Poll Res. 41 (1) : 78-85 (2022)

ISSN 0257–8050
DOI No.: http://doi.org/10.53350/PR.2022.v41i01.011

INDUSTRIAL SPATIAL DISTRIBUTION AND HEAVY METAL CONCENTRATION OF RIVER WATER IN PALEMBANG CITY

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(Received 2 June, 2021; Accepted 10 July, 2021)

ABSTRACT

Water is very important for human life, especially drinking water. River is a water resource that is used to supply drinking water for households and residences. There are several activities and industries in the Musi River, Komering River, Ogan River and Keramasan River. These various activities have the potential to contribute to pollutants such as heavy metals. The industries located along the river in the city of Palembang are The Crumb Rubber Industry, PT. Pertamina, PT. Pusri, PT. Bukit Asam and PT. Semen Baturaja as well as fabric coloring. Some activities that have the risk of producing liquid waste containing heavy metals are coal mining industry and dyeing fabrics. Several parameters that exceed the quality standard are temperature, turbidity, water color, pH, and organics ($KMnO_4$). Heavy metals concentration is still in accordance with the required quality standards. Sediment serves as an absorber as well as a source of heavy metals. Heavy metals in sediments can be lost or re-suspended to cause secondary pollution in water bodies. Accumulation of heavy metals in sediments directly affects organisms. Therefore, it is very important to study the accumulation of heavy metals in sediments and organisms such as shellfish.

KEY WORDS : Water, River, Heavy metal, Waste, Industry

INTRODUCTION

Water is very important for human life, especially for drinking (Adilah and Nadia, 2020). River is a water resource that is used to supply drinking water for households and residences (Dunca, 2018). The Musi River is the longest river in South Sumatera. The length of this river reaches 750 km with a discharge varying from 4,000 to 7,000 m^3 per/second (Husnah *et al.*, 2007). In addition, there are several other large rivers, namely the Komering River with an average width of 236 meters; The Ogan River with an average width of 211 meters, and the Keramasan River with an average width of 103 meters. All of these rivers disembogue into the Musi River (Rosyidah, 2018).

Industrial and urban development is always followed by the problem of water environmental pollution (Azizi *et al.*, 2018). Several industries along the Musi River include wood processing, rubber, fertilizer, ceramics, boat docks, detergent, oil, gas, cold storage, electroplating and the soft drink industry. Most of these industries are known not to have an optimal waste water treatment plant. In addition, The Musi River is also a shipping channel for various types of ships (Putri *et al.*, 2015). Synthetic dyes for Batik and Jumputan fabrics produce dangerous chemical effects (Felaza, 2016). Solid or liquid waste was discharged into river bodies can result in water toxicity, eutrophication, and damage to aquatic life (Chen *et al.*, 2019). These various activities may potentially contribute pollutants such as heavy metals (Indrayani, 2018; Putri *et al.*, 2015). This journal describes industrial pollutant distribution along the river in Palembang City and the heavy metals concentration in Musi and Ogan River.

MATERIALS AND METHODS

Location and Time

Measurement was performed in Ogan and Musi River at 5 (five) points. Water samples were taken in 22nd December 2020.

Sample preparation

Plastic bottles and the caps were cleaned with detergent and rinsed with clean water, then they were rinsed with nitric acid (HNO_3) 1:1, afterwards re-rinsed with analyte free water for 3 times. If the bottles and the caps have dried, they were closed tightly. The plastic bottles were used as sampling tools. Sample was loaded into the 2 litters bottle. Sampling location was done based on testing purpose (National Standardization Board, 2008).

Arsenic (As)

50 ml sample was dispensed into 100 ml digestion flask. That sample was added with 1 ml H_2SO_4 2,5 N and 5 ml 5% $K_2S_2O_8$. That solution was heated slowly until boiled for 30 to 40 minutes, until the volume reached 10 ml. Afterward the solution is cooled. 50 ml of demineralized water was added until 50 ml. 5 ml concentrated HCl was added, and then homogenized. 5 ml pre-reductant NaI/KI was added, and then homogenized and let it still for 30 minutes. The measurement was performed at 193,7 nm wavelength. Arsenic level was calculated using following formula (National Standardization Board, 2018a):

$$As(mg/l) = \frac{C \text{ x } fp}{1000}$$

Annotation:

C : level obtained by measurement results (µg/l);

fp : dilution factor;

1000 : conversion factor from microgram per liter to milligram per liter.

Cyanide (Cn)

10 ml sample from the distillation was dispensed into a 50 ml volumetric flask. Sample was diluted with 0,16% NaOH as diluent solution until the volume reached 40 ml. 1 ml Acetate buffer was added and homogenized. Chloramine-T which has been inversed twice was added 2 ml into the sample and left to stand for 2 minutes. Barbituric acid pyridine solution was added as much as 5 ml and homogenized. The sample was maximized into the mark using demineralized water and homogenized inversely. That solution was left to stand for 8 minutes until the stable color complex compound was formed. Measurement was performed using spectrophotometer UV-Vis at 575-582 nm wavelength. Cyanide Level (Cn) was calculated using the formula as follows (National Standardization Board, 2011):

$$(mgCN^-/l) = \frac{(C \text{ x } 50 \text{ x } 250)}{(500 \text{ x } V)}$$

Annotation:

C : cyanide content of the test sample obtained from calibration curve (mg/l);

V : volume of test sample taken for analysis (ml);

50 : obtained from volumetric flask that is used for test sample analysis;

250 : obtained from the volume of distillate;

500 : obtained from the volume of test sample used for distillation..

Iron/Ferric (Fe)

100 ml sample was dispensed into beaker glass and then homogenized. That solution was added with Nitric Acid as much as 5 ml. The sample solution was heated until almost dry. 50 ml distilled water was added into 100 ml volumetric flask through filter paper. Standard solution of ferrous metal, Fe 100 mg/l as much as 50 ml was taken into 500 ml volumetric flask. Then 0 ml; 5 ml; 10 ml; 20 ml; 30 ml; 40 ml and 60 ml Iron standard metal solution were dispensed into 100 ml volumetric flask. Dilution solution was added until exactly the mark to get 0.0 mg/l; 0.5 mg/l; 1.0 mg/l; 2.0 mg/l; 3.0 mg/l; 4.0 mg/l; 5.0 mg/l an 6.0 mg/l Iron metal concentration. Measurement was performed at 248.3 nm wavelength. Iron content (Fe) was calculated with formula, as follows (American Public Health Association, 2017; National Standardization Board, 2004):

$$Fe(mg/l) = C \text{ x } fp$$

Annotation:

C : concentration obtained from measurement result (mg/l)

fp : dilution factor

Cadmium (Cd)

125 ml sample was taken with duplo method.

Liquid was dispensed into 200 ml glass bottle. NaOH 1 N was added until pH became 3. 100 ml test sample was dispensed into separating funnel. 1 ml Ammonium Pyrrolidine Dithiocarbamate solution was added and shaken, and then 10 ml of Methyl Isobutyl Ketone was added and shaken for 30 seconds.

Sample was rested until there was phase separation between organic and water layer. The water layer was removed through the spout. The organic layer was transferred into glass tube with sharpening lid. The organic layer was filtered with filter paper treated with anhydrate Na_2SO_4. Measurement was performed at 229.8 nm wavelength. Cadmium level (Cd) was calculated using formula, as follows (American Public Health Association, 2017; National Standardization Board, 2005a):

$$(\mu g/l) = C \times fp$$

Annotation:
C : content/level obtained from measurement result (µg/l)
fp : dilution factor

Zinc (Zn),

125 ml sample was extracted with Duplo method. Solution was taken into 200 ml glass bottle and then NaOH 1 N was added until the pH level became 3. 100 ml test sample was taken and put into a separation funnel. The test sample was added with 1 ml Ammonium Pyrrolidine Dithiocarbamate ($C_5H_9NS_2.NH_3$) solution and shaken, and then added another 10 ml of Methyl Isobutyl Ketone($C_6H_{12}O$) and shaken for 30 seconds. Sample was rested until the separation phase of organic and water layer occurred. The water layer was removed through the spout. The organic layer was moved into the glass tube with stopper and then strained with filter paper which was given anhydrous Na_2SO_4 powder. Measurement was performed at 213.9 nm wavelength. Zinc concentration (Zn) was calculated using formula as follows, (American Public Health Association, 2017; National Standardization Board, 2005b):

$$(mg/l) = C \times fp$$

Annotation:
C : level obtained from measurement result (mg/l)
fp : dilution factor

Lead (Pb)

The sample was filtered with 0.45 µm porous membrane. Sample was aspired into an Atomic Absorption Spectrophotometer, and the absorption was measured at 283.3 nm wavelength. Lead content was calculated using the formula, as follows: (American Public Health Association, 2017; National Standardization Board, 2009b):

$$Pb\ (mg/l) = C \times fp$$

Annotation:
C : concentration obtained from measurement result (mg/l)
fp : dilution factor

Selenium (Se)

50 ml sample was extracted into 100 ml digestion flask. Sample was added with 1 ml 2.5 N H_2SO_4 and 5 ml 5% $K_2S_2O_8$. Sample was heated for 30-40 minutes until the volume reached 10 ml and cooled. Demineralized water was added until the volume reached 30 ml. 15 ml concentrated HCl was added and homogenized. Solution was heated at 100ºC for 40 minutes and then cooled. Atomic Absorption Spectrophotometer was operated and optimized equipped with hydride generation unit. Working solution was aspirated until the absorption value could be read. The measurement was performed at 196,0 nm wavelength. Selenium level (Se) was calculated using formula, as follows (American Public Health Association, 2017; National Standardization Board, 2018b):

$$Se(mg/l) = \left(\frac{C \times fp}{1000}\right)$$

Annotation:
C : Concentration obtained from measurement results (µg/l);
fp : dilution factor;
1000 : conversion factor from microgram per liter to milligram per liter

Manganese (Mn)

Sample was filtered with 0.45 µm porous membrane and then aspired into a flaming AAS. The absorption measurement of the sample was performed at 279.5 nm. Manganese concentration (Mn) was calculated using formula, as follows (American Public Health Association, 2017; National Standardization Board, 2009a):

$$Mn\ (mg/l) = C \times fp$$

Annotation:
C : concentration obtained from measurement result (mg/l)
fp : dilution factor

Hexavalent Chromium (Cr+6)

Sample was strained with 0.45 μm porous membrane. l0 ml Sample from distillation was poured into 100.0 ml volumetric flask. 0.25 ml H_3PO_4 was added into the solution. 0.2 N Sulfuric Acid was added until pH became 2.0 ± 0,5. Test sample solution was removed into a 100 ml volumetric flask until the mark by adding demineralized water, subsequently 2.0 ml diphenylcarbazide solution was added, shaken and rested until 10 minutes. The absorption of the sample was measured at 540 nm. Hexavalent Chromium (Cr-VI) concentration was calculated using formula, as follows (National Standardization Board, 2009):

$$\text{Cr-VI}\left(\frac{mg}{l}\right) = C \times \frac{120}{V}\ fp$$

Annotation:
C : hexavalent chromium concentration obtained from measurement result (mg/l);
102: final volume (ml);
V : test sample volume, declared in milliliter (ml);
Fp : dilution factor (if needed).

RESULTS AND DISCUSSION

Industrial Distribution

This study was conducted in Musi River and Ogan River in Palembang City, South Sumatera. There are many industries located on the banks of Musi and Ogan River. These industries have the risk to compromise the environment by polluting the river. The location of these industries can be seen in Figure 1 below:

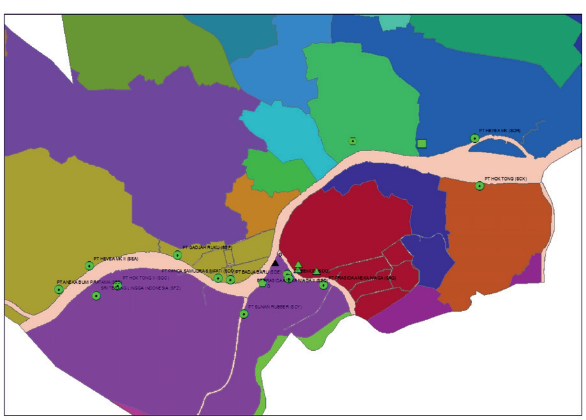

Fig. 1. Distribution of Industries along the river in Palembang City

The most dominant industry on the banks of the Musi, Ogan and Keramasan River is crumb rubber. There are also some big industries such as PT Pertamina, PT Pusri, PT Bukit Asam and PT Semen Baturaja. Besides that, there are also some communities which activities are colouring jumputan fabrics. The most dominant liquid waste produced by crumb rubber industry are H_2S and NH_3, while for heavy metals were not detected (Oktriyedi *et al*., 2021). The parameters exceeded quality standard in stockpile of PT Batu bara were TSS, pH, Fe and Mn (E. Suoth and Nazir, 2014); Fitriyanti 2014, 2015). The most dominant parameter in liquid waste of PT Pusri was ammonia (Kosim *et al*., 2015; Rahman, 2019). Oil, fat, H_2S, NH_3 and total phenol were the most dominant parameters in liquid waste of PT Pertamina (Igirisa *et al*., 2016). Heavy metals found in liquid waste of fabric dyeing were Hg, Cd, Pb, Ni, Cu, Cr, Fe and Al (Indrayani, 2018; Karim and Juniar, 2018; Nopilda, 2019).

Human activity greatly affects the presence of heavy metals (Wei *et al*., 2019). Kind of activities which affects the presence of heavy metals are industry and mining (Ezugwu *et al*., 2019). Heavy metals contamination is more worrying than other pollutants, due to bio-accumulative characteristics of heavy metals which are not biodegradable (Mukhtar and Chisti, 2018). Therefore, physicochemical parameters and heavy metals concentration are measured to evaluate water quality (Liang *et al*., 2020). Heavy metals pollute natural water bodies, sediment, and soil. Heavy metals are persistent in the environment, they are accumulated into biota or dissolved into ground water. Different physicochemical and climatic factors influence overall dynamics and biogeochemical heavy metals cycles in environment (Ali *et al*., 2019).

River water characteristics

Sample was taken at five points. Those five points were at PT Remco, Ki Merogan Mosque, Shipping pier, estuary of Musi and Ogan river, and Jumputan center. The results obtained were summarized in Table 1 (River water characteristics) and Table 2 (Heavy metals content).

Based on Table 1, there were some parameters that exceeded quality standard, namely temperature, turbidity, water color, pH and organics ($KMnO_4$), while other parameters such as odor, TDS or TS, taste, fluoride, total hardness, chloride, N as

Table 1. River Water Characteristics

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5	Quality Standard*
Odor	Odorless	Odorless	Odorless	Odorless	Odorless	Odorless
Temperature (C)	22.1	22.1	22.1	22	22	Air Temperature± 3 °C
TDS/TS (mg/l)	20.7	20.45	20.62	20.59	21.1	1000
Turbidity (NTU scale)	37.1	35.9	37.2	38.3	36.2	25
Taste	Tasteless	Tasteless	Tasteless	Tasteless	Tasteless	Tasteless
Water color (PtCo Scale)	62.453	67.475	64.813	84.723	74.492	50
Water pH	6.12	6.18	6.16	6.22	6.14	6.5-8.5
Flourida (mg/l)	0.148	0.074	0.085	0.062	0.098	1.5
Total Hardness (mg/l)	< 5.407	< 5.407	< 5.407	< 5.407	< 5.407	500
Chloride (mg/l)	4.374	1.999	< 1.521	1.749	1.749	-
Organic ($KMnO_4$) (mg/l)	27.527	27.527	27.37	26.901	26.588	10
N as nitrite (mg/l)	< 0.036	< 0.036	< 0.036	< 0.036	< 0.036	1
N as nitrate (mg/l)	7.52	7.016	8.214	8.65	7.532	10
Sulfate (mg/l)	13.086	13.77	10.605	14.545	11.435	400

*Quality standard was based on minister of health regulation of Republic of Indonesia No. 32, 2017.

nitrite, N as nitrate and sulfate is still in accordance with the required quality standards.

Good physical or chemical conditions, such as: pH, redox potential, temperature, organic matter decomposition, leaching and ion exchange process, affect changes in the form of metal associations in sediments (Rumhayati *et al.*, 2016). The most important parameters in assessing variations in river water quality are alkalinity or acidity, salinity, Mg, Ca, dissolved organic carbon and total organic carbon (Amiæand Tadiæ, 2018).

Physical-chemical characteristic of the river influences the entry of heavy metals. Heavy metals will be adsorbed onto the suspended particulate matter and then deposited into the sediment (Lafabrie *et al.*, 2007). TSS concentration has a strong correlation with Cu, As, Fe and Ni. Heavy metals are carried along with organic and/or sediment loads. Suspended sediments carry Cu, As, Fe and Ni into the canal through surface runoff. Surface sediments carry heavy metals from anthropogenic sources into river water (Bhaskar and Dixit, 2013; Liang *et al.*, 2020).

Heavy metals charasteristics are persistence, environmental toxicity, bioaccumulation in aquatic ecosystems (Jordanova *et al.*, 2018). Heavy metals usually quickly settle into sedimen after entering river (Shyleshchandran *et al.*, 2018). Heavy metals are also more concentrated in sediments than in water bodies of river systems (Liu *et al.*, 2018). River sediments serve as reservoirs for heavy metals. This results in increased concentration in sediment compared to river systems. If the hydrodinamic conditions change or if there is a change in the physico-chemical equilibrium, the metals present in the sediment can be released back into the water,

Table 2. Heavy Metals Concentration

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5	Quality Standard
Arsenic (mg/l)	Negative/ < 0.008	Negative/ < 0.008	Negative/ < 0.008	Negative/ < 0.008	Negative/ < 0.008	0.05
Cyanida (mg/l)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.1
Iron (mg/l)	414.628	450.33	470.157	687.872	669.957	1000
Cadmium (µ/l)	< 2.643	< 2.643	< 2.643	< 2.643	< 2.643	5
Zinc (µ/l)	5.223	12.967	15.152	6.218	5.088	15000
Lead (µ/l)	7.727	9.166	8.775	8.396	8.472	50
Selenium (µ/l)	< 3.558	< 3.558	< 3.558	< 3.558	< 3.558	10
Hexavalent Chromium (mg/l)	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	0.05
Mangan (µ/l)	28.355	26.298	26.163	28.373	24.544	500

causing secondary pollution (Hill *et al.*, 2013). Therefore, where sediment acts as "Sink" or "secondary source" for heavy metals, there is potential to use sediment as an effective environmental medium for monitoring and evaluating the magnitude and source of heavy metal pollution in the aquatic environment (Cui *et al.*, 2019).

Shellfish is used as environmental pollution indicator. This is due to their wide geographic distribution, sedimentary life style, filter feeding behavior, concentrate different microorganism and multiple chemical pollutant in their tissue and tolerance to wide variety of environmental conditions. Shellfish can withstand a high degree of variation in their environment. Shellfish have been used extensively to monitor pollution in aquatic environment (Azizi *et al.*, 2018; Oliveira *et al.*, 2016).

Metals are known to easily get accumulated in sediments, which serve as a storage area for pollutant. Sedimentary contaminant can be released to the surface of the water, resulting in potential adverse health effect for aquatic organisms. Heavy metals accumulated in aquatic organism which the concentration is greatly higher than in water, and can undergo biomagnification in the food chain to the level of causing physiological damage to human consumer (EL-Shenawy *et al.*, 2016).

Heavy metals tend to accumulate in human organ and neural systems and disturb the normal function. In the current past years, heavy metals such as Lead (Pb), Arsenic (As), Magnesium (Mg), Nickel (Ni), Copper (Cu), and Zinc (Zn) has gained significant attention due to the effect of human health. Moreover, cardiovascular disease, kidneys related problems, neurocognitive disease, and metals trace cancer related such as Cadmium (Cd) and Chromium (Cr). Lead (Pb) is known to slow down physical growth and mental problems in infants, while Arsenic (As) and Mercury (Hg) can cause serious toxicity in case of derma and cancer pathology and further damage in kidneys and liver (Rahmanian *et al*., 2015)

CONCLUSION

The Industries located along the river of Palembang city is crumb rubber industry, PT Pertamina, PT Pusri, PT Bukit Asam and PT Semen Baturaja and also fabric dyeing. Activities those are at the risk of producing liquid waste containing heavy metals are coal mining industry and fabric dyeing. Several parameters that exceed the quality standard, namely temperature, turbidity, water color, pH, and organic ($KMnO_4$). Heavy metals concentration is still in accordance with the required quality standards.

Sediment serves as both an absorber and a source of heavy metals. Heavy metals in sediments can be lost or resuspended to cause secondary pollutant in water bodies. Heavy metals accumulation in sediment directly affects organisms. Therefore, it is very important to study heavy metals accumulation in sediments and organisms such as shellfish (Huang *et al.,* 2020).

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