Assessment of heavy metals pollution in the sediment of Ciliwung river

T R Mulyaningsih¹, M Irmawati², Istanto¹ and Alfian¹
1 Center For Science and Technology of Advanced Materials, BATAN Indonesia
2 Faculty of Pharmacy, Pancasila University, Indonesia
E-mail: thrinam@batan.go.id

Abstract. Thirteen (13) rivers flowing in the city of Jakarta and Ciliwung is one of them. This river flows through residential, offices, industrial and factories. Activities that exist around the river can cause rivers to become polluted. River sediments act as a potential sink for many hazardous chemicals that can be used as indicators for pollution monitoring of the river. The objective of this study is to assess the heavy metal contamination in the Ciliwung river sediment based on single and combination indices. For the assessment of the Ciliwung sediment quality, measurements of metal concentration in river sediments have been performed. Sampling was carried out at four sampling locations, namely in Kelapa Dua, Kalibata, Condet, and Depok. Analysis of heavy metals in the sample was carried out using instrumental neutron activation analysis method. The analysis result shows that the detected elements in sediment include: Br, Al, As, Ca, Ce, Cr, Co, Cs, Mg, Mn, Na, Sb, Eu, Fe, Hf, K, Sc, Sm, Ta, Tb, Th, Yb, and Zn. The assessment based on the value of the enrichment factor indicates that there has been an increase in the concentration of heavy metals As, Cr, Sb, and Zn in moderate levels due to anthropogenic factors. Based on the geo accumulation index value, it is known that the sampling area is not polluted to moderate contamination. Heavy metals As, Cr, Sb, and Zn in sediments provide a low level of ecological risk to the aquatic environment. Based on the pollution load index value (PLI), all sampling locations are in no pollution conditions. From the evaluation, it can be seen that even for some heavy metals namely As, Cr, Sb, and Zn has been an increase in the concentration value but has not yet reached the polluted level and the ecological risk of heavy metals in the sediments also still provides a low ecological risk.

1. Introduction
Ciliwung River is one of the rivers that flow in Jakarta. This river has many important functions, such as raw water sources for drinking water, fisheries, livestock, agriculture, and urban businesses [1]. Heavy metal pollution in the aquatic environment is one of the critical issues due to the toxic and persistent characters [2–4]. Heavy metals in water reservoir originate from both natural processes and anthropogenic sources. Anthropogenic sources are mainly from industrial processing, urban, sewage, mining activity, and agricultural run-off [5,6]. Sediment plays a vital role in the aquatic environment. Sediment can be used as an indicator for monitoring contaminant in aquatic environments [7–9]. Many researchers have used sediment to study the behavior of metals [10–12].

The presence of heavy metals in sediments can result in a decrease in the quality of waters, which is a long time can a negative impact on aquatic organisms and public health. Heavy metals in the sediments of the Ciliwung River can come from activities around the river. To evaluate water quality:
monitoring, quantification, and analysis of water quality need to be done. The concentration of heavy metals in sediments is usually in low concentration. For analysis, it needs sensitive analytical techniques. Neutron activation analysis with all its excess is a suitable technique used in this study [7,13,14].

The objective of this study is to assess the heavy metal contamination in the Ciliwung river sediment. Some quantitative indices were used to assess heavy metal contamination. These indices included Enrichment factor (Ef), Contamination factor (Cf), Contamination degree (Cd), Ecological risk assessment (Er), Geo-accumulation index (I_{geo}), and Potential ecological risk factor (RI) [5,8,9,11,12].

2. Research methods

2.1. Sampling
Sediment sampling was obtained from 12 (twelve) observation points in 2017. Observation sites along the Ciliwung River (Figure 1) include Depok, Kelapa Dua, Condet, and Kalibata. The surface sediments samples were collected by coring sediment sampler. Sediment samples were stored into a plastic bag that has been coded, then brought to the laboratory. The samples were air-dried at room temperature and then grinded and sifted through 100 mesh sieve, and stored in brown bottles.

![Sampling location along Ciliwung river](image)

**Figure 1.** Sampling location along Ciliwung river

2.2. Sample preparation, Irradiation, and Counting
Weigh 20-100 mg sediment samples, respectively place in 0.3 ml vial low-density polyethylene (LDPE). The sample that has been weighed in an LDPE vial was wrapped in aluminum foil and arranged into a target that is ready to be activated. Targets consist of sediment samples, standard reference material (SRM) 2704 Buffalo river
sediment from NIST (National Institute of Science and Technology), and 2-3mg Al-Au 0.1 % flux monitor from IRRM (Institute for Reference Materials and Measurement).

Targets were inserted into irradiated capsules. Irradiation was carried out in Rabbit system of G.A. Siwabessy Multy Purpose Reactor at Serpong, at a neutron flux of \( \sim 10^{13} \) n cm\(^{-2}\) s\(^{-1}\). Post irradiated samples were counted by high purity germanium detector from Canberra with 1.8 keV of resolution for 1332 keV of 60Co and 25% relative efficiency. The spectra were evaluated with the program Genie 2000 software version 3.2. Quantitative analysis was carried out by comparative- INAA for short half live radionuclides and ko-IAEA software for medium and long half live radionuclides. The condition data of irradiation and counting were shown in Table 1.

| T irradiation | T decay | T counting | Radioisotope       |
|---------------|---------|------------|--------------------|
| 15 s          | ±5 min  | 200 s and 5 min | Al, Mn, Mg, K, Na   |
| 10 min        | 4-7 d   | 15-30 min   | As, La             |
| 3 h           | 10-20 d | 1-2 h       | Cr, Fe, Co, Sb, Sc, Th, Zn, Ta, Tb |

### 2.3. Evaluation Method

The quality of sediments was evaluated based on several methods, including enrichment factors (Ef), contamination factors (Cf), ecological risk factors(Er), and index of geo-accumulation (I\(_{\text{geo}}\)). These indicators can be used to estimate the level of contamination based on single metal. To estimate sediment quality based on a combination of several heavy metals using a contamination degree (Cd), the potential ecological risk index (RI) and pollution load index (PLI) [5,9,12,13,15]. According to this method, the single and integrated indices can be calculated via the following equations:

\[
\text{Ef} = \frac{(C_{\text{Fe}})_{\text{sample}}}{(C_{\text{Fe}})_{\text{standard}}} \tag{1}
\]

\[
C_f = \frac{C_i}{C_{\text{Fe}}} \tag{2}
\]

\[
I_{\text{geo}} = \log_2 \left[ \frac{C_i}{1.5 \times C_{\text{Fe}}} \right] \tag{3}
\]

\[
E_r = T_r \times C_f \tag{4}
\]

\[
C_{\text{cd}} = \sum_{i=1}^{m} C_f^i \tag{5}
\]

\[
RI = \sum_{i=1}^{m} E_r^i \tag{6}
\]

\[
\text{PLI} = \sqrt[\sum_{i=1}^{m} C_f^2} \tag{7}
\]

Ef is the enrichment factor for heavy metals in sediment, C a metal concentration in the sample and unpolluted sediments, and Fe was the content of Fe in a sample and unpolluted sediments. Fe selected as an element for normalization because of its high concentration in nature [8,16]. Cf describes the condition of contamination caused by toxic substances in river sediment. Ci is the mean concentration of an individual examined, and Cn is the background concentration of individual metal. The criteria
for contamination factor its classification shows Table 2. Cd is a combined index used to describe the level of contamination of several toxic Thr criteria for contamination degree its classification shows Table 2.

Table 2. Criteria for enrichment factor, contamination factor, and ecological risk factor

| Ef   | Classification | Cf   | Classification | Er   | Classification |
|------|----------------|------|----------------|------|----------------|
| Ef<2 | No enrichment  | Cf<1 | Low            | Er<30| Slight         |
| 2≤Ef<5 | Moderate     | 1≤Cf<3 | Moderate     | 30≤Er<60 | Medium     |
| 5≤Ef<20 | Considerable | 3≤Cf<6 | Considerable | 60≤Er<120 | Strong     |
| 20≤Ef<40 | Very high    | Cf≥6  | Very high     | 120≤Er<240 | Very strong |
| Ef>40 | Extremely strong |      |                | Er≥240 | Extremely strong |

Er is a potential ecological risk index, where Tr is the response coefficient for the toxicity of single heavy metal, which is determined for As=10, Zn=1, and Cr=2 [17]. RI is a comprehensive potential ecological risk index. Table 3 shows Risk grades indexes and grades of potential ecological risk of heavy metal pollution. PLI is a combined risk index. PLI <1 means no pollution, PLI>1 is polluted, and PLI=0 is baseline level [18–20].

Table 3. Criteria for index of geo-accumulation, contamination degree (Cd), and the potential ecological risk index (RI)

| Cd   | Classification | RI   | Classification | PLI   | Classification |
|------|----------------|------|----------------|-------|----------------|
| Cd<m  | Low            | Cf<1 | Low            | Er<30 | Slight         |
| m≤Cd<2m | Moderate    | 1≤Cf<3 | Moderate     | 30≤Er<60 | Medium     |
| 2m≤Cd | Considerable  | 3≤Cf<6 | Considerable | 60≤Er<120 | Strong     |
| Cd>4m  | Very high     | Cf≥6  | Very high     | 120≤Er<240 | Very strong |
|       |                |      |                | Er≥240 | Extremely strong |

3. Result and discussion
Elemental data were validated by simultaneously analyzing reference material NIST 2704 buffalo river sediment. The validation results were shown in Figure 2. From this figure, it can be seen the ratio of the measured to certified. The analysis method was valid if the result was equal to or almost the same as the certificate value or ratio ~ are Some elements had zeta-score in range ±3 except Yb. From this result, the neutron activation analysis technique was a reliable method to determine the elements except Yb in the sediment.

Figure 2. Validation results of the NAA method using NIST SRM 2704 buffalo river sediment.
The content of elements in the sediments from four different monitoring locations along the Ciliwung river was presented in Table 4. From this table could be known the types of elements contained in the samples. The concentration of the elements is almost the same both sampled from Condet, Depok, Kelapa Dua, and Kalibata. Al, Ca, Fe, K, Mg, Mn, and Na concentrations more than 1000 µg/g, while other metals have concentrations lower than 100 µg/g. Arsenic concentration were in range of 6.83-8.18 ug/g, Cr: 36.53-54.33 µg/g, Sb:0.92 -1.52 µg/g and Zn : 205.56 – 243.73 µg/g.

The enrichment factor was calculated to determine the anthropogenic effect on sediment quality. The enrichment factor in the sediments from 4 different monitoring locations along the Ciliwung river was presented in Figure 3. From this Figure can be known that almost all elements (Al, Ca, Ce, Co, Cs, have enrichment factors \( \leq 1 \), that means no enrichment from these elements [12]. The enrichment factor for some heavy metals was \( 1 < \text{Ef} \leq 1 \) for As, Cr, Fe, Mn, Sb, and Zn, that means was minor enrichment [12]. The enrichment degree of As was highest, the range value of Ef was 2.34-2.81. It means that at all four sampling locations, it has been enriched by As at a moderate level [12]. This enrichment can be sourced from activities around the river, such as industrial waste and garbage disposal activities. The enrichment degree of Cr was lower than As, the range Ef was 1.57-2.51. Kalibata has Ef<2, while the other three locations the Enrichment factor was >2. The range enrichment factor of Sb 1.67-2.96.

The enrichment degree of Zn was lowest, the maximum was 2.17 (Condet) and minimum 1.85 (Kelapa Dua).

### Table 4. Elements content in the sediment from four sampling locations

| Elements | Condet | Depok | Kelapa Dua | Kalibata |
|----------|--------|-------|------------|----------|
| Al       | 35,890.50±17.60 | 3,129.90±16.00 | 33,004.30±26.00 | 53,278.60±599.00 |
| As       | 6.83±0.73 | 7.46±0.77 | 8.18±0.56 | 7.43±0.45 |
| Ca       | 14,546.60±150.50 | 6,352.90±153.90 | 7,505.80±59.70 | 11,940.80±51.40 |
| Ce       | 30.11±2.61 | 33.11±1.48 | 31.80±1.53 | 42.57±1.92 |
| Cr       | 54.33±0.95 | 49.06±1.11 | 52.62±0.86 | 36.53±1.38 |
| Co       | 42.12±0.45 | 36.29±0.47 | 36.53±0.40 | 35.27±0.48 |
| Cs       | 2.30±0.12 | 2.21±0.12 | 2.04±0.11 | 2.12±0.24 |
| Eu       | 1.27±0.03 | 1.18±0.04 | 1.22±0.03 | 1.72±0.08 |
| Fe       | 120,999±31.24 | 98,755±29.8 | 95,325±23.40 | 88,933±33.31 |
| Hf       | 3.46±0.12 | 4.04±0.12 | 3.46±0.12 | 4.21±0.24 |
| K        | 3,825.19±186.92 | 2,848.91±104.55 | 3,527.33±160.13 | 3,120.87±134.12 |
| La       | 22.96±0.45 | 28.47±0.36 | 26.37±0.32 | 26.82±0.32 |
| Mn       | 1,584.80±10.20 | 1,574.90±9.30 | 2,121.40±15.30 | 1,409.50±9.70 |
| Na       | 6,245.10±82.92 | 3,337.53±49.32 | 3,798.76±73.71 | 5,729.52±16.23 |
| Sb       | 1.04±0.24 | 0.98±0.14 | 1.52±0.10 | 0.92±0.15 |
| Sc       | 27.45±0.28 | 25.48±0.28 | 27.39±0.26 | 29.49±0.32 |
| Sm       | 6.20±0.20 | 10.41±0.50 | 6.41±0.21 | 6.82±0.15 |
| Ta       | 0.55±0.06 | 0.42±0.04 | 0.46±0.06 | 0.54±0.11 |
| Tb       | 0.65±0.06 | 0.66±0.07 | 0.72±0.07 | 0.65±0.10 |
| Th       | 5.32±0.18 | 5.99±0.18 | 5.92±0.16 | 7.48±0.27 |
| Yb       | 2.31±0.11 | 2.02±0.13 | 2.42±0.13 | 3.07±0.19 |
| Zn       | 241.65±6.04 | 206.11±5.55 | 205.56±3.69 | 243.73±7.67 |
Figure 3. Enrichment Factors of elements in the sediments from four sampling locations

The geo-accumulation index ($I_{geo}$) is used to determine and define metals contamination in sediments, while contamination factor (Cf) and the degree of contamination (Cd) were used to determine the contamination status of sediment in the study area. Geo-accumulation index, contamination factor, contamination degree, and pollution load index were list in Table 5. Combine some heavy metals contained in sediments, evaluated based on the calculation of the combined index, which includes: contamination degree, pollution load index, and potential toxicity response index for various heavy metals in the sediment.

Table 5. Pollution index of heavy metals in sediment

| Element | Condet $I_{geo}$ | Condet Cf | Depok $I_{geo}$ | Depok Cf | Kelapa dua $I_{geo}$ | Kelapa dua Cf | Kalibata $I_{geo}$ | Kalibata Cf |
|---------|------------------|-----------|-----------------|---------|----------------------|--------------|-------------------|------------|
| As      | 0.09             | 0.46      | 0.10            | 0.50    | 0.11                 | 0.55         | 0.10              | 0.50       |
| Cr      | 0.12             | 0.60      | 0.11            | 0.55    | 0.12                 | 0.58         | 0.08              | 0.41       |
| Zn      | 0.28             | 1.38      | 0.24            | 1.18    | 0.24                 | 1.17         | 0.28              | 1.39       |

Contamination degree 2.44 2.22 2.30 2.29
Pollution load index 0.38 0.32 0.37 0.28

Annotation: In Table 5, $I_{geo}$ stands for the geo-accumulation index, and Cf stands for contamination factor

According to the calculation result (Table 5), geo-accumulation index in sediment for all location and all metals As, Cr, Zn had value $0 < I_{geo} \leq 1$. Evaluation based on standard had from unpolluted to moderately polluted by these metals [10,20].

The contamination factor for As and Cr were lower than 1, that means in four locations had low contamination by As and Cr. Sediment has contaminated by Zn at a moderate level, this is indicated by the value of the contamination factor was $1 \leq Cf \leq 3$ [19]. The range of Zn contamination factor was 1.17-1.39.

Contamination degree is the sum of all contamination heavy metals in sediment, used to describe the level of some toxic heavy metals in sediment, while the pollution load index is used to estimate the level of pollution from the combination of several toxic heavy metals in sediment. From Table 3. can be known that contamination degree from As, Cr and Zn were $< 3$ [19], this means that the level of
contamination because they combine three metals are still low. The range of pollution index was 0.28 – 0.38. This index value low than 1, this means that in all four locations, it has not been contaminated by a combination of all three metals As, Cr and Zn.

The purpose of ecological risk assessment is to assess the ecological effects of human activities through scientifically credible evaluation (chemical assessment and individual bioassay) to protect and manage the environment. The assessment of ecological risks of heavy metals in the sediment samples was done using the Ecological Risk Assessment (Er) and Risk Index (RI). Potential ecological risk indices and potential toxicity response indices of heavy metals in the sediment along Ciliwung river was shown in Table 6.

| Location | Potential ecological risk indices for single heavy metals (Er) | Potential toxicity response indices of heavy metals (RI) |
|----------|---------------------------------------------------------------|--------------------------------------------------------|
|          | As Cr Zn                                                     |                                                        |
| Condet   | 9.54 1.40 -0.38                                              | 10.56                                                  |
| Depok    | 9.50 1.45 -0.18                                              | 10.78                                                  |
| Kelapa Dua| 9.45 1.42 -0.17                                              | 10.70                                                  |
| Kalibata | 9.50 1.59 -0.39                                              | 10.71                                                  |
| average  | 9.50 1.47 -0.28                                              | 10.69                                                  |

In this table, the potential ecological risk indices of As, Cr, and Zn in four locations were lower than 40 [21], which indicated low potential ecological risk of all three metals in 4 locations. The potential toxicity response indices of heavy metals on all four locations almost the same were the range of 10.56-10.78. The RI average was 10.69. This value was lower than 150 [21]. According to the evaluation standard, all location had low ecological risk.

4. Conclusion
Evaluation based on the calculation of single and combined element pollution index shows that at the four sampling locations has occurred minor enrichment by metals, Cr, Fe, Mn, Sb, and Zn. Sampling locations were in unpolluted conditions to moderately polluted by As, Zn, and Cr metals. All four locations, it has not been contaminated by a combination of all three metals As, Cr and Zn.

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References
[1] Satmoko Y 2010 Kondisi Kualitas Air Sungai Ciliwung di Wilayah DKI Jakarta Ditinjau dari Parameter Organik, Amoniak, Fosfat, Deterjen dan Bakteri Coli J. Air Indones. 6 34–42
[2] Islam M S, Ahmed M K, Raknuzzaman M, Habibullah -Al- Mamun M and Islam M K 215 Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country Ecol. Indic.
[3] Cheung K C, Poon B H T, Lan C Y and Wong M H 2003 Assessment of metal and nutrient concentrations in river water and sediment collected from the cities in the Pearl River Delta, South China Chemosphere
[4] Rahman M S, Saha N, Molla A H and Al-Reza S M 2014 Assessment of Anthropogenic Influence on Heavy Metals Contamination in the Aquatic Ecosystem Components: Water, Sediment, and Fish Soil Sediment Contam.
[5] Mohammed F K, Sieuraj J and Seepearsaud M 2017 A preliminary assessment of heavy metals in sediments from the Cipero and South Oropouche Rivers in Trinidad, West Indies Environ.
[6] Mulyaningsih T R and Suprapti S 2016 Penaksiran Kontaminasi Logam Berat dan Kualitas Sedimen Sungai Cimadur, Banten *Gnendra Maj. IPTEK Nukl.*

[7] Bounouira H, Embarch K, Amsil H, Bounakhlia M, Foudeil S, Ait Ilyazidi S, Benyaich F, Haddad M and Said F 2018 Study of heavy metal assessment in the Gharb plain along Sebou river (Morocco) using k0-NAA method at the Moroccan Triga Mark II research reactor *Ann. Agrar. Sci.*

[8] Harikumar P S and Jisha T S 2010 Distribution pattern of trace metal pollutants in the sediments of an urban wetland in the southwest coast of India *Int. J. Eng. Sci. Technol.*

[9] Islam M S, Ahmed M K, Habibullah-Al-Mamun M and Hoque M F 2015 Preliminary assessment of heavy metal contamination in surface sediments from a river in Bangladesh *Environ. Earth Sci.*

[10] Awadh S M 2018 A preliminary assessment of the geochemical factors affecting groundwater and surface water quality around the rural communities in Al-Anbar, Western Desert of Iraq *Environ. Earth Sci.*

[11] Ali M M, Ali M L, Islam M S and Rahman M Z 2016 Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh *Environ. Nanotechnology, Monit. Manag.*

[12] Elias M S, Hamzah M S, Rahman S A, Salim N A A, Siong W B and Sanuri E 2014 Ecological risk assessment of elemental pollution in sediment from Tunku Abdul Rahman National Park, Sabah *AIP Conference Proceedings*

[13] Rocha F R, Silva P S C, Castro L M, Bordon I C C L, Oliveira S M B and Fávaro D I T 2015 NAA and XRF technique bottom sediment assessment for major and trace elements: Tietê River, São Paulo State, Brazil *J. Radioanal. Nucl. Chem.*

[14] Moon J H, Kim S H, Chung Y S, Lee Y N, Kim H J and Kim Y E 2008 Determination of the elemental contents in stream sediments collected from Cheongiu city by instrumental neutron activation analysis *Anal. Chim. Acta*

[15] Banu Z, Chowdhury M S A, Hossain M D and Nakagami K 2013 Contamination and Ecological Risk Assessment of Heavy Metal in the Sediment of Turag River, Bangladesh: An Index Analysis Approach *J. Water Resour. Prot.*

[16] Mireles F, Davila J I, Pinedo J L, Reyes E, Speakman R J and Glascock M D 2012 Assessing urban soil pollution in the cities of Zacatecas and Guadalupé, Mexico by instrumental neutron activation analysis *Microchem. J.* 103 158–64

[17] Hakanson L 1980 An ecological risk index for aquatic pollution control.a sedimentological approach *Water Res.*

[18] Suresh G, Sutharsan P, Ramasamy V and Venkatachalapathy R 2012 Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India *Ecotoxicol. Environ. Saf.*

[19] Vu C T, Lin C, Shern C C, Yeh G, Le V G and Tran H T 2017 Contamination, ecological risk and source apportionment of heavy metals in sediments and water of a contaminated river in Taiwan *Ecol. Indic.*

[20] Salem D M S A, Khaled A, El Nemr A and El-Sikaily A 2014 Comprehensive risk assessment of heavy metals in surface sediments along the Egyptian Red Sea coast *Egypt. J. Aquat. Res.*

[21] Pejman A, NabiBidhendi G, Ardestani M, Saeedi M and Baghvand A 2015 A new index for assessing heavy metals contamination in sediments: A case study *Ecol. Indic.*