value are presented in Table 6.3.

c. Consensus-based Sediment Quality Guidelines (SQGs) $Q_{m\text{-}PCA}$

Consensus-based SQGs was developed by Macdonald et al. (MacDonald, Ingersoll, and Berger 2000) to determine the toxicity of certain contaminants to sediment-dwelling organisms in freshwater environment. The concentration of contaminant in samples was compared to the consensus-based

probable effect concentration (PECs). It is a value above which adverse effects are expected to occur more often than not (Fu et al. 2014). The mean PEC quotient ($Q_{m\text{-}PEC}$) was proposed to assess the combined effects of multiple contaminants (Zhu et al. 2017) by using the following equation:

$$Q_{m-PEC} = \overline{\sum C_n / PEC_n} \quad (6.3)$$

Where Cn is the concentration of contaminant in the sediment sample and PECn is the corresponding PEC for that contaminant. The PEC value for contaminant discussed in this study are only for Cd, Cr, Cu, and Pb as no PEC available for Fe. Those PEC values are 4.98, 111, 149 and 128 mg/kg for Cd, Cr, Cu, and Pb respectively. The evaluation criteria for the derived $Q_{m\text{-}PEC}$ are presented in Table 6.3.

d. Heavy metal Pollution Index (HPI)

HPI was initially developed by Mohan et.al (1996) to assess drinking water quality with respect to the content of heavy metals (Venkata Mohan, Nithila, and Jayarama Reddy 1996; Wulan, Marganingrum, and Yoneda 2020; Milivojević et al. 2016). Recently, it is also applied for quality assessment of groundwater and surface water. This pollution index uses weighted arithmetic mean method to assess the total influence of various heavy metals content in water body. The equation to calculate HPI value is as following:

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \quad (6.4)$$

$$Qi = \sum_{i=1}^{n} \frac{|Mi-Ii|}{Si-Ii} \; x \; 100 \quad (6.5)$$

Where W*i* is the unit weightage of the *i*th parameter, while n is the number of parameters of concern. W*i* is the reciprocal value of highest permitted value or referred standard symbolled as Si. Qi is sub index of the *i*th parameter and calculated by using equation 6.5. Mi is the concentration of heavy metal *i* in sample, and I*i* is the ideal concentration. For this study, referred standard for S*i* is Indonesian national stream standard, on the other hand, WHO guideline for drinking water was referred for I*i* value. The critical value for HPI is 100, however previous study proposed a modified index classification as presented in Table 6.3.

e. Nemerow Pollution Index (PN)

Nemerow pollution index (PN) is another indexing method to assess degree of pollution caused by several heavy metals at one particular site and has been used to assess groundwater (Zhong et al.

2015; Bodrud-Doza et al. 2016) and surface water (Vu et al. 2017). This index considers the average and highlights the pollutant with high pollution degree (Zhong et al. 2015). The following equation is used to calculate NI:

$$PN = \sqrt{\frac{(avgCf)^2+(maxCf)^2}{2}} \quad (6.6)$$

Where avgCf is the arithmetic mean of contamination factor of all contributed heavy metals at the site and maxCf is the maximum contamination factor among all contributed heavy metals. Contamination factor is the ratio of measured heavy metal concentration and its associated standard. The evaluation criteria of the derived PN value are presented in Table 6.3.

Table 6.3 Evaluation criteria of degree of contamination and risk assessment methods

Geo-accumulation index (Igeo) (Wu, Qi, and Xia 2017)		
I_{geo}	Class of I_{geo}	Pollution level
<0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly to very strongly polluted
>5	6	Very strongly polluted

Enrichment Factor (EF) (Wu, Qi, and Xia 2017)	
≤ 2	Deficiency to minimal enrichment
2-5	Moderate enrichment
5-20	Significant enrichment
20-40	Very high enrichment
>40	Extremely high enrichment

Consensus-based SQGs	
$Q_{m\text{-}PEC}$	Sediment Quality
< 0.5	Not toxic
> 0.5	Toxic

Heavy metal pollution index (Edet and Offiong 2002)	
HPI value	Pollution level
< 15	Low
15 - 30	Medium
> 30	High

Nemerow Pollution Index (Vu et al. 2017)	
PN value	Contamination degree
< 1	Unpolluted
1 ≤ PN ≤ 2.5	Slightly polluted
2.5 ≤ PN < 7	Moderately polluted
≥ 7	Heavily polluted

6.2.7 The effect of batik wastewater discharge on river water quality

Monte Carlo approach is employed to simulate the probability of heavy metal concentration in river exceed the stream standard due to batik effluent discharge according to dilution formula of:

$$Cr\alpha = \frac{Cr.Qr+Cw.Qw}{Qr+Qw} \qquad (6.7)$$

In which,

Crα = α element concentration of river water after effluent discharge
Cr = river water concentration
Qr = river discharge
Cw = concentration of element α in wastewater
Qw = effluent discharge

The input parameter for the simulation is presented in Table 6.4. Simulation is conducted 1000 times under the assumption that the initial concentration of heavy metal element of concern in river water is neglected. Simulation is for single effluent point which means that it does not simulate more than one point of effluent discharge occurred at the same time. It is also assumed that wastewater from batik industry is collected for 1 (one) month before released to river through pipe diameter of 90 mm, PVC pipe with Manning coefficient 0.012, slope 0.5% and ratio of water depth and pipe diameter (d/D) 0.8. This pipe specification is considered to be affordable by most batik factories in study area. Elements Fe, Cd, Cu, Pb, and Zn are selected for this simulation considering their association with batik effluent characteristic and the availability of maximum allowable limit of these elements in stream standard. Cr is associated with batik effluent characteristics, but it is not simulated because no referred concentration limit is available in stream standard. The stream standard referred in this study is Indonesian Government Regulation No. 22/2021 on Stream Standard for Class 1 and presented in Table 6.5. Uniform distribution is used for all input parameter during Monte Carlo simulation. The simulation is conducted using Microsoft Visual Basic for Application (VBA) in Microsoft Excel 365 version 2111.

Table 6.4 Input parameter for Monte Carlo simulation of batik wastewater dilution in Winongo River

Parameter	Symbol	Value	Source of data
River discharge	Qr	0.04 – 4.61 m^3/s	Dinas Lingkungan Hidup dan Kehutanan Daerah Istimewa Yogyakarta 2021
Wastewater discharge	Qw	80 – 90 % of water consumption for batik production	Zaenuri and Dwidayati 2020
Water consumption	Qwater	0.004 – 1.25 m^3/month	Primary data (chapter 3)
Element concentration in wastewater	Cw		

Parameter	Symbol	Value	Source of data
Fe		$5.6\ 10^2 – 1.2\ 10^4$ µg/L	Primary data (chapter 4)
Pb		0.03 – 42.7 µg/L	Primary data (chapter 4)
Cd		$0.05 – 2.2\ 10^2$ µg/L	Primary data (chapter 4)
Cu		$20.9 – 1.9\ 10^3$ µg/L	Primary data (chapter 4)
Zn		$0.11 – 1.8\ 10^2$ mg/L	Primary data (chapter 4)

Table 6.5 Referred stream standards

Parameter	Standard (µg/L)
Fe	300
Pb	30
Cd	10
Cu	20
Zn	50

6.2.8 Statistical analysis and map works

The statistical analysis in this study was performed using the R program version 4.0.3 (R Core Team 2020). Basic R package “base” was used to present summary statistics (R Core Team 2020). Correlation among parameter was measured by using “stats” Package (R Core Team 2020), while “Corrplot” Package was used for correlation matrix visualization (Wei and Simko 2017). For multivariate analysis, “MVN” Package was used to check multivariate normality (Korkmaz, Goksuluk, and Zararsiz 2014). For sediment data, as all variable are normally distributed, Hierarchical Cluster Analysis (HCA) was conducted using “Euclidian” distance measure and “Average” clustering method available in “stats” package (R Core Team 2020). Prior to Principal Component Analysis (PCA) for sediment data, Kaiser-Meyer-Olkin test in “psych” Package (Revelle 2021) and Bartlett test in “stats” Package (R Core Team 2020) were conducted to measure sampling adequacy and variance equality, respectively. To ensure comparability among datasets, standardization was performed before PCA and HCA. Dendrogram visualization of HCA was performed by using “factoextra” Package (Kassambara and Mundt 2020).

Map works was produced by using QGIS open-source software version 3.16 Hannover (QGIS Development Team 2009). Basic maps were provided by Indonesia Geospatial Portal (BIG 2020).

6.3 Results and Discussion

6.3.1 Physicochemical characteristics of samples

The physicochemical characteristics including pH, temperature and COD of water samples is presented in Table 6.6. According to Regulation of Governor of Yogyakarta Special Province No. 22/2007, sampling

location in Winongo River for this study is along the Class 1 section, meaning that the quality should be appropriate as raw water for drinking water purposes.

*Table 6.6 Physicochemical characteristics of water samples *)*

	1	2	3	4	5	6	7	8	9	10	11	12
T (°C)	28.5	29.2	31.5	32.1	30.6	26.5	27.7	28.5	28.9	29.6	30.4	30.5
pH	6.7	7.1	7.5	7.5	6.9	7.9	7.4	7.2	6.7	7.1	7.3	7.0
COD (mg/L)	31.1	30.7	30.5	45.1	47.5	35.9	46.3	32.9	41.6	28.9	38.1	33.8

**)* This data was obtained with the cooperation of Environmental Engineering Program of Universitas Islam Indonesia (UII) and is shared with UII students and researchers

According to Government Regulation No. 22/2021 on Stream Standard, COD for Class 1 River should be below 10 mg/L. Compared to this value, all sample exceed the permissible value and do not meet the criteria for Class 1 river quality standard. COD value at points 4, 5 and 7 are among the highest. The source of COD can be from domestic wastewater. The coverage of wastewater treatment service in Yogyakarta City, Bantul and Sleman Regency actually has reached more than 97% (Badan Pusat Statistik Provinsi Daerah Istimewa Yogyakarta 2021). The service consists of regional, communal, and individual wastewater treatment facilities. However, despite the high coverage, the treatment efficiency of especially communal and individual treatment plant is in question. Study by (Rahmawati, Yulianto, and Wijayaningrat 2019) revealed that more than 56% samples from effluent of communal wastewater treatment plants in Bantul area were exceed effluent quality standard. Other possible source was from non-domestic activities, including home industries. Point 4 is tributary from the direction of Yogyakarta City center with high intensity of anthropogenic activities, while point 5 is the meeting point of that tributary and main river. In the case of point 7, it is where many organic-wastewater-generator-home industries including batik factories were located. COD represent organic concentration in sample. Heavy metal content have positive association with organic material for its high tendency to attach to organic matter (Liu et al. 2016).

For pH, the value at each sampling point is within the neutral pH range and meet the standard criteria of 6 – 9. The pH is important abiotic parameter determining metal bioavailability and partitioning (Ribeiro et al. 2017). Dissolution and precipitation of various metal element affected by pH values. Cr, Ni, Pb, and Zn tend to precipitate in pH 6 – 10, while for Cu minimum release from sediment is within pH 5-9 (Martín-Torre et al. 2015).

6.3.2 Distribution of heavy metal in samples

Concentration of heavy metal in water and sediment samples of Winongo River is presented in Table 6.7. Compared to relevant stream standard, concentration of Cd in water samples in almost all sampling points exceed maximum value of 10 µg/L, except at sampling point 6 and 11. Another parameter that exceed standard is Pb at sampling point 5, 8 and 12. In sediment samples, concentration of these 2 heavy metals also exceed their corresponding concentration in global average shale.

Distribution of heavy metal in water samples along sampling points are plotted in map and presented in Figure 6.2. Concentration of iron at upper sampling points were relatively high and decreasing at point 5 even after getting inflow from point 4 which is one of tributaries of Winongo River. The concentration increased again at point 9 where many batik factories were located along its riparian area. For Pb, concentration relatively low until point 4 and then rise at point 5 onwards. This indicates the probable impact of anthropogenic activities along this area onward.

Compared to heavy metal concentration in other rivers from various studies as presented in Table 6.8, Cd and Pb in this study are in the similar range of those in Korotoa River in Bangladesh but higher than river in other part of Java Island. For other parameters, concentration in this study is relatively lower.

Distribution of heavy metal content in sediment samples are plotted in map and presented in Figure 6.2 and Figure 6.3. High concentration in sediment samples is observed to occur around point 4 and 5. Sampling point 4 is one of tributaries of Winongo River flowing from the eastern part of Winongo Watershed which is a high-density populated area.

Compared to other studies on river sediment in Indonesia, concentration of cadmium was relatively high, only less than Tajum River in which sampling location of this study was affected by artisanal gold mining activities. Cadmium concentration was only a bit higher than that of Bremi River which is also affected by batik industry. For chromium, concentration in Brantas River was almost ten times higher than in Winongo River. Meanwhile, concentration of copper in Winongo River was below those in Brantas River and Tajum River. For iron, concentration in Winongo River was a fiftieth of that in Brantas River but around 10 times higher than iron concentration in Citarum River. For lead, concentration in Winongo River was relatively high and only below that of gold mining contaminated Tajum River. Compared to studies in other countries, average cadmium concentration in this study was among the highest. However, for iron and chromium, concentrations were the lowest. Meanwhile for copper and lead, concentration in this study was within the medium level. Comparison with other studies is presented in Table 6.9.

*Table 6.7 Concentration of heavy metals in water and sediment samples *)*

Sampling point	Water (µg/L)					Sediment (mg/kg)				
	Cd	Cr	Cu	Fe	Pb	Cd	Cr	Cu	Fe	Pb
1	11.1	<LoD	5.1	121.4	9.2	2.3	2.8	27.8	2663.3	16.3
2	12.0	<LoD	4.7	114.6	7.6	2.2	3.2	15.4	2226.8	18.2
3	12.5	<LoD	4.7	97.1	8.7	1.9	12.6	29.6	1512.7	32.9
4	12.0	<LoD	6.8	55.0	8.7	3.2	7.2	46.3	2787.4	41.8
5	12.2	<LoD	4.0	43.9	30.2	3.3	4.4	27.8	3237.6	49.0
6	8.9	<LoD	5.6	91.8	15.3	2.7	8.9	24.2	2578.2	45.2
7	12.5	<LoD	3.6	46.9	18.9	1.9	0.5	28.5	1645.3	31.4
8	12.2	<LoD	5.6	53.0	54.9	2.5	4.4	25.1	2273.1	32.3
9	13.1	<LoD	4.8	115.3	21.5	2.1	3.4	18.5	2117.6	26.7
10	14.4	<LoD	3.0	44.6	24.1	3.1	5.7	34.9	2116.4	29.0
11	9.9	<LoD	3.6	43.1	9.7	2.5	3.8	23.0	2206.2	27.3
12	10.1	<LoD	4.3	42.8	40.5	1.7	3.1	29.4	1473.4	24.2
Min	8.9		3.0	42.8	7.6	1.7	0.5	15.4	1473.4	16.3
Max	14.4		6.8	121.4	54.9	3.3	12.6	46.3	3237.6	49.0
SD	11.7		4.6	72.4	20.8	2.5	5.0	27.5	2236.5	31.2
Standard[1]	10.0	NA	20.0	300.0	30.0					
Average shale[2]						0.3	90.0	45.0	47,200.0	20.0

[1] Indonesia Government Regulation No.22/2021 on Stream Standard for Class I

[2] Global average shale value (Turekian and Wedepohl 1961)

*) This data was obtained with the cooperation of Environmental Engineering Program of Universitas Islam Indonesia (UII) and is shared with UII students and researchers

Based on its mean, distribution of heavy metal in water samples was following the order of Fe>Pb>Cd>Cu>Cr. Meanwhile, distribution of heavy metal in sediment samples was following the order of Fe>Pb>Cu>Cr>Cd. The order in both compartments is the same for Fe and Pb, but different for the other 3 metals. In water sample, Cr is even not detected by the method due to very low concentration, but it has detectable concentration in sediment and even higher than Cd. Some metals including Cr, Pb and Ni tend to accumulate in sediment so that their concentration in water are relatively lower (Ribeiro et al. 2017). Adsorption, complexation, precipitation and other processes in water bodies stimulate the accumulation of heavy metal in the surface sediment, so that the concentration in sediment is far higher than in water (Zhang et al. 2019). The change in environmental condition such as in pH may release the accumulated heavy metal in sediment back to water bodies (Zhang et al. 2019).

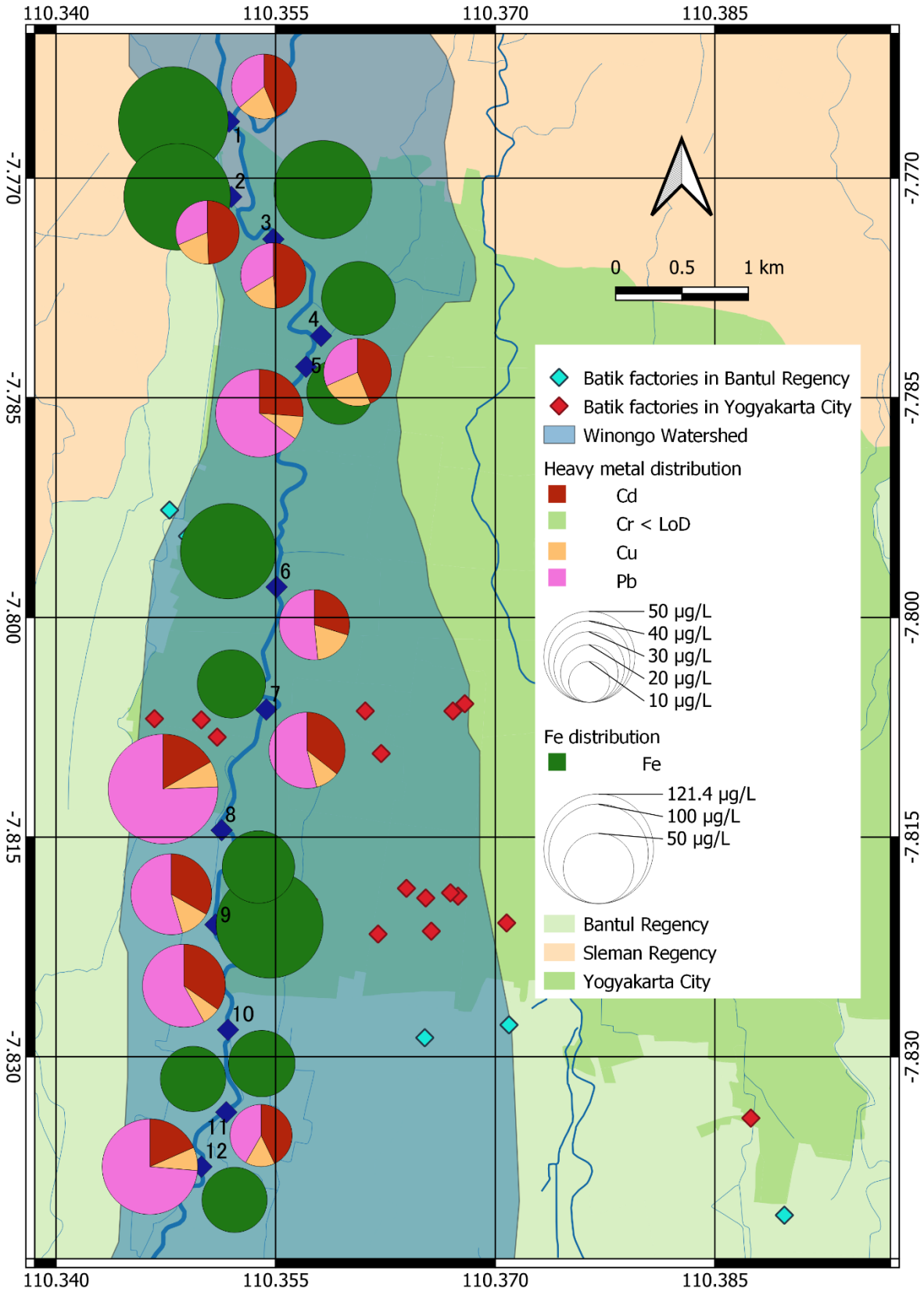

Figure 6.2 Distribution of heavy metal in water samples

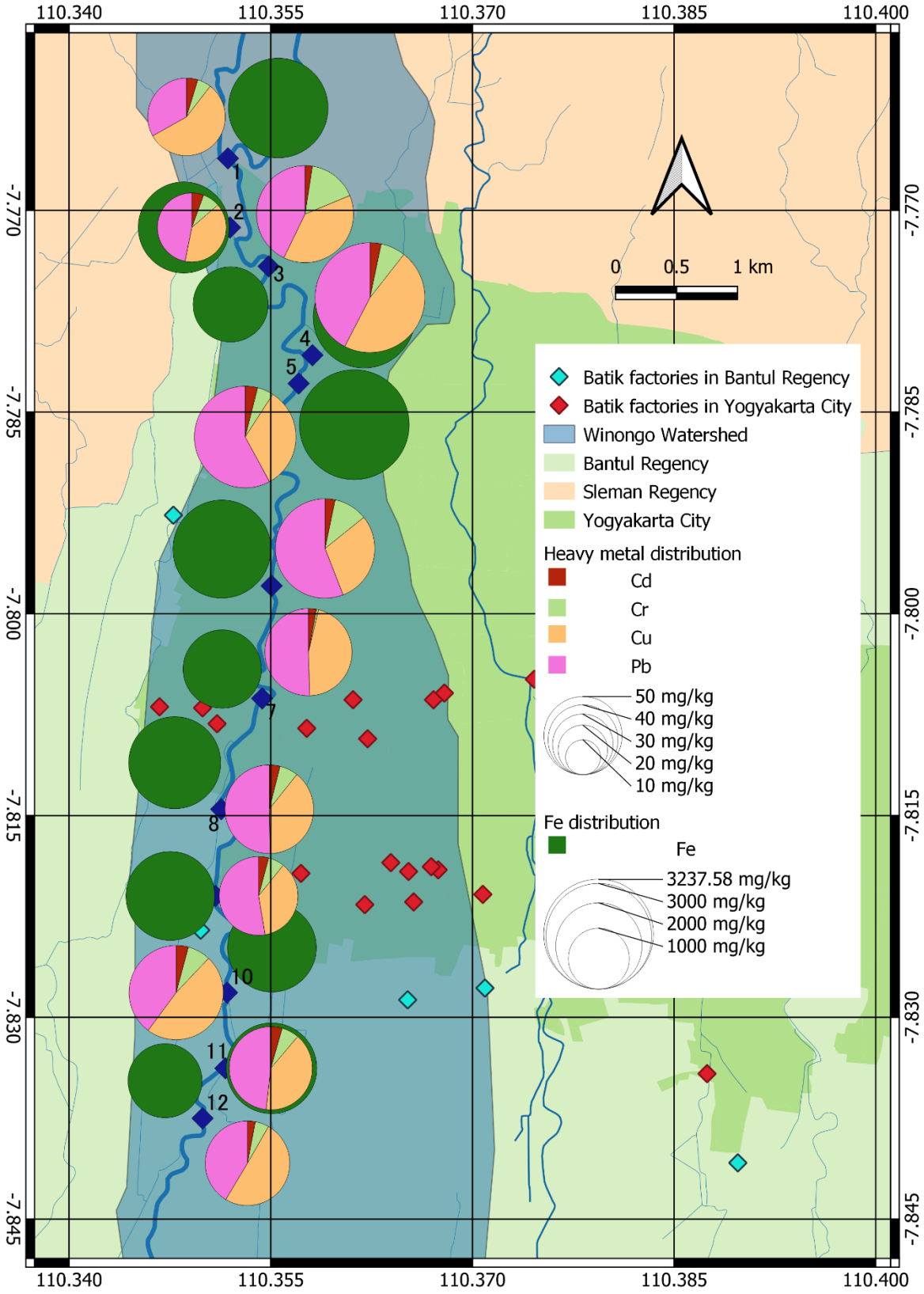

Figure 6.3 Distribution of heavy metal in sediment samples

Table 6.8 Summary statistics of heavy metal concentration in river water sample (µg/L) and comparison with other studies

Metal element	Cd		Cr		Cu		Fe		Pb	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
This study	11.7	8.9-14.4	<LoD	<LoD	4.6	3.0-6.8	72.4	42.8-121.4	20.8	7.6-54.9
Cipeles River, West Java, Indonesia [a)]	-	-	0.9	0.3-1.6	6.3	2.7-21.4	1,358.1	633.0-3,965.0	3.8	0.8-14.0
Uglješnica River, Serbia [b)]										
Spring	15.8	3.0-29.0	-	-	9.0	4.0-14.0	204.8	134.0-250.0	29.3	2.0-102.0
Autumn	276.5	2.00-1,098.0	-	-	224.5	5.0-862.0	277.0	133.0-656.0	1,134.8	7.0-4,510.0
Houjing River, Taiwan [c)]	2.0		35.0		401.0		-		475.0	
Ajay River, India [d)]	30.0	-	-	-	72.0		1,951.0		53.0	
Karnaphuli River [e)]										
Summer	6.5	2.5-11.7	69.6	46.1-96.1					9.9	5.3-18.2
Winter	10.5	3.18-18.3	86.9	55.4-112.4					16.8	10.7-27.5
Hengshi River [f)]										
Wet season	62.7	1.3-174.2			1,930.0	120.0-4,960.0			188.8	0. 8-545.2
Dry season	90.0	1.8-242.1			2,470.0	120.0-5,820.0			222.0	1.6-596.3
Korotoa River, Bangladesh [g)]										
Summer	8.0	0.9-18.0	73.0	41.0-103.0	61.0	23.0-96.0			27.0	8.0-52.0
Winter	11.0	1.0-22.0	83.0	43.0-126.0	73.0	31.0-119.0			35.0	11.0-64.0

a) (Wulan, Marganingrum, and Yoneda 2020)

b) (Milivojević et al. 2016)

c) (Vu et al. 2017)

d) (Singh and Kumar 2017)

e) (Ali et al. 2016)

f) (Liao et al. 2017)

g) (Islam et al. 2015)

Table 6.9 Comparison of concentration of heavy metals in sediment sample (mg/kg dry weight) with other studies

Metal element	Cd		Cr		Cu		Fe		Pb	
	Mean	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**
This study	2.5	1.7-3.33	5.0	0.5-12.6	27.5	15.4-46.3	2,236.5	1,473.4-3,237.6	31.2	16.3-49.0
Other studies in Indonesia										
Bremi River, Central Java [a)]	1.8	1.3-2.2								
Tajum River, Central Java [b)]	4.5	1.5-6.5			128.8	87.0-210.0			71.8	34.0-110.0
Citarum River, West Java [c)]	0.02	0.01-0.05			0.4	0.2-0.6	159.8	125.0-204.0	0.4	0.2-0.6
Brantas River, East Java [d)]			50.0	13.0-108.0	49.0	27.0-82.0	$10.2\ 10^3$	$(6.6\text{-}20.2)\ 10^4$		
Krueng Sabee River, Aceh Jaya [e)]	*)	0-0.27			9.60	4.41-14.82			*)	0-15.40
Other studies global										
Daliao River System, China [f)]	0.3	0.1-0.9	61.4	12.9-151.6	24.6	4.6-86.0			25.2	11.6-67.1
Karnaphuli River, Bangladesh [g)]										
Summer	1.5	0.6-2.5	70.1	37.2-131.1					38.3	22.0-61.9
Winter	2.5	0.9-3.6	92.1	55.4-112.4					49.0	27.7-73.4
Red River, Vietnam [h)]	0.4	0.1-1.4	85.7	23.9-113.1	83.0	20.0-332.0	$37.6\ 10^3$	$(15.1\text{ -}56.6)\ 10^3$	66.0	27.0-188.0
Zahuapan River, Mexico [i)]			121.6		12.6		$21.6\ 10^3$		9.0	
Atoyac River, Mexico [i)]			181.8		14.2		$16.6\ 10^3$		12.2	
Brisbane River, Australia [j)]		0.6-0.9		82.0-332.0		20.0-110.0		$(51.2\text{-}77.3)\ 10^3$		25.0-126.0
Oder River, Poland [k)]	0.9	0.1-4.0	22.8	2.7-65.6	27.6	1.2-105.0	$13{,}6\ 10^3$	$(1.8\text{-}32.2)\ 10^3$	64.2	2.5-579.0
Vistula River, Poland [k)]	1.6	0.1-17.1	37.3	1.5-538.0	15.3	0.4-77.9	$10{,}2\ 10^3$	$(1.1\text{-}25.7)\ 10^3$	40.7	1.0-361.0
Franco River, Brazil [l)]										
Rainy season			40.6		16.5				28.5	
Dry season			13.3		2.2				5.9	

*) cannot calculate due to some non-detect data,

a) Batik industry (Siregar, Prayogo, and Harisam 2019)
b) Artisanal gold mining (Budianta 2021)
c) (Sudarningsih et al. 2019)
d) (Mariyanto et al. 2019)
e) (Nasir et al. 2021)
f) (Lin et al. 2013) contain reference
g) (Ali et al. 2016)
h) (Thu et al. 2016)
i) (Rodríguez-Espinosa et al. 2018)
j) (Duodu, Goonetilleke, and Ayoko 2016)
k) (Jaskuła and Sojka 2022)
l) (Ribeiro et al. 2017)

6.3.2.1 Contamination and risk assessment

Several evaluation index methods were employed to assess the degree of contamination in water and sediment samples in this study. For water samples, degree of contamination was assessed by 2 indexes, Heavy metal Pollution Index (HPI) and Nemerow Pollution Index (PN) as presented in Figure 6.4 and Figure 6.5. According to HPI value, all samples were categorized as highly polluted. For PN value, only 4 sampling points were categorized as polluted which are sampling point 8, 9, 10 and 12. Apart from the difference, both indexes agreed that points 8, 9, and 10 are of the most polluted. Sampling points 8 and 9 are especially associated to home industry including batik industry. The biggest contributor to high value for both indexes are Cd and Pb.

For sediment samples, degree of contamination was assessed by comparison to background concentration using I_{geo} index and the result is presented in Table 6.10. I_{geo} value for Cd is 2.42 indicating a moderate to strongly polluted condition. For the other 4 metals, I_{geo} are below 0 indicating unpolluted condition. Different approach to estimate anthropogenic enrichment through EF value calculation was also used and the result is presented in Table 6.8. EF shows different evaluation compared to I_{geo} with increasing degree of polluted condition for all assessed metal elements. Extreme enrichment occurred for Cd with EF value of 174.74. For other assessed metal elements, sediment environment gets minimum enrichment for Cr and Fe, significant enrichment for Cu, and very high enrichment for Pb. As EF determination is based on ratio to normalization element, the relatively low concentration of Fe as normalization element for this study resulted in high EF value. Both I_{geo} and EF index assess single element effect in the environment while it is more likely that heavy metals give synergistic effect in the environment (Vu et al. 2017). Consensus-based Sediment Quality Guidelines (SQGs) $Q_{m\text{-}PCA}$ is an alternative to assess effect of various metal elements simultaneously. As it is considering the toxicity to sediment dwelling organisms, this index serves as a simple ecological risk assessment index. The result of assessment is presented in Figure 6.5. Based on this assessment, all sampling point are considered toxic to sediment dwelling organisms as the value in all sampling points exceed the 0.5 limit. It may pose threat to human if it goes into aquatic food chain through the bio accumulative and bio magnification nature of various heavy metal (Fu et al. 2014). The highest contributor to this high value of $Q_{m\text{-}PCA}$ is Cd as it has very low PEC value compared to other metals. Cadmium is also stated as human carcinogen by WHO - International Agency for Research on Cancer (IARC) (National Institute of Technology and Evaluation 2016) and regulation in many countries (Velusamy et al. 2021).

Comparing contamination index of HPI and PN in water and ecological risk index $Q_{m\text{-}PCA}$ in sediment, there is a difference on which sampling points is of the highest concern. Sampling point 8 is of the most contaminated according to HPI and PN but the highest ecological risk is at point 4. In general, for all assessment index employed in this study, Cd consistently become the biggest contributor to high contamination degree or high ecological risk. As in the case of sediment, it shared the equal toxic level for all sampling points. This difference also indicates the distinct in the balance of heavy metal in aquatic and sedimentary systems (Varol and Şen 2012). Considering the potential long-term threat to human health, monitoring of Cd and its possible source should be prioritized.

Table 6.10 Average Igeo value for heavy metals in this study

	Cd	Cr	Cu	Fe	Pb
Igeo	2.42	-5.09	-1.35	-5.02	-0.02
	Moderately to strongly polluted	Unpolluted	Unpolluted	Unpolluted	Unpolluted
EF	174.76	1.25	13.59	1	33.85
	Extremely high enrichment	Deficiency to minimal enrichment	Significant enrichment	Deficiency to minimal enrichment	Very high enrichment

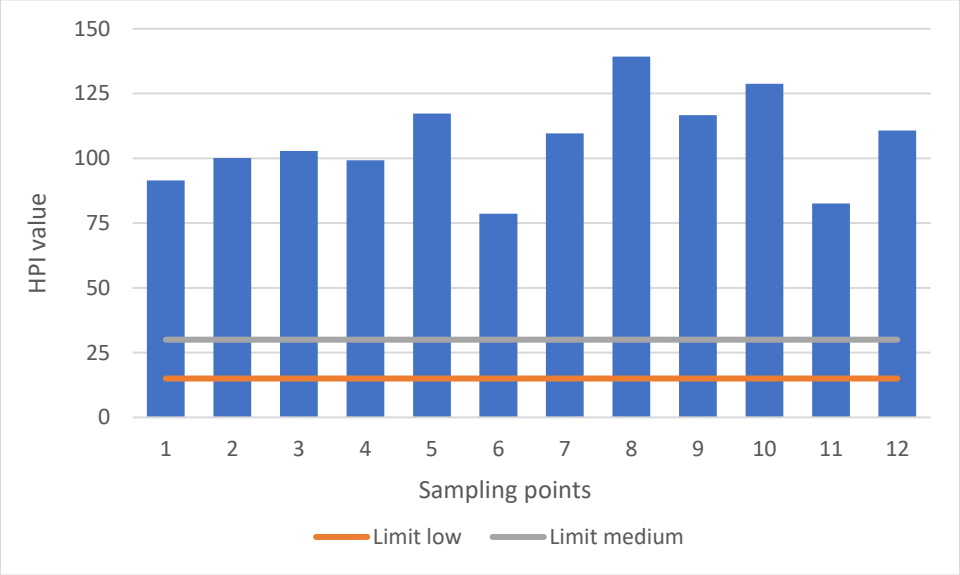

Figure 6.4 HPI value for each sampling point

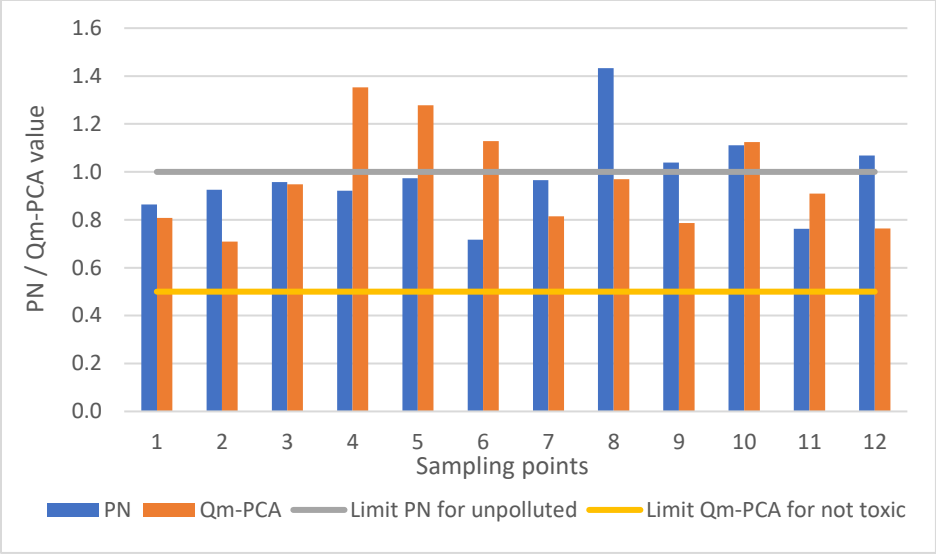

Figure 6.5 PN and Qm-PCA value for each sampling point

6.3.2.2 Source identification of heavy metal in sample

Correlation analysis (CA), hierarchical cluster analysis (HCA), and principal component analysis (PCA) were used to identify source of heavy metals in this study. PCA was conducted to sediment samples after Kaiser-Meyer-Olkin test resulted in overall MSA of 0.57 (>0.5) and Bartlett test's p-value <0.05. Factor loadings with a varimax rotation and the eigenvalues is presented in Table 6.11. PC1, PC2 and PC3 explain 90.6 % of the total variance. To interpret the loading, three categories are used. Value of > 0.75 indicates strong loading, 0.50-0.75 indicate moderate loading, and 0.30-0.50 indicates weak loading (Rezaei et al. 2019).

Table 6.11 Rotated loading matrix

	PC1	PC2	PC3
Cd	**0.56**	-0.27	0.08
Cr	0.27	**0.69**	-0.46
Cu	0.37	0.36	**0.81**
Fe	0.46	**-0.54**	-0.17
Pb	**0.51**	0.16	-0.29
Eigenvalues	2.62	1.20	0.84
% Variance	52.47	24.03	14.09
% Cumulative variance	52.47	76.50	90.60

PC1 explained 52.47 % of the total variance showing moderate positive loading on Cd (0.56), Pb (0.51) and low positive loading for Fe (0.46). This association may be attributed to anthropogenic sources as I_{geo} value for Cd and EF value for Cd and Pb (Table 6.10) indicate possible enrichment from non-natural sources. The sources may be from local industries as high concentration of Cd and Pb occur at point 4, 5 and 10. Point

4 is affected by high intensity of anthropogenic activities from the direction of Yogyakarta City center. On the other hand, there was one manufacture industry located near point 4 in the time of sampling campaign. Point 5 is the meeting point of point 4 and main river body. High concentration of Cd occurred also at point 10 which is probably from home industries located at the upstream of this sampling point. The source of Pb and Fe is most probably from anthropogenic activity such as agriculture from the use of fertilizer. In Indonesia, organic and inorganic fertilizers are enriched with zinc, copper, cobalt, lead, iron, and manganese as micronutrients (Wulan, Marganingrum, and Yoneda 2020). Various studies reported the Pb concentration of 30 – 969 mg/kg in manure fertilizer (Setyorini et.al 2003 in Erfandi and Juarsah 2014), 216 mg/kg in compost fertilizer from Piyungan landfill facility in Yogyakarta Area (Sudaryono 2011), 1.3 – 2240 mg/kg in another compost fertilizer sample (Karamina, Widowati, and Mudjoko 2019), and 5 mg/kg in NPK fertilizer (Prasetyawati, Siaka, and Rita 2021). Agriculture activity can also be the source Cd, as it sometimes presents or added to phosphate fertilizer or pesticide (Briffa, Sinagra, and Blundell 2020). These metals enter river body through drainage outlet to the river or non-point-source-run-off from agriculture area in the Sleman Regency in the north and Bantul Regency in the south part of the watershed.

The second principal component (PC2) accounted for 24.03% of total variance. This PC contain Cr with moderate positive loading (0.69) and Fe with moderate negative loading (-0.54) indicating metal originated both from natural and anthropogenic sources. Fe can be from natural source as it is one of main components of rock and soil. Heavy metal in surface water and river sediment was affected by many factors including surrounding soil type (Zhang et al. 2019). One study conducted in the same area as this study presents data on the major chemical composition of soil in the study area are Si, Al, Ca and high quantity of Fe (Xaixongdeth et al. 2015). For Cr, it is most probably from dye-based home industries such as batik factories.

The third PC explained 14.09% of the total variance contain Cu with strong positive loading (0.81). The possible source of Cu is probably from automotive workshops located along the river. Other possible source is livestock farming. Together with Zn, Cu is commonly used as mineral additives for animal feed to enhance immune system of the livestock. This contribute to the presence of considerable concentration of these 2 metals in the manure (Hejna et al. 2020). In 2020, around 46% of supply of around 15 million livestock population in Yogyakarta Special Province come from livestock farms in Bantul Regency, Sleman Regency and small portion in Yogyakarta City area (Badan Pusat Statistik Provinsi Daerah Istimewa Yogyakarta 2021).

Pearson correlation analysis confirmed the significant correlation between Fe-Cd and Pb-Cd as presented in Table 6.12. As explained above, this can be associated with agricultural activity from the use of fertilizer or pesticide washed out during rainfall event and goes into river body via drainage outlet or non-point source run-off.

Table 6.12 Correlation matrix of heavy metal parameter in sediment samples of Winongo River

	Cd	Cr	Cu	Fe	Pb
Cd	1				
Cr	0.18	1			
Cu	0.46	0.31	1		
Fe	0.83*	-0.01	0.14	1	
Pb	0.61*	0.44	0.39	0.46	1

* Statistically significant at $p<0.05$

HCA was conducted upon water samples data to examine possible cluster among heavy metal parameters except for Cr, and organic parameter. Parameters in one cluster may indicate the possible common of source. HCA generated 3 (three) clusters in which the first cluster consists of Fe, Cd, and Cu. This cluster can be associated with agriculture activities from the use of fertilizer and pesticide. Pb and COD belong to different clusters, but they are connected with higher linkage distance. It is probably associated with Pb-containing-organic waste from local industries along Winongo river.

Spearman rank correlation analysis (CA) was employed to observe relationship among heavy metals except for Cr and physicochemical parameters as presented in Table 6.13. Correlation is significant at 90% and 95% confidence interval for some pairs as indicated in the table. Significant strong negative relationship is shown by pH and temperature, so that pH tends to decrease at the increasing temperature. Fe showed significant positive correlation with pH and negative correlation with temperature. Positive correlation occurs between Pb and temperature. Significant correlation between metal parameters occurs on Fe and Cu in positive manner and Fe and Pb in negative manner. Correlations between different heavy metals in water may suggest similar contamination levels or same source of pollution, mutual dependency, and similar transfer behavior through the river system (Ali et al. 2016).

Table 6.13 Correlation matrix of parameters in river water

	pH	T	Cd	Cu	Fe	Pb	COD
pH	1						
T	-0.80*	1					
Cd	0.04	0.22	1				
Cu	0.22	-0.23	-0.31	1			
Fe	0.55**	-0.53**	0.13	0.58*	1		
Pb	-0.36	0.55**	0.20	-0.22	-0.55**	1	
COD	0.19	-0.27	-0.12	0.04	-0.27	0.19	1

*Statistically significant at p<0.05

**Statistically significant at p<0.1

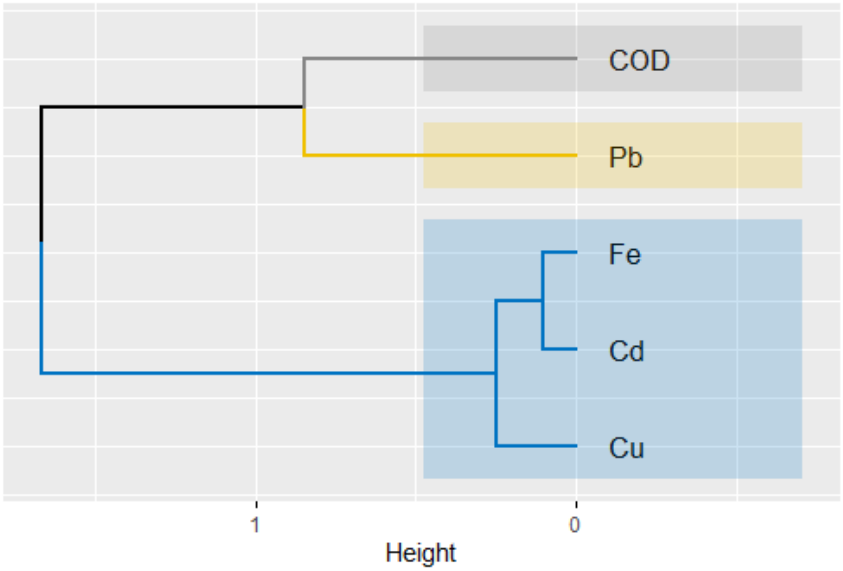

Figure 6.6 Cluster dendrogram of heavy metal and organic parameter in river water

6.3.3 The effect of batik wastewater discharge on the river quality

Monte Carlo approach is employed to simulate the probability of heavy metal concentration in river water exceed the corresponding stream standard due to batik wastewater effluent discharge. The result of the simulation is presented in Figure 6.7 and Table 6.14. From 1000 times simulation, probability of batik wastewater effluent to cause Pb concentration in river water exceed the standard of 30 µg/L is 0 (zero). Pb concentration in wastewater is low compared to other heavy metal of concern. For Cd, Cu, and Fe probability are 0.7, 1.3, and 4.6 respectively. The value is high For Zn, with probability of 77.7 % to cause Zn concentration in river water exceed the standard of 0.05 mg/L. In general, the probability of batik effluent discharge to cause river quality exceed stream standard is low for heavy metal Pb, Cd, Cu and Fe. This is due to low concentration and discharge of wastewater. However, the very high concentration of

Zn in batik wastewater is possible to cause Zn concentration of river water exceed stream standard. This simulation was conducted under the assumption of single effluent discharge. It means that the probability can be higher when several factories released their wastewater at the same time, especially for Zn. This result can be confirmed with monitoring data. However, heavy metal has not been put as priority parameter for routine monitoring by local Environmental Agency. Analysis of Zn on various environmental media in river water, sediment or soil surrounding of batik factory location may confirm this finding. A consistent result may suggest Zn as indicator pollutant for batik industry.

Table 6.14 Simulation result

	Probability* (%)	Simulated concentration		
		Unit	Maximum	Average
Fe	1.3	µg/L	$9.3\ 10^2$	31.7
Pb	0	µg/L	5.8	0.11
Cd	0.7	µg/L	17.8	0.57
Cu	4.6	µg/L	$1.9\ 10^2$	5.18
Zn	77.7	mg/L	16.5	0.44

*Probability of concentration of metal element in river water exceed stream standard

6.4 Conclusion

Analysis on 12 water and sediment samples from Winongo River showed the distribution of various heavy metal in river water was following the order of Fe>Pb>Cd>Cu>Cr. Range of concentration were 42.8-121.4 µg/L for Fe, 7.6-54.9 µg/L for Pb, 8.9-14.4 µg/L for Cd, 3.0-6.8 µg/L for Cu, and <5.5 µg/L for Cr. For concentration in sediment samples following order occurred, Fe>Pb>Cu>Cr>Cd. Range concentration in sediment were 1473.4-3237.6 mg/kg for Fe, 16.3-49.0 mg/kg for Pb, 15.4-46.3 mg/kg for Cu, 0.5-12.6 mg/kg for Cr, and 1.7-3.3 mg/kg for Cd. Assessment of the degree of contamination by using Geo-accumulation index (I_{geo}) and Enrichment Factor (EF) suggested a serious contamination by Cd and Pb in river sediment. In addition, ecological risk index by using consensus-based sediment quality standard ($Q_{m\text{-}PCA}$) categorized sediment sample from all sampling points were toxic to sediment dwelling organisms. For water samples, Heavy metal Pollution Index (HPI) suggested a highly polluted state for all sampling points but according to Nemerow Pollution Index (PN) only 4 sampling points were categorized as polluted. Both indexes agreed upon which sampling points were the mostly polluted which includes sampling points in the area where many home industries including batik factories were located. In general, for all assessment index employed in this study, Cd consistently become the biggest contributor to high contamination degree or high ecological risk suggestion the prioritization of Cd monitoring. Source identification by using Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA) and Correlation Analysis (CA)

revealed the heavy metal possible sources were agricultural activities from the using of fertilizer, pesticides, and metal-enriched cattle fodder and also from home industries along the river including batik industries. Monte Carlo simulation showed the low probability of contribution of batik wastewater to cause the concentration of river water exceed stream standard for parameter Pb, Cd, Fe and Cu, but high probability for Zn.

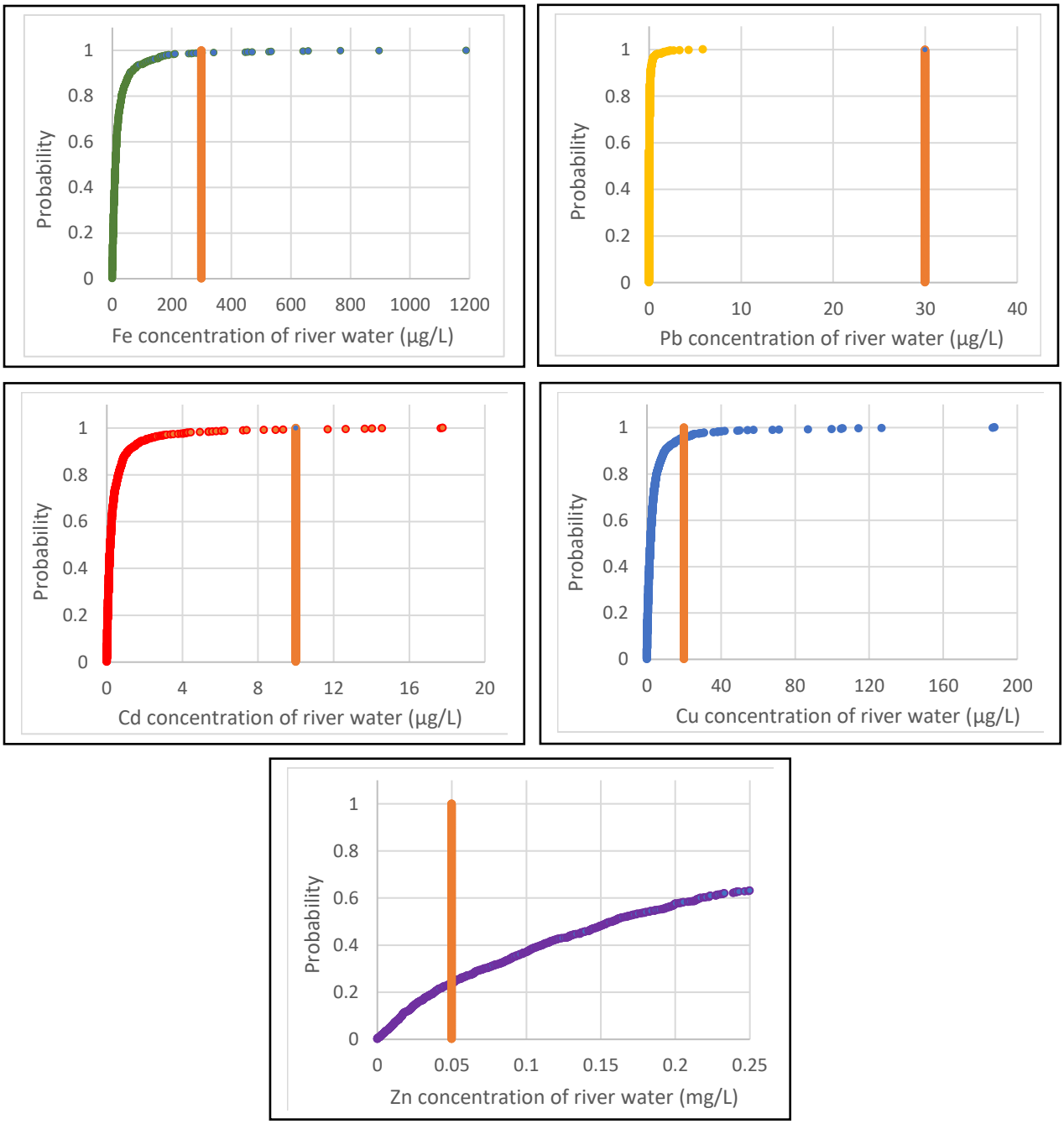

Figure 6.7 Probability of concentration of heavy metal Fe, Pb, Cd, Cu and Zn to exceed stream standard due to batik effluent discharge

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CHAPTER 7 : RISK ANALYSIS OF HEAVY METAL IN EDIBLE FISH FROM RIVER RECEIVING EFFLUENT FROM BATIK INDUSTRY

Abstract

Winongo River is one of important rivers flowing across Yogyakarta City which serves various roles including as the source of edible fish for the people daily diet. On the other hand, this river received various contamination load from its watershed including from batik factories. Most batik factories just released their wastewater without proper treatment into environment including Winongo River. Heavy metal content in wastewater may eventually goes into human body through the consumption of contaminated fish. This chapter is aimed to investigate heavy metal concentration in samples of edible fish samples taken from Winongo River followed by risk analysis of its consumption by human. Ten fish samples were taken from Winongo River and analyzed for the concentration of Cr, Cr, Cu, Fe, and Cd in the flesh part of the fish. The distribution of heavy metal concentration is following the order of Fe>Cu>Cr>Cd>Pb with the range of 0.02-0.34 mg/kg for Pb, 0.03-0.51 mg/kg for Cr, 0.04-0.33 mg/kg for Cu, 0.05-0.17 mg/kg for Cd, and 0.62-6.68 mg/kg for Fe. Concentration of Cd and Pb exceed the relevant standard at some sampling points. The highest concentration occurred at the meeting point of main river and tributary from the direction of Yogyakarta City Center. Risk analysis on the consumption of this contaminated fish revealed the safe level for non-carcinogenic effect with Risk Quotients below 1 but not safe level for carcinogenic effect, since the ECR value for Cd and Cr are above 10^{-4}. This result is the indication of the urgency to conduct risk management program upon Winongo River and the various parties involved.

7.1 Introduction

Wastewater from batik industries has been a long-time concern. The application of wax, dye and other supporting chemicals results in wastewater characteristic of high color, pH, organic and solid. The use of azo dyes by most batik factories raises concern on the carcinogenic organic and toxic heavy metal release to environment (Syuhadah, Muslim, and Rohasliney 2015; Moradi et al. 2016). Some azo dyes are complexed with metal to improve fastness to fabric and the commonly employed metal for this purpose are chromium, cobalt and copper (Maria et al. 2014). The use of this metal complex dye could lead to the discharge of especially chromium which is potentially carcinogenic into the environment (Islam and Mostafa 2018).

In Indonesia, Batik is mostly produced by medium to small-scale companies classified as home or cottage industries. One distinguishing feature of home industry is their poor capacity in a variety of areas,

including its wastewater handling. Most batik factories discharge their wastewater into the environment without sufficient treatment. In Indonesia, it is common for batik industry to discharge their wastewater into nearby river. Heavy metals in wastewater can be accumulated in sediments and biota along the aquatic food chain (Fu et al. 2014) through higher mobility and bioavailability of anthropogenic metals compared to those from geogenic origin (Sojka, Jaskula, and Siepak 2018). Meanwhile river in many cities in Indonesia is the source of water, income, and fish for food. Heavy metals from contaminated river may go into fish commonly consumed by human. Once the fish is consumed, the metal would be transferred to human body. A long-term effect may result in serious health problem.

Winongo river is one of the three main rivers flowing in Yogyakarta City area and the main river of Winongo Watershed. This river plays important role as the source of water for domestic purposes, irrigation, fishery, tourism (Dinas Lingkungan Hidup Kabupaten Bantul 2020). Apart from domestic houses, small-scale industries including batik industries are situated along the river. Hence, this river became one of the receiving water bodies for the discharge of untreated batik wastewater which contain considerable amount of heavy metal. This chapter is aimed to investigate heavy metal concentration in samples of edible fish samples taken from Winongo River followed by risk analysis of its consumption by human.

7.2 Materials and Methods

7.2.1 Site description and sampling points

Fish samples were taken from Winongo River. Winongo River is the main river of Winongo Watershed. It is a 49.12 km long river with maximum and minimum discharge were 4.61 m^3/sec. and 0.04 m^3/sec respectively (Dinas Lingkungan Hidup dan Kehutanan Daerah Istimewa Yogyakarta 2021). The upstream of this river is from two small streams originates from Mount Merapi flows across three administrative areas of Sleman Regency, Yogyakarta City, and Bantul Regency and eventually empties into Opak River. Winongo River is one of the 3 main rivers flowing in Yogyakarta City Area.

Sampling points were located along the middle section of Winongo River. A total of 10 sampling points were selected for this study. Coordinate of sampling points is presented in Table 7.1, while the location in the map is presented in Figure 7.1.

Table 7.1 Coordinate of fish sampling points

Sampling point	Location	Coordinate	
1	Jambon Bridge	-7.76629343	110.35175275
2	Panggungan	-7.77008516	110.35118546
3	Jatimulyo Bridge	-7.77417222	110.35483611
4	Bumijo, Jetis Subdistrict	-7.78077778	110.35809443
5	Merah Bridge	-7.79670664	110.35517927
6	Ngampilan	-7.80629722	110.35435278
7	Tamansari Bridge	-7.80855821	110.35365377
8	Arumina	-7.81666135	110.35110533
9	Jogonalan Kidul	-7.83379722	110.35162222
10	Winongo Bridge	-7.83740196	110.3499094

7.2.2 Chemical and reagents

Standard stock for each element to be analyzed were the product of Supelco - Merck Chemical. Concentrated HNO_3 used for sample preservation, standard and sample dilution and sample pretreatment was from Merck (grade for heavy metal analysis, 65%). Perchloric acid $HClO_4$ for sample pretreatment also purchased from Merck (for analysis, 70-72%). Filter paper 0.45 µm from Whatman was used for sample filtration.

7.2.3 Sample collection

Fish sampling was conducted during rainy season within the period between December – Februari. Fish samples were taken using fishing rod directly from the river or from fish farming pond along Winongo River in which the source of water for these ponds were from Winongo River. Local fishers and pond owners were asked to assist during sampling. Samples were put inside cool box during transportation from sampling point to the laboratory. All samples were kept in -18°C until pretreatment.

7.2.4 Sample preparation and pretreatment

Heavy metal analysis was only conducted upon the flesh part which is the most consumed part of the fish. Sample preparation was started with the determination of the type of the fish and its species, then measuring the length and the wet weight of the fish sample. Fish sample was oven dried at 105°C (Memmert UN series) for 24 hours. The sample was then put in desiccator and remeasured to obtain dry weight and water content. The sample were ground in a mortar to enhance meat dissolution during acid digestion.

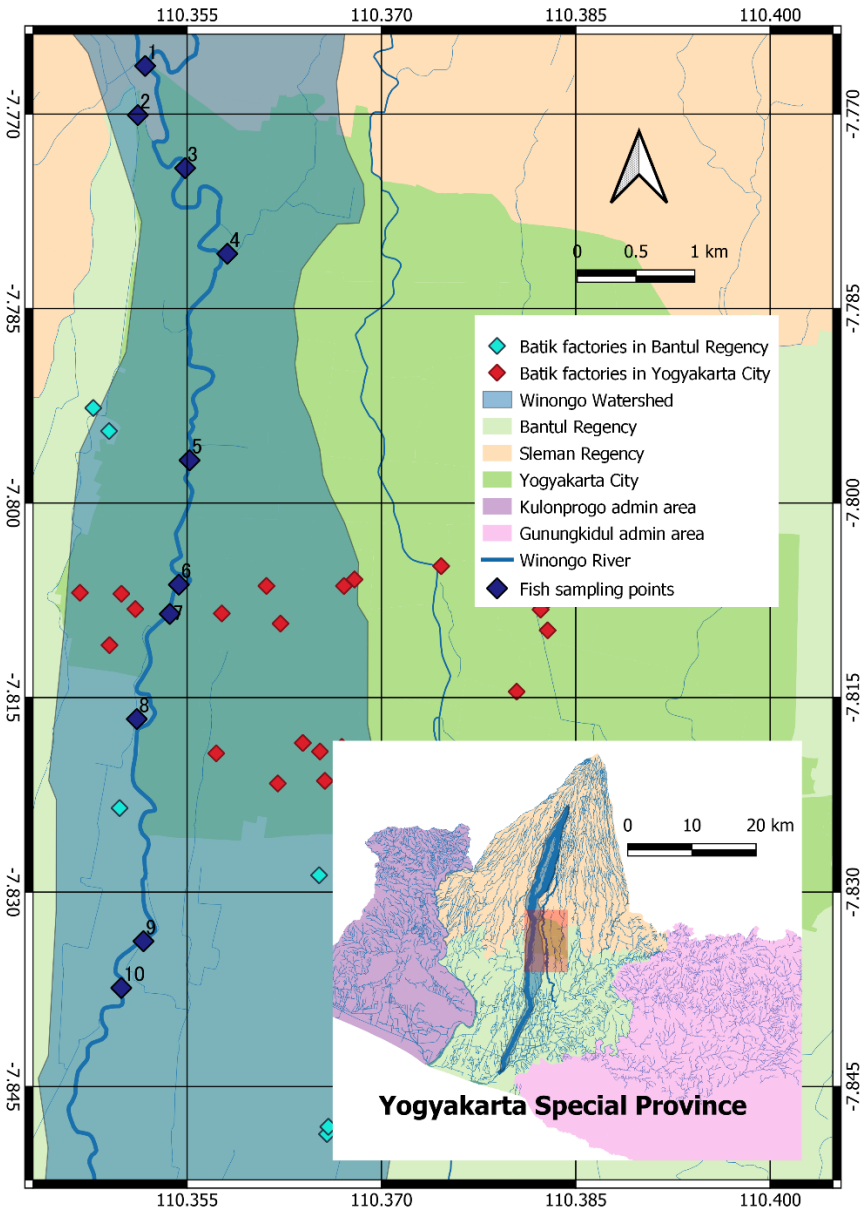

Figure 7.1 Fish sampling points

Prior to instrument analysis, fish samples were pretreated following Indonesian Standard Method (SNI) for analysis by using Atomic Absorption Spectrometer (AAS) for each target element. In general pretreatment was conducted using open acid digestion method.

Acid digestion was conducted by addition of 25 ml distilled water and 5 ml concentrated HNO_3 into 3 grams homogenous fish sample. The mixture then heated over 105 – 120°C hot plate until the remaining 10 ml. Another 5 ml of concentrated HNO_3 and 2 ml $HClO_4$ were then added. Heating using hot plate was

continued until white smoke appear and clear solution was obtained. Sample was allowed to cool until room temperature and then filtered using Whatman paper 40. Filtered sample was then transferred into 100 ml volumetric flask. Distilled water was added until 100 ml mark.

7.2.5 Sample analysis

Prior to instrument analysis, a series of standard solutions was generated by diluting each element's standard stock in HNO_3 solution. The concentration of Cr, Fe, Cu, Cd, and Pb and was determined by using Atomic Absorption Spectrometry/AAS (series GBC Sigma Avanta A 6840). Wavelength used for each element is 357.9 nm for Cr, 248.3 nm for Fe, 324.7 nm for Cu, 228.8 for Cd, and 283.3 for Pb.

7.2.6 Risk analysis

Health risk analysis in this study was conducted by following environmental health risk analysis guidance issued by Indonesia Ministry of Health (Indonesian Ministry of Health 2012). In general, it covers 4 (four) basic steps: hazard identification, dose-response assessment, exposure assessment and risk characterization. In this study, hazard identification was conducted by analysis of heavy metal concentration in fish sample. The purpose of this study is to estimate the risk posed by the consumption of heavy metal contaminated fish from Winongo River, hence the exposure pathway is through oral/ingestion method. Reference dose (RfD), reference concentration (RfC) or slope factor (SF) from EPA (Environmental Protection Agency (EPA) 2022) were used during dose-response assessment for 5 concerned heavy metals in this study. RfD and RfC are safe reference value for non-carcinogenic effect, while SL is safe reference value for carcinogenic effect. For exposure assessment, intake for every heavy metal agent was calculated for oral/ingestion type of exposure. The last step is risk characterization and conducted by determination of Risk Quotient (RQ) for non-carcinogenic effect and Excess Cancer Risk (ECR) for carcinogenic effect. Risk is considered 'safe' if RQ ≤ 1 or ECR ≤ 10^{-4}.

7.2.6.1 Concentration in fish sample

Data of concentration of heavy metal obtained from AAS analysis was used to calculate concentration of heavy metal in fish sample in mg/kg by using the following equation:

$$C = \frac{Ci \; x \; Fc \; x \; Vt}{W \; x \; Fp} \qquad (7.1)$$

Where,

C = concentration in fish sample (mg/kg)
Ci = concentration from AAS

Fc = dilution factor
W = dry weight (kg)
Fp = concentration factor
Vt = volume after digestion (L)

7.2.6.2 Exposure Intake

Calculation of Intake value for exposure assessment was conducted by using equation (2) (Indonesian Ministry of Health 2012). Input value for all variables is presented in Table 7.2.

$$I = \frac{C \; x \; R \; x \; fe \; x \; Dt}{Wb \; x \; tavg} \qquad (7.2)$$

Where,

I = intake (mg/kg.day)
C = concentration of agent or in this case heavy metal in fish sample (mg/kg)
R = rate of consumption (gr/day)
Fe = frequency of exposure (days/year)
Dt = duration time of exposure (year)
Wb = body weight (kg)
tavg = averaging time (days)

7.2.6.3 Risk characterization

Determination of RQ and ECR for risk characterization was conducted by using following equation (Indonesian Ministry of Health 2012):

$$RQ = \frac{I}{RfD} \qquad (7.3)$$

$$ECR = I \; x \; SF \qquad (7.4)$$

Where,

RQ = Risk Quotient
RfD = reference dose
ECR = Excess Cancer Risk
SF = Slope Factor
I = Intake

Table 7.2 Input variable to calculate intake

Variable	Unit	Input value		Assumptions and reference
C	mg/kg	RQ	ECR	
- Cd		0.171	0.171	Primary data
- Cr		0.513	0.513	Primary data
- Cu		0.331	0.331	Primary data
- Fe		6.675	6.675	Primary data
- Pb		0.338	0.338	Primary data

Variable	Unit	Input value		Assumptions and reference
Wb	kg			
- Adult		50	50	Average ideal weight for Indonesian at age above 6 according to regulation of Minister of Health
- Child		13	13	Average weight of Indonesian child aged 1 – 6 (Pulungan et al. 2018)
R x Fe	kg/year			
- Adult		25.48	25.48	Average annual fish consumption in Yogyakarta Special Province (Bappeda Daerah Istimewa Yogyakarta 2022)
- Child		12.74	12.74	Half of adult annual consumption (assumption)
Dt	years			Fish consumption was started at the age of 1 year old. For carcinogenic risk until the age of 70 years old, based on average life expectancy of Indonesian people
- Adult		30	64	
- Child		5	5	
Tavg	days			For RQ = Dt (year) X 365 (days/year) For ECR = 70 (years) X 365 (days/year)
- Adult		30	70	
- Child		5	70	

Table 7.3 RfD and SF to calculate risk

		Cd	Cr	Cu	Fe	Pb
RfD	mg/kg.day					
- Adult		0.001	0.003	0.141	0.7	0.0035
- Child		0.001	0.003	0.111	0.7	0.0035
SF	mg/kg.day	6.3	0.5	-	-	0.0085

(Iresha et al. 2021)

7.2.7 Statistical analysis and map works

Descriptive statistical analysis was performed by using Microsoft Excel 365 version 2111. Map works was created using the open-source QGIS software version 3.16 Hannover (QGIS Development Team 2009). Basic maps were provided by Indonesia Geospatial Portal (BIG 2020).

7.3 Results and Discussion

7.3.1 Fish samples identification

Sampling campaign during December 2020 – Februari 2021 had obtained fish samples from 10 sampling points. The name of species, description of fish sample and the specific source of the sample is presented in Table 7.4. Figure 7.2 shows condition at sampling point 5 and 8. Sampling point 5 is located under a bridge connecting two settlement areas. Fishing and small-scale aquaculture was commonly practiced by people living in this area. The fish obtained from these two activities were usually for self-consumption purposes. At sampling point 8, a bigger-scale aquaculture existed using the water from Winongo River.

Fishes from these ponds were for commercial purposes. Figure 7.3 shows sample fish obtained from point 6 (*Colossoma bramidae)* and 9 (*Oreochromis niloticus)*.

*Table 7.4 Fish sample identification *)*

Point	Local name	Species	Length (cm)	Wet weight (gr)	Dry weight (gr)	Water content (%)	Source of sample
1	Nila	*Oreochromis niloticus*	22	98.6	21.4	78	River body
2	Nila	*Oreochromis niloticus*	21	46.3	12.7	73	Fishpond
3	Nila	*Oreochromis niloticus*	18	25.2	9.2	63	River body
4	Wader	*Rasbora argyrotaenia*	12	12.8	4.4	66	River body
5	Nilem	*Osteochilus vittatus*	21	39.1	9.9	75	River body
6	Bawal	*Colossoma bramidae*	12	18.9	7.2	62	River body
7	Nilem	*Osteochilus vittatus*	21	54.5	14.3	74	River body
8	Nila	*Oreochromis niloticus*	21	34.7	9.3	73	Fishpond
9	Nila	*Oreochromis niloticus*	15	24.9	9.0	64	River body
10	Wader	*Barbodes binotatus*	12	13.8	5.0	64	River body

*) This data was obtained with the cooperation of Environmental Engineering Program of Universitas Islam Indonesia (UII) and is shared with UII students and researchers

Figure 7.2 Sampling point 5 (left) and 8 (right)

Figure 7.3 Sample fish from point 6 (left) and point 9 (right)

7.3.2 Concentration of heavy metal in fish samples

Concentration of heavy metal in fish samples from 10 sampling points is presented in Table 7.5 and Figure 7.4 and 7.5 along with relevant standards to evaluate the finding. Comparison with other studies in Indonesia or other countries is presented in Table 7.6.

Table 7.5 Concentration of heavy metal in fish samples)*

Sample	Concentration (mg/kg)				
	Cd	Cr	Cu	Fe	Pb
Nila 1	0.08	0.18	0.05	2.51	0.02
Nila 2	**0.10**	0.08	0.33	1.61	0.02
Nila 3	**0.10**	0.04	0.14	3.51	0.02
Wader 4	**0.17**	0.51	0.32	6.68	**0.34**
Nilem 5	0.07	0.03	0.04	0.62	0.02
Bawal 6	0.05	0.04	0.05	2.95	0.02
Nilem 7	**0.11**	0.04	0.14	2.33	0.02
Nila 8	0.09	0.04	0.05	1.10	0.02
Nila 9	**0.12**	0.04	0.31	2.26	0.10
Wader 10	0.08	0.04	0.05	1.14	0.02
Max	0.17	0.51	0.04	0.62	0.02
Min	0.05	0.03	0.33	6.68	0.34
Mean	0.09	0.10	0.15	2.47	0.06
Standard 1	0.1[a)]	12[b)]	30[c)]	100[d)]	0.3[a)e)]

[a)] SNI 7387:2009 on maximum allowable heavy metal contaminant in food
[b)] USFDA (Kawser Ahmed et al. 2016)
[c)] FAO/WHO (Töre et al. 2021)
[d)] WHO (Töre et al. 2021; Javed and Usmani 2013)
[e)] FAO and WHO 1995

*) This data was obtained with the cooperation of Environmental Engineering Program of Universitas Islam Indonesia (UII) and is shared with UII students and researchers

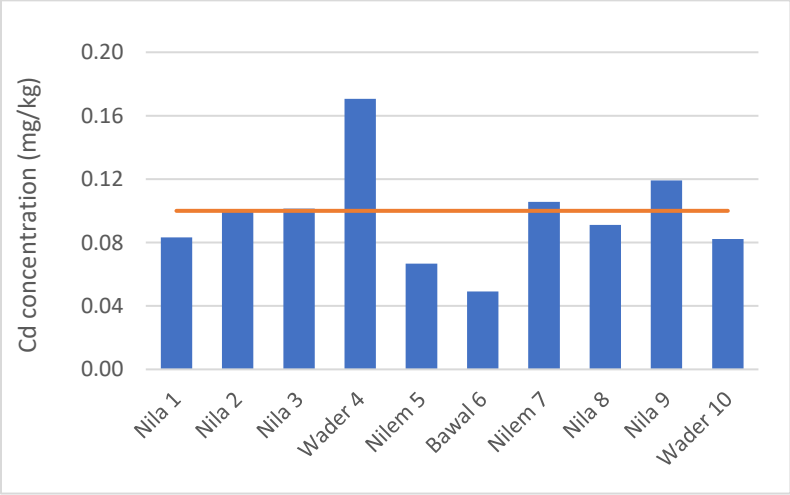

Figure 7.4 Concentration of Cd in fish samples compared to Indonesian standard

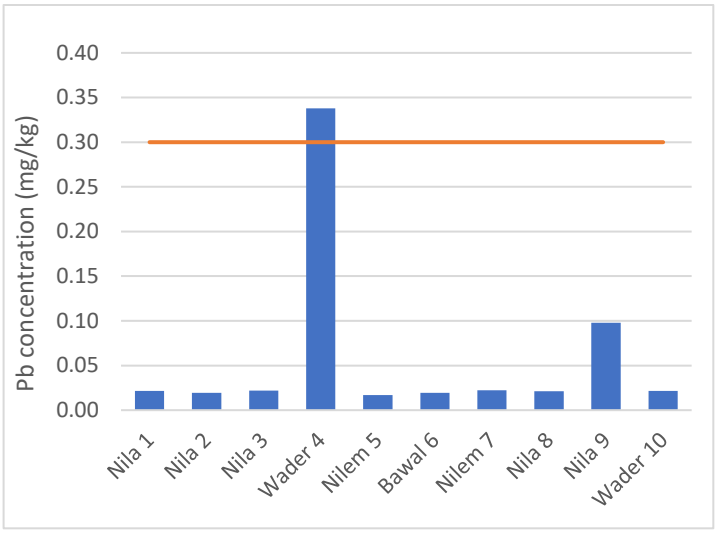

Figure 7.5 Concentration of Pb in fish samples compared to Indonesian standard

Concentration of heavy metal in fish samples for Cr, Cu and Fe do not exceed the maximum value set by relevant standards. However, for Cd and Pb, some samples exceed the standard. At point 2, 3, 7, 9 this occurred only for Cd. At point 4, concentration of Cd and Pb are the highest for both metals and eventually exceed the standard. Point 4 is located at the meeting point of main river body and one of Winongo tributary from the direction of Yogyakarta City center with high intensity of anthropogenic activities. This point then received cumulative load from the main river body and high load from the tributary giving the highest concentration of heavy metal in fish living around this point.

According to their mean, concentration of heavy metal in fish samples in this study is following the order of Fe>Cu>Cr>Cd>Pb. Fe becomes the highest accumulated metal in the fish because of high concentration of Fe in the water or sediment of the river. Fe can be from natural origin as it is one of the main components of rock and soil. Surrounding soil type may affect the heavy metal in surface and river sediment (Zhang et al. 2019). The source can also from anthropogenic origin such as from the use of metal-enriched fertilizer which goes into the river through run-off. However, the metal that goes into the aquatic food chain is mainly from anthropogenic origin as it is usually have higher mobility and bioavailability (Vu et al. 2017). On the other hand, high concentration of Fe in the fish can be due to the characteristic of iron metabolism for there is no route for total excretion of Fe from the body (Javed and Usmani 2013).

Compared to similar study conducted by Handayani, et.al, at Winongo River in 2014, concentration of Cr in this study is much lower. This is probably because sampling for this study was conducted during rainy season while the other was in dry season. Low water level and dilution during dry season may increase

the exposure of contaminants from the water and sediment upon the fish (Ribeiro et al. 2017). Compared to other studies both in Indonesia and other countries as presented in Table 7.6, Cd was relatively high, while it is relatively low for Cr, Cu, Pb, and Fe.

Table 7.6 Comparison of concentration of heavy metal in fish sample (mg/kg) to other studies

	Cd	**Cr**	**Cu**	**Fe**	**Pb**
This study	0.05-0.17	0.03-0.51	0.04-0.33	0.62-6.68	0.02-0.34
Other study in Indonesia					
Oreochromis spp. Winongo River [a)]		9.23-10.23			
Sardinella gibbosa, Makasar [b)]			0.01–0.02		
Sillago sihama, Cilacap [c)]	0.11-0.56		0.360-1.39		<0.005-9.19
Saguling Dam, West Java [d)]	0.002-0.07		0.003-0.25		0.002-0.04
Other study global					
Poonch River, India [e)]		0.07-0.22	0.001	0.08-0.26	ND
Tigris River, Turkey [f)]	0.05	1.68	2.81	175.88	0.33
Buriganga River, Bangladesh [g)]	0.01-0.04	3.57-18.84	5.90-18.77		1.77-6.98

[a)] (Handayani, Dewi, and Priyono 2014)
[b)] (Mu'nisa and Nurham 2010)
[c)] (Cah yani, Lumban Batu, and Sulistiono 2017)
[d)] (Murtini and Rachmawati 2007)
[e)] (Aziz et al. 2021)
[f)] (Töre et al. 2021)
[g)] (Kawser Ahmed et al. 2016)

7.3.3 Risk Quotient (RQ) and Excess Cancer Risk (ECR)

Concentration of Cd and Pb in fish sample taken from several sampling points in this study exceed the maximum allowable concentration in edible fish. It means that these fishes are not safe for human consumption. Risk Quotient (RQ) and Excess Cancer Risk (ECR) for the long-term consumption of these fishes were conducted to examine the associated risk both non-carcinogenic and carcinogenic effect. Maximum concentration of each heavy metal considered in this study were used for the calculation of exposure intake using equation (2). For variable rate of exposure, the average annual consumption of fish in Yogyakarta Special Province of 25.48 kg/year (Bappeda Daerah Istimewa Yogyakarta 2022) was used for Adult group, while the assumption of 50% of this number was used for Child group. Average weight of 50 kg and 10 kg were used for Adult and Child group, respectively. For non-carcinogenic hazard, Reference Dose or RfD was used, while for carcinogenic hazard, oral Slope Factor for suspected cancer-causing heavy metals was used instead. The result is presented in Table 7.7 and 7.8.

Table 7.7 non-carcinogenic hazard/Risk Quotient (RQ)

No.	Heavy metal	Concen-tration C (mg/kg)	Age group	Duration non-carcinogenic Dt (year)	Average weight Wb (kg)	*Refence Dose RfD (mg/kg.day)	Exposure Intake (mg/kg.day)	Risk Quotient
1	Cd	0.171	Adult	30	50	$1\ 10^{-3}$	$2.4\ 10^{-4}$	$2.4\ 10^{-1}$
			Child	5	13	$1\ 10^{-3}$	$7.7\ 10^{-5}$	$0.8\ 10^{-1}$
2	Cr	0.513	Adult	30	50	$3\ 10^{-3}$	$7.2\ 10^{-4}$	$2.4\ 10^{-1}$
			Child	5	13	$3\ 10^{-3}$	$2.8\ 10^{-4}$	$0.9\ 10^{-1}$
3	Cu	0.331	Adult	30	50	$1.4\ 10^{-1}$	$4.6\ 10^{-4}$	$3.3\ 10^{-3}$
			Child	5	13	$1.1\ 10^{-1}$	$1.8\ 10^{-4}$	$1.6\ 10^{-3}$
4	Fe	6.675	Adult	30	50	0.7	$9.3\ 10^{-3}$	$1.3\ 10^{-2}$
			Child	5	13	0.7	$3.6\ 10^{-3}$	$0.5\ 10^{-2}$
5	Pb	0.338	Adult	30	50	$3.5\ 10^{-3}$	$4.7\ 10^{-4}$	$1.3\ 10^{-1}$
			Child	5	13	$3.5\ 10^{-3}$	$1.8\ 10^{-4}$	$0.5\ 10^{-1}$

Table 7.8 Carcinogenic risk

No.	Heavy metal	Concen-tration C (mg/kg)	Age group	Duration carcinogenic Dt (year)	Average weight Wb (kg)	*Slope Factor SF (mg/kg.day)	Exposure Intake (mg/kg.day)	Excess Cancer Risk ECR
1	Cd	0.171	Adult	64	50	6.3	$2.2\ 10^{-4}$	**$1.3\ 10^{-3}$**
			Child	5	13	6.3	$3.3\ 10^{-5}$	**$0.2\ 10^{-3}$**
2	Cr	0.513	Adult	64	50	0.5	$6.5\ 10^{-4}$	**$3.3\ 10^{-4}$**
			Child	5	13	0.5	$9.8\ 10^{-5}$	**$4.9\ 10^{-5}$**
3	Cu	0.331	Adult	64	50	-	$4.2\ 10^{-4}$	-
			Child	5	13	-	$6.3\ 10^{-5}$	-
4	Fe	6.675	Adult	64	50	-	$8.5\ 10^{-3}$	-
			Child	5	13	-	$1.3\ 10^{-3}$	-
5	Pb	0.338	Adult	64	50	$8.5\ 10^{-3}$	$4.3\ 10^{-4}$	$3.7\ 10^{-6}$
			Child	5	13	$8.5\ 10^{-3}$	$6.5\ 10^{-5}$	$5.5\ 10^{-7}$

*(Iresha et al. 2021)

For non-carcinogenic effect, RQ for each heavy metal are still below 1 which means that it is still safe for 50 kg adult and 13 kg child to consume fish containing heavy metal at the above concentration. However, from the calculation of ECR, Cd shows ECR value above 10^{-4} which means unacceptable or not safe. So, the consumption of fish containing Cd at the above concentration is not safe for 50 kg adult and 13 kg child for exposure duration of 70 years. This is also applied for ECR value of consumption of Cr contaminated fish by adult. In the case of Cd contaminated fish, the ECR is $13\ 10^{-4}$ for adult which means there is risk of 13 cancer cases in 10.000 persons. In the case of high ECR, risk management become urgent to conduct. It can cover all variable determining the intake exposure including concentration of heavy metal in the edible fish, consumption rate and exposure duration. To manage the consumption rate and exposure duration, the biggest portion is on the people. Meanwhile, for the variable of concentration of

heavy metal in edible fish, it involves the management of river environment which require strong will and integration of various aspects and parties.

7.4 Conclusion

To conduct health risk analysis for the consumption of contaminated fish, ten fish samples were taken from Winongo River and analyzed for the concentration of Cr, Cr, Cu, Fe, and Cd in the flesh part of the fish. The distribution of heavy metal concentration is following the order of Fe>Cu>Cr>Cd>Pb with the range of 0.02-0.34 mg/kg for Pb, 0.03-0.51 mg/kg for Cr, 0.04-0.33 mg/kg for Cu, 0.05-0.17 mg/kg for Cd, and 0.62-6.68 mg/kg for Fe. Concentration of Cd and Pb exceed the relevant standard at some sampling points. The highest concentration occurred at the meeting point of main river and tributary from the direction of Yogyakarta City Center. Risk analysis on the consumption of this contaminated fish revealed the safe level for non-carcinogenic effect with Risk Quotients below 1 but not safe level for carcinogenic effect, since their ECR value for Cd and Cr are above 10^{-4}. This result is the indication of the urgency to conduct risk management program upon Winongo River and the various parties involved.

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CHAPTER 8 : GENERAL CONCLUSION AND RECOMMENDATION

8.1 General Conclusion

The use of synthetic dyes and other chemical by batik industry in Indonesia raises concern on its potential negative impact to the environment and eventually human health. The magnitude of the impact would be greater because the majority of batik factories were small-scale industry with insufficient capacity for occupational health and environmental management. This study examines the effect of the batik industry on the quality of the aquatic environment in Yogyakarta, one of Indonesia's centers of batik industry.

Studies on 24 batik factories in Yogyakarta City and 53 factories in Bantul Regency showed that 92 % and 89% batik factories in each of these 2 areas used synthetic dyes in their production. Of this synthetic dyes, azo dyes especially naphthol have been used by more than 88% and 70 % of batik factories in Yogyakarta City and Bantul Regency, respectively. Regarding water consumption, average amount of water required for production of one sheet of batik product was 7.5 liter. Compared to other study, this amount is relatively low. Apart from different dyeing technique used, the practice of reusing dye solution multiple times can be another reason. It is usually practiced in producing lower quality batik product. Related to wastewater handling, 50 % factories in Yogyakarta City and 34 % factories in Bantul Regency did not have any kind of wastewater treatment plant. Hence, wastewater was just released into environment without prior treatment. This would lead to serious environmental pollution as well as direct and long-term threat to human health. One of the concerns was the implication of the widely used azo dyes. Laboratory analysis detected 11 toxic aromatic amines in varied concentration from reduced naphthol dye samples and 5 compounds in reduced wastewater samples. It is confirmed that azo dyes widely used by batik factories in study area are those potentially release carcinogenic aromatic amines under reduction favorable environment.

The total concentration of some heavy metals elements in 18 wastewater samples were measured by using inductively coupled plasma mass spectrophotometry (ICP-MS). The result was compared to other studies and relevant local and international effluent standards. Hierarchical Cluster Analysis (HCA) was then performed to observe group of samples or parameters with similar characteristics that represent

similar production method which affects their wastewater characteristics. The results shows that concentration of Al, Si, Fe, Zn, Cr, Co, Ni, Cu, As, Se, Cd, and Pb ranged from 0.11 to 300 mg/L, 25 to 280 mg/L, 0.56 to 12 mg/L, 0.11 to 180 mg/L, 11.7 to 100 µg/L, 0.6 to 17.7 µg/L, 7.2 to 82.8 µg/L, 20.9 to 1.9 10^3 µg/L, 1.5 to 21.2 µg/L, 7.6 to 2.6 10^3 µg/L, and <0.05 to 220 µg/L respectively. No sample exceed relevant effluent standard in Indonesia as the only heavy metal parameter regulated is Cr. However, concentration of Cd, Se, Fe and Zn exceed relevant effluent standard in Japan and Malaysia. Compared to other studies, concentration of Cr, Pb and Si in this study were relatively lower. However, the concentration of Cu, Cd, Fe and especially Al and Zn were much higher than other studies. Hierarchical Cluster Analysis (HCA) produced dendrograms showing cluster of strong similarity among parameters Ni, Cr and Co which indicates that the source of these metals is from dyes. Other clusters indicated various sources such as fixation agent, groundwater or another supporting chemical. HCA also indicates that factors other than the type of dye and production stage may affect heavy metal content in batik wastewater which represent the high variability of production process among batik factories.

Analysis on 32 groundwater samples taken from dug wells at and around batik factories revealed that the water quality is still within the acceptable level. Heavy Metal Contamination Index (HCI) confirmed this condition with very low HCI value. Numerical simulation using one dimensional contaminant transport equation showed very low concentration at groundwater table level which indicate that no groundwater contamination occurred from batik wastewater seepage. This is supported by the lithological and hydrogeological condition of alternating clay and sand layer that prevent the pollutant to seep into the groundwater.

Distribution of various heavy metal in river water was following the order of Fe>Pb>Cd>Cu>Cr. Range of concentration were 42.8-121.4 µg/L for Fe, 7.6-54.9 µg/L for Pb, 8.9-14.4 µg/L for Cd, 3.0-6.8 µg/L for Cu, and <5.5 µg/L for Cr. For concentration in sediment samples following order occurred, Fe>Pb>Cu>Cr>Cd. Range concentration in sediment were 1473.4-3237.6 mg/kg for Fe, 16.3-49.0 mg/kg for Pb, 15.4-46.3 mg/kg for Cu, 0.5-12.6 mg/kg for Cr, and 1.7-3.3 mg/kg for Cd. Assessment of the degree of contamination by using Geo-accumulation index (I_{geo}) and Enrichment Factor (EF) suggested a serious contamination by Cd and Pb in river sediment. In addition, ecological risk index by using consensus-based sediment quality standard ($Q_{m\text{-}PCA}$) categorized sediment sample from all sampling points were toxic to sediment dwelling organisms. For water samples, Heavy metal Pollution Index (HPI) suggested a highly polluted state for all sampling points but according to Nemerow Pollution Index (PN) only 4 sampling points were categorized as polluted. Both indexes agreed upon which sampling points were the mostly polluted which includes

sampling points in the area where many home industries including batik factories were located. In general, for all assessment index employed in this study, Cd consistently become the biggest contributor to high contamination degree or high ecological risk suggestion the prioritization of Cd monitoring. Source identification by using Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA) and Correlation Analysis (CA) revealed the heavy metal possible sources were agricultural activities from the using of fertilizer, pesticides, and metal-enriched cattle fodder and also from home industries along the river including batik industries. Monte Carlo simulation showed the low probability of contribution of batik wastewater to cause the concentration of river water exceed stream standard for parameter Pb, Cd, Fe and Cu, but high probability for Zn. Zn may be suggested to be indicator parameter for pollution from baik industry.

Ten fish samples were taken from Winongo River and analyzed for the concentration of Cr, Cr, Cu, Fe, and Cd in the flesh part of the fish. The distribution of heavy metal concentration is following the order of Fe>Cu>Cr>Cd>Pb with the range of 0.02-0.34 mg/kg for Pb, 0.03-0.51 mg/kg for Cr, 0.04-0.33 mg/kg for Cu, 0.05-0.17 mg/kg for Cd, and 0.62-6.68 mg/kg for Fe. Concentration of Cd and Pb exceed the relevant standard at some sampling points. The highest concentration occurred at the meeting point of main river and tributary from the direction of Yogyakarta City Center. Risk analysis on the consumption of this contaminated fish revealed the safe level for non-carcinogenic effect with Risk Quotients below 1 but not safe level for carcinogenic effect, since the ECR value for Cd and Cr are above 10^{-4}. This result is the indication of the urgency to conduct risk management program upon Winongo River and the various parties involved.

In conclusion, in regard to heavy metal, effluent from batik industry did not cause groundwater contamination in study area. Batik industry may contribute to heavy metal concentration in river water and sediment, but more data is required to confirm this finding, especially for parameter Zn. In regard to organic, batik industry is confirmed to potentially generate toxic aromatic amine due to the type of dye being used for production. Further study is necessary to investigate its potential problems to environment and human health in study area.

8.2 Future Recommendation

Recommendation for future research related to this topic are as following:

a) There is indication that pollutants in batik wastewater were adsorbed into the soil, hence the analysis on soil samples from areas exposed to batik wastewater is necessary to be conducted

b) Groundwater contamination may occur in batik center in Bantul area as it has different hydrogeology and lithological condition

c) Study on aromatic amines which covers 3 (three) objects:
   - Environmental sample (soil, groundwater)
   - Batik product for its potential release of aromatic amines to expose to human body
   - Batik factory worker which are the mostly exposed to various chemicals used during production but with minimum occupational safety measure

APPENDIX A

Toxicity Classification of 22 Aromatic Amines According to European Union (EU), Japan Regulation, and WHO-IARC

STOT = Target Organ Systemic Toxicity
RE = Repeated Exposure
SE = Single Exposure

No	CAS No	Substances	Health/Environment Hazard	EU	Japan	IARC
1	92-67-1	4-aminobiphenyl	Acute Toxicity	Oral 4	Oral 4	
			Mutagenicity		2	
			Carcinogenicity	1A	1A	1
2	92-87-5	benzidine	Acute toxicity	Oral 4	Oral 4	
			Mutagenicity		2	
			Carcinogenicity		1A	1
			STOT		RE 1 (liver, brain) RE 2 ((bone marrow, spleen, ovary, urinary, bladder)	
			Hazard to aquatic environment	Acute 1 Chronic 1	Chronic 2	
3	95-69-2	4-chloro-o-toluidine	Acute toxicity	Oral 3 Dermal 3 Inhalation 3	Oral 4 Dermal 4	
			Mutagenicity	2	2	
			Carcinogenicity	1B	1B	2A
			STOT		Single Exposure/SE 1 (urinary, bladder, blood) RE 1 (urinary, bladder, blood system)	
			Hazard to aquatic environment	Acute 1 Chronic 1		
4	91-59-8	2-naphtylamine	Acute toxicity	Oral 4		
			Mutagenicity		2	
			Carcinogenicity		1A	1
			Hazard to aquatic environment	Chronic 2	Acute 1 Chronic 1	

No	CAS No	Substances	Health/Environment Hazard	EU	Japan	IARC
5	97-56-3	o-aminoazotoluene	Skin sensitization	1	1	
			Mutagenicity		2	
			Carcinogenicity	1B	1B	2B
6	99-55-8	5-nitro-o-toluidine	Acute toxicity	Inhalation 3 Dermal 3 Oral 3	Oral 4	
			Carcinogenicity	2	2	3
			STOT		SE 1 (blood system, liver) RE 1 (liver)	
			Hazard to aquatic environment	Chronic 3		
7	106-47-8	4-chloroaniline	Acute toxicity	Inhalation 3 Dermal 3 Oral 3		
			Skin sensitization	1		
			Carcinogenicity	1B		2B
			Hazard to aquatic environment	Acute 1 Chronic 1	Acute 1 Chronic 1	
8	615-05-4	4-methoxy-m-phenylenediamine	Acute toxicity	Oral 4	Oral 4	
			Mutagenicity	2	2	
			Carcinogenicity	1B	1B	2B
			STOT		RE 2 (thyroid)	
			Hazard to aquatic environment	Chronic 2		
9	101-77-9	4,4'-methylenedianiline	Acute toxicity		Oral 4 Dermal 3	
			Eye damage/irritation		2	
			Skin sensitization	1	1	
			Mutagenicity	2	2	
			Carcinogenicity	1B	1B	2B
			STOT	SE 1 RE 2	SE 1 (central nervous system, liver, kidney, heart, visual organ) RE 1 (heart, liver, kidney) RE 2 (haemal system)	

No	CAS No	Substances	Health/Environment Hazard	EU	Japan	IARC
			Hazard to aquatic environment	Chronic 2	Acute 1 Chronic 1	
10	91-94-1	3,3'-dichlorobenzidine	Acute toxicity	Dermal 4		
			Skin sensitization	1		
			Carcinogenicity	1B		2B
			Hazard to aquatic environment	Acute 1 Chronic 1	Acute 1 Chronic 1	
11	119-90-4	3,3'-dimethoxybenzidine	Acute toxicity	Oral 4	Oral 4	
			Mutagenicity		2	
			Carcinogenicity	1B	1A	2B
			STOT		RE 1 (liver, haemal system, respiratory organs)	
12	119-93-7	3,3'-dimethylbenzidine	Acute toxicity	Oral 4		
			Carcinogenicity	1B		2B
			STOT		RE 1 (liver, kidney) RE 2 (haemal system)	
			Hazard to aquatic environment	Chronic 2		
13	838-88-0	4,4'-methylenedi-o-toluidine	Acute toxicity	Oral 4		
			Skin sensitization	1		
			Carcinogenicity	1B	1B	2B
			Hazard to aquatic environment	Acute 1 Chronic 1		
14	120-71-8	P-cresidine	Acute toxicity	Oral 4	Oral 4	
			Eye damage/irritation		2A	
			Skin corrosion/irritation		2	
			Carcinogenicity	1B	2	2B
			STOT		SE 2 (haemal system)	
15	101-14-4	4,4'-methylenebis (2-chloroaniline)	Acute toxicity	Oral 4		
			Mutagenicity		2	
			Carcinogenicity	1B	1B	1
			STOT		SE 1 (blood) RE 2 (blood system, liver)	

No	CAS No	Substances	Health/Environment Hazard	EU	Japan	IARC
			Hazard to aquatic environment	Acute 1 Chronic 1	Acute 1 Chronic 1	
16	101-80-4	4,4'-oxydianiline	Acute toxicity	Inhalation 3 Dermal 3 Oral 3	Oral 4	2B
			Skin sensitization		1	
			Mutagenicity	1B	2	
			Carcinogenicity	1B	1B	
			Reproductive toxicity	2	2	
			STOT		RE 1 (haemal system) RE 2 (pituitary, thyroid, liver, kidney, genetic organ (men))	
			Hazard to aquatic environment	Chronic 2	Acute 1 Chronic 1	
17	139-65-1	4,4'-thiodianiline	Acute toxicity	Oral 4	Oral 4	
			Carcinogenicity	1B	2	2B
			Reproductive toxicity		2	
			STOT		RE 2 (thyroid, lung, liver)	
			Hazard to aquatic environment	Chronic 2		
18	95-53-4	O-toluidine	Acute toxicity	Inhalation 3 Oral 3	Inhalation 4 Oral 4	
			Eye damage/irritation	2	2A	
			Mutagenicity		2	
			Carcinogenicity	1B	1A	1
			STOT		SE 1 (central nervous system, haemal system, urinary bladder SE 3 (narcotic effect) RE 1 (haemal system, urinary bladder)	
			Hazard to aquatic environment	Acute 1	Acute 1 Chronic 1	
19	95-80-7	2,4-diaminotoluene	Acute toxicity	Oral 3 Dermal 4	Oral 3 Dermal 4	

No	CAS No	Substances	Health/Environment Hazard	EU	Japan	IARC
			Eye damage/irritation		2	
			Skin sensitization	1	1	
			Mutagenicity	2	2	
			Carcinogenicity	1B	1B	2B
			Reproductive toxicity	2	2	
			STOT	RE 2	SE 1 (central nervous system, liver, haemal system) SE 3 (respiratory tract irritation) RE 1 (immune system, liver, testis)	
			Hazard to aquatic environment	Chronic 2	Acute 1 Chronic 1	
20	137-17-7	2,4,5-trimethylaniline	Acute toxicity	Inhalation 3 Dermal 3 Oral 3	Oral 4	
			Carcinogenicity	1B	2	3
			Hazard to aquatic environment	Chronic 2		
21	90-04-0	O-anisidine	Acute toxicity	Inhalation 3 Dermal 3 Oral 3	Oral 4	
			Skin sensitization		1	
			Mutagenicity	2	2	
			Carcinogenicity	1B	2	2A
			STOT		SE 2 (blood, central nervous system) RE 2 (blood)	
			Hazard to aquatic environment		Acute 2	
22	60-09-3	4-amino azobenzene	Acute toxicity		Oral 4	
			Skin sensitization		1	
			Mutagenicity		2	
			Carcinogenicity	1B	2	2B
			STOT		SE 2 (blood)	
			Hazard to aquatic environment	Acute 1 Chronic 1	Acute 1 Chronic 1	

APPENDIX B

Globally Harmonized System of Classification and Labelling of Chemicals (GHS Classification) on Health Hazard and Environmental Hazard

A. **Physical**
B. **Health Hazard**

B.1. Acute toxicity

Exposure route	Category 1	Category 2	Category 3	Category 4	Category 5
Oral (mg/kg bodyweight) *See notes (a) and (b)*	5	50	300	2000	5000 *See detailed criteria in Note (g)*
Dermal (mg/kg bodyweight) *See notes (a) and (b)*	50	200	1000	2000	
Gases (ppmV) *See notes (a), (b) and (c)*	100	500	2500	20000	*See detailed criteria in Note (g)*
Vapours (mg/l) *See notes (a), (b), (c), (d) and (e)*	0.5	2.0	10	20	
Dusts and Mists (mg/l) *See notes (a), (b), (c) and (f)*	0.05	0.5	1.0	5	

***Note**: Gases concentration are expressed in parts per million per volume (ppmV).*

Source: UN GHS Purple Book

B.2. Skin Irritation/Corrosion

Category 1 Corrosive	• Human experience showing irreversible damage to the skin; • Structure/activity or structure property relationship to a substance or mixture already classified as corrosive; • pH extremes of <=2 **and** >=11.5 including acid/alkali reserve capacity; • Positive results in a valid and accepted in vitro skin corrosion test; or • Animal experience or test data that indicate that the substance/mixture causes irreversible damage to the skin following exposure of up to 4 hours.
Category 2 Irritant	• Human experience or data showing reversible damage to the skin following exposure of up to 4 hours; • Structure/activity or structure property relationship to a substance or mixture already classified as an irritant; • Positive results in a valid and accepted in vitro skin irritation test; or • Animal experience or test data that indicate that the substance/mixture causes reversible damage to the skin following exposure of up to 4 hours, mean value of ≥ 2.3 < 4.0 for erythema/eschar or for oedema, or inflammation that persists to the end of the observation period, in 2 of 3 tested animals.
Category 3 Mild Irritant	• Animal experience or test data that indicates that the substance/mixture causes reversible damage to the skin following exposure of up to 4 hours, mean value of ≥ 1.5 < 2.3 for erythema/eschar in 2 of 3 tested animals.

B.3. Serious Eye Damage/Eye Irritation

Category 1 (Causes serious eye damage)	• Classification as corrosive to skin; • Human experience or data showing damage to the eye which is not fully reversible within 21 days; • Structure/activity or structure property relationship to a substance or mixture already classified as corrosive; • pH extremes of < 2 **and** > 11.5 including buffering capacity; • Positive results in a valid and accepted in vitro test to assess serious damage to eyes; or • Animal experience or test data that the substance or mixture produces either (1) in at least one animal, effects on the cornea, iris or conjunctiva that are not expected to reverse or have not reversed; or (2) in at least 2 of 3 tested animals a positive response of **corneal opacity ≥ 3 and/or iritis > 1.5,** calculated as the mean scores, following grading at 24, 48, and 72 hours
Category 2A (Irritant)	• Classification as severe skin irritant; • Human experience or data showing production of changes in the eye which are fully reversible within 21 days; • Structure/activity or structure property relationship to a substance or mixture already classified as an eye irritant; • Positive results in a valid and accepted in vitro eye irritation test; or • Animal experience or test data that indicate that the substance/mixture produces a positive response in at least 2 of 3 tested animals of: **corneal opacity ≥ 1, iritis ≥ 1, or conjunctival edema (chemosis) ≥ 2,** calculated as the mean scores, following grading at 24, 48, and 72 hours
Category 2B (Mild irritant)	• Human experience or data showing production of mild eye irritation; • Animal experience or test data that indicate that the lesions are fully reversible within 7 days.

B.4. Respiratory or skin sensitization

Category 1 Skin Sensitization	**Category 1 Respiratory Sensitization**
For substances and tested mixtures: • If there is evidence in humans that the individual substance can induce sensitization by skin contact in a substantial number of persons, or **where there are positive results from an appropriate animal test.** • If any individual skin sensitizer in the mixture has a concentration of: Subcategory 1B≥ 1.0% Solid/Liquid/Gas or Subcategory 1A≥ 0.1% Solid/Liquid/Gas	For substances and tested mixtures: • If there is human evidence that the individual substance induces specific respiratory hypersensitivity, and/or **Where there are positive results from an appropriate animal test.** • If any individual respiratory sensitizer in the mixture has a concentration of: ≥ 1.0% Solid/Liquid and ≥ 0.2% Gas

B.5. Germ Cell Mutagenicity

Category 1A	**Chemicals known to induce or regarded as if they induce heritable mutations in human germ cells** Known to induce heritable mutations –positive evidence from human epidemiological studies. Mixtures containing ≥ 0.1% of such a category 1A mutagen.
Category 1B	**Chemicals known to induce or regarded as if they induce heritable mutations in human germ cells** Regard as if they induce heritable mutations – positive results from *in vivo* heritable germ cell or somatic cell mammalian mutagenicity tests, or positive results showing mutagenic effects in the germ cells of humans without demonstration of transmission to progeny. Mixtures containing ≥ 0.1% of such a category 1B mutagen.
Category 2	**Chemicals that may induce heritable mutations in human germ cells** Positive evidence obtained from *in vivo* somatic cell mutagenicity or somatic cell genotoxicity tests in mammals and in some cases with support from *in vitro* experiments Mixtures containing ≥ 1% of such a category 2 mutagen.

B.6. Carcinogenicity

Category	Criteria
Category 1A	**Chemicals known to have carcinogenic potential to humans - largely based on human evidence** Mixtures containing ≥ 0.1% of such a category 1A carcinogen.
Category 1B	**Chemicals presumed to have carcinogenic potential to humans - largely based on animal evidence.** Mixtures containing ≥ 0.1% of such a category 1B carcinogen.
Category 2	**Suspected human carcinogen - evidence from human and/or animal studies is limited** Mixtures containing ≥ 0.1% of such a category 2 carcinogen. (Note: Some countries have different concentration limits. For example, EU's concentration limit for category 2 carcinogen is **1%**).

B.7. Reproductive toxicity

Category	Criteria
Category 1A	**Known human reproductive toxicants** Mixtures containing ≥ 0.1% or ≥ 0.3 % of such a substance. (EU's value is 0.3%).

Category	Criteria
Category 1B	**Presumed human reproductive toxicants - largly based on animal studies** Mixtures containing ≥ 0.1% or ≥ 0.3 % of such a substance. (EU's value is 0.3%. USA's value is 0.1%)
Category 2	**Suspected human reproductive toxicant - Evidence from animal and/or human studies is limited** Mixtures containing ≥ 0.1% or ≥ 3 % of such a substance. (EU's value is 3% while USA's value is 0.1%).
Effects on via lactation	**Effects on via lactation** Toxicants which may interfere with lactation or which may be present in breast milk and may cause harm to breast-fed children Mixtures containing ≥ 0.1% or ≥ 0.3 % of such a substance.

B.8. Target Organ Systemic Toxicity – Single Exposure

		Guidance value ranges for:		
Route of exposure	**Units**	**Category 1**	**Category 2**	**Category 3**
Oral (rat)	mg/kg body weight	C ≤ 300	2000 ≥ C > 300	Guidance values do not apply[b]
Dermal (rat or rabbit)	mg/kg body weight	C ≤ 1000	2000 ≥ C > 1000	
Inhalation (rat) gas	ppmV/4h	C ≤ 2500	20000 ≥ C > 2500	
Inhalation (rat) vapour	mg/l/4h	C ≤ 10	20 ≥ C > 10	
Inhalation (rat) dust/mist/fume	mg/l/4h	C ≤ 1.0	5.0 ≥ C > 1.0	

Source: UN GHS Purple Book

Ingredient classified as:	**Cut-off/concentration limits triggering classification of a mixture as:**	
	Category 1	**Category 2**
Category 1 Target organ toxicant	≥ 1.0% (note 1)	1.0 ≤ ingredient < 10% (note 3)
	≥ 10% (note 2)	
Category 2 Target organ toxicant	--	≥ 1.0% (note 4)
		≥ 10% (note 5)

Source: UN GHS Purple Book

B.8. Target Organ Systemic Toxicity – Repeated Exposure

Category	Classification Criteria and Guidance Value
Category 1	Reliable evidence on the substance or mixture (including bridging) of an adverse effect on specific organ/systems or systemic toxicity in humans or animals. May be named for specific organ/system. For tested substances and mixtures: • **Guidance value C** (oral, rat) ≤ 10 mg/kg bw/d • Guidance value C (dermal, rat or rabbit) ≤20 mg/kg bw/d • Guidance value C (inhalation, rat, gas) ≤ 50ppm/6h/d • Guidance value C (inhalation, rat, vapour) ≤ 0.2 mg/l/6h/d

	• Guidance value C (inhalation, rat, dust/mist/fume) ≤ 0.02mg/l/6h/d Mixture that lack sufficient data, but contains Category 1 ingredient: ≥ 1 to ≤ 10% for some authorities; and ≥ 10% for all authorities.
Category 2	Evidence on the substance or mixture (including bridging) of an adverse effect on specific organ/systems or systemic toxicity from animal studies or humans. May be named for specific organ/system. For substances and tested mixtures: • 10<Guidance value C (oral, rat) ≤ 100 mg/kg bw/d • 20<Guidance value C (dermal, rat or rabbit) ≤200 mg/kg bw/d • 50<Guidance value C (inhalation, rat, gas) ≤ 250ppm/6h/d • 0.2<Guidance value C (inhalation, rat, vapor) ≤ 1 mg/l/6h/d • 0.02<Guidance value C (inhalation, rat, dust/mist/fume) ≤ 0.2mg/l/6h/d Mixture that lack sufficient data, but contains Category 1 ingredient: ≥ 1.0 but ≤ 10% for some authorities and/or contains Category 2 ingredient: ≥ 1.0 or ≥ 10%.

B.9. Aspiration toxicity

Categories	Criteria
Category 1: Chemicals known to cause human aspiration toxicity hazards or to be regarded as if they cause human aspiration toxicity hazard	A substance is classified in Category 1: (a) Based on reliable and good quality human evidence (see note 1); or (b) If it is a hydrocarbon and has a kinematic viscosity ≤ 20.5 mm^2/s, measured at 40° C.
Category 2: Chemicals which cause concern owing to the presumption that they cause human aspiration toxicity hazard	On the basis of existing animal studies and expert judgment that takes into account surface tension, water solubility, boiling point, and volatility, substances, other than those classified in Category 1, which have a kinematic viscosity ≤ 14 mm^2/s, measured at 40° C (see note 2).

Source: UN GHS Purple Book

For mixture

Category	Criteria
Category 1	Contains >=10% category 1 ingredient and has a kinematic viscosity<=20.5mm^2/s (measured at 40 celcius degrees);
Category 2	Contains >=10% category 2 ingredient and has a kinematic viscosity<=14mm^2/s (measured at 40 celcius degrees);

C. Environmental Hazards

C.1. Hazardous to aquatic environment (Acute/Chronic)

Classification categories			
Short-term (acute) hazard (*Note 1*)	**Long-term (chronic) hazard** (*Note 2*)		
	Adequate chronic toxicity data available		**Adequate chronic toxicity data not available** (*Note 1*)
	Non-rapidly degradable substances (*Note 3*)	**Rapidly degradable substances** (*Note 3*)	
Category: Acute 1 $L(E)C_{50} \leq 1.00$	**Category: Chronic 1** NOEC or $EC_x \leq 0.1$	**Category: Chronic 1** NOEC or $EC_x \leq 0.01$	**Category: Chronic 1** $L(E)C_{50} \leq 1.00$ and lack of rapid degradability and/or BCF ≥ 500 or, if absent log $K_{ow} \geq 4$
Category: Acute 2 $1.00 < L(E)C_{50} \leq 10.0$	**Category: Chronic 2** $0.1 <$ NOEC or $EC_x \leq 1$	**Category: Chronic 2** $0.01 <$ NOEC or $EC_x \leq 0.1$	**Category: Chronic 2** $1.00 < L(E)C_{50} \leq 10.0$ and lack of rapid degradability and/or BCF ≥ 500 or, if absent log $K_{ow} \geq 4$
Category: Acute 3 $10.0 < L(E)C_{50} \leq 100$		**Category: Chronic 3** $0.1 <$ NOEC or $EC_x \leq 1$	**Category: Chronic 3** $10.0 < L(E)C_{50} \leq 100$ and lack of rapid degradability and/or BCF ≥ 500 or, if absent log $K_{ow} \geq 4$
	Category: Chronic 4 *(Note 4)* Example: (*Note 5*) No acute toxicity and lack of rapid degradability and BCF ≥ 500 or, if absent log Kow ≥ 4, unless NOECs > 1 mg/l		

Source: UN GHS Purple Book

Table 4.1.3: Classification of a mixture for short-term (acute) hazards based on summation of the concentrations of classified ingredients

Sum of the concentrations (in %) of ingredients classified as:		Mixture is classified as:
Acute 1 × M[a]	≥ 25%	Acute 1
(M × 10 × Acute 1) + Acute 2	≥ 25%	Acute 2
(M × 100 × Acute 1) + (10 × Acute 2) + Acute 3	≥ 25%	Acute 3

Table 4.1.4: Classification of a mixture for long-term (chronic) hazards based on summation of the concentrations of classified ingredients

Sum of the concentrations (in %) of ingredients classified as:	Mixture is classified as:
Chronic 1 × M[a] ≥ 25%	Chronic 1
(M × 10 × Chronic 1) + Chronic 2 ≥ 25%	Chronic 2
(M × 100 × Chronic 1) + (10 × Chronic 2)+ Chronic 3 ≥ 25%	Chronic 3
Chronic 1 + Chronic 2 + Chronic 3 + Chronic 4 ≥ 25%	Chronic 4

[a] *For explanation of the M factor, see 4.1.3.5.5.5.*

Source: UN GHS Purple Book

Acute toxicity	M factor	Chronic toxicity	M factor	
$L(E)C_{50}$ value		NOEC value	NRD[a] ingredients	RD[b] ingredients
$0.1 < L(E)C_{50} \leq 1$	1	$0.01 < NOEC \leq 0.1$	1	-
$0.01 < L(E)C_{50} \leq 0.1$	10	$0.001 < NOEC \leq 0.01$	10	1
$0.001 < L(E)C_{50} \leq 0.01$	100	$0.0001 < NOEC \leq 0.001$	100	10
$0.0001 < L(E)C_{50} \leq 0.001$	1000	$0.00001 < NOEC \leq 0.0001$	1000	100
$0.00001 < L(E)C_{50} \leq 0.0001$	10000	$0.000001 < NOEC \leq 0.00001$	10000	1000
(continue in factor 10 intervals)		(continue in factor 10 intervals)		

[a] *Non-rapidly degradable*
[b] *Rapidly degratdable*

Source: UN GHS Purple Book

C.2. Hazardous to the ozone layer

Category	Criteria
Category 1	Any of the controlled substances in the annexes to the Montreal Protocol; or any mixture containing at least 1 ingredient listed in the annexes to the Montreal protocal, at a concentration>=0.1%;