Effect of redox gradients on Cu and Zn concentrations in water of Blanakan River, West Java

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Abstract. Metal concentrations in water threat adjacent ecosystems due to the potential of metal mobilization and the subsequent uptake into water. Here, contents of heavy metals Cu and Zn were determined for river waters. We used factorial analysis (FA) to determine the metal contents in relation to environmental factors such as redox potential (Eh), dissolved oxygen (DO), pH, salinity, temperature and turbidity in the Blanakan river. The Zn was ranging from 0.44 to 2.13 mg/L. The FA categorized Zn with salinity and temperature. Meanwhile, the Cu was ranging from 0.02 to 0.05 mg/L. The FA categorized Cu with Eh, turbidity, DO and pH. Such discrepancy in metal concentrations highlighted that redox gradient has more effects on Cu than Zn. Respectively, decrease of Eh from -38 to -41 mV can increase the Cu up to 0.05 mg/L. Correlation of Eh with Cu contents indicating that Cu was influenced by terrestrial inputs. Conversely, correlation of temperature and salinity with Zn contents indicating that Zn was influenced by aquatic inputs.

Keywords: heavy metals, gradients, redox

1. Introduction
Heavy metal contents in environment are known influenced by surrounding environmental parameters. Correspondingly, redox (reduction and oxidation/Eh) potential has been acknowledged as one of important environmental parameters that influenced heavy metal. The pH and Eh of surface waters and sediments are important to the regulatory processes affecting the solubility of heavy metals and their distribution among various geochemical forms. Changes in pH or Eh of a sediment water system can result in chemical transformations of metals between geochemical forms affecting their availability to aquatic and benthic organisms [1]. The increasing of Eh (from +400 mV to +503 mV) resulted in a rise of solubility of heavy metals in all sediments [2]. Such increase in Eh led to a solubility of about 1% of Cr, Cu, Pb, and Zn. The Eh gradients are known having different effects on Cu and Zn contents. For example, Eh has more correlations with Cu rather than Zn [2, 16].

The relations of heavy metal and redox gradients were also observed in the aquatic environment [3]. In the aquatic environment, water is a major vector of transport of heavy metals in the lithosphere. The solids present in soils, aquifers and surface water bodies can trap significant quantities of toxic heavy metals and act as reservoirs in the various hydro cycles taking place at the earth’s surface. Respectively, pH and Eh conditions are prominent variables controlling the potential release of stored...
pollutants to the aqueous phase and therefore their dispersion in the environment and their availability to biota.

River pollution in Indonesia, especially in Java island has been reported intensively. For example, the Cr, Cu, Pb and Zn in Angke, Ciliwung, Sunter, Cakung and Bekasi rivers have exceeded the Canadian Standard for Contaminated Sediments [4, 5]. The recorded ranges for Cr, Cu, Pb and Zn in those rivers were 24-290 mg/kg, 63-157 mg/kg, 28-198 mg/kg and 150-910 mg/kg. While the thresholds according to Canadian Standard for Contaminated Sediments were 90 mg/kg for Cr, 197 mg/kg for Cu, 91 mg/kg for Pb and 315 mg/kg for Zn [17].

However, a study emphasizing on relationship between heavy metals with Eh in water mainly in river is still limited. Hence, this research aiming to study the Cu and Zn concentration over Eh gradients in water of Blanakan river, West Java. Blanakan river is known as an important river. This river provides water for every requirement. Thus, a research confirming the relationship of Eh gradients with Cu and Zn contents will provide significant contributions for mitigations of heavy metal contamination in river.

2. Methodology
The samples were collected from 9 stations that located along Blanakan river. The sample collection activities were conducted in April 2019. The samples that collected and measured directly from the river were water for heavy metal, redox (Eh), dissolved oxygen (DO), pH, salinity, temperature and turbidity [6]. Moreover, the waters were sampled, transported and analysed in the laboratory for measuring the heavy metal contents.

2.1. Study site
The Blanakan river is located in Subang district, West Java province. The station geocoordinates were from upstream at latitude: -6.277444, long: 107.6599 (station 1) to downstream (river mouth) latitude: -6.240083, long: 107.667472 (station 9) (figure 1). The geocoordinates of stations were recorded using hand held GPS Garmin Etrex and mapped by using Geographical information system (GIS) software (ArcView 3.3).

![Figure 1. The location of 9 stations across the Blanakan river.](image-url)
2.2. **Physico-chemical parameters**

The parameters including Eh, dissolved oxygen (DO), pH, salinity, temperature and turbidity were measured directly in the field. DO and temperature measured using DO meter (Lutron DO 5510), pH and Eh with pH and ORP (oxidation/reduction potential) meter (Lutron PH 208), salinity with refractometer (Atago) and turbidity with turbidity meter (Ezdo TUB-430) respectively.

2.3. **Heavy metal sampling and analysis**

Water were sampled from the river and put in the polyethylene bottle. The bottle was cleaned and sterilized from any contaminants including metal contents. The bottle containing water then transported by using cooler box to the laboratory. In the laboratory, water samples then analysed by using atomic absorption spectrophotometer (AAS) Shimadzu 6300 with detection limit up to 0.01 mg/L.

2.4. **Statistical and factorial analysis**

Factorial analysis was used to analyse the relationship of Cu and Zn with Eh gradients. For statistical analysis, the 9 stations were grouped into 3 group, they are upstream (station 1,2,3), middle (station 4,5,6) and downstream (station 7,8,9). Furthermore, the average, minimum and maximum values of Cu, Zn and Eh are visualized by using box plots. The statistical and factorial analyses were performed using XLStat software.

3. **Results and Discussion**

The average maximum and minimum concentration of Cu and Zn in water were summarized in Figure 2 and 3. The contents for Cu and Zn from water in all parts of Blanakan river have not exceeded the permissible limit issued by WHO [6], which is 2 mg/L for Cu and 5 mg/L for Zn [6]. For Cu, the content was lower in the downstream and higher in the upstream. The high Cu content near the upstream related to the existence of settlement in that areas. Cu particulates are released into the water through volcanic eruptions and anthropogenic sources. Conversely, Zn content was higher in the downstream than in upstream. The Zn order in water was downstream > middle > midstream. The Zn ranges was 0.44-2.13 mg/L.

![Figure 2](image-url)

**Figure 2.** The box plots of Cu (mg/L) (left) and spatial gradient of Cu (mg/L) (right) in Blanakan river. The x axis is the locations of stations in Blanakan river (upstream, middle, downstream) and the y axis is the contents of Cu (mg/L) in water.
The Figure 4 summarizes the Eh value. From the results, the upstream has poor Eh value (more negative). In contrast, the downstream has better Eh value. The Figure 5 explains the pH, DO, temperature and salinity values in Blanakan river. In general, those parameters have value higher in downstream than upstream.

The Factor Analysis (FA) (figure 6, table 1) has been applied to determine the correlation between the partition of Cu and Zn and environmental factors such as Eh, DO, pH, salinity, temperature and turbidity. The FA results suggest that heavy metals and environmental parameters could be grouped into 2 factors (table 1). The first factor components showed a correlation of Zn with temperature and salinity. Meanwhile, the second factors showed correlation of Cu with Eh, DO, pH and turbidity.

Figure 3. The box plots of Zn (mg/L) (left) and spatial gradient of Zn (mg/L) (right) in Blanakan river. The x axis is the locations of stations in Blanakan river (upstream, middle, downstream) and the y axis is the contents of Zn (mg/L) in water.

Figure 4. The box plots of Eh (mV) in Blanakan river. The x axis is the locations of stations in Blanakan river (upstream, middle, downstream) and the y axis is the values of Eh (mV) in water.
The correlation of Cu with Eh indicates that the Cu contents in water is influenced by redox gradients. The content of metal was increasing along with decreasing redox potential [7]. In this research, when the redox was decreasing from -38 to -41 mV (figure 4), the Cu was increasing from 0.03 to 0.05 mg/L (Figure 2). When the redox has positive value, the Cu in water was decreasing. This trend was also observed from other studies. For instance, when the Eh changed from -343 mV toward positive values equal to -175 mV, the Cu was reduced [17]. The low Cu in water happens because Cu was bound in sediments. Positive redox value will reduce the mobility of sediment-to-water of Cu [2]. Moreover, Cu is also known as a metal with low mobility [14]. Correlation of Cu with Eh and lack of correlation of Cu with temperature and salinity indicating that terrestrial inputs strongly contributed to the distributions of Cu. Respectively, high Eh values were related with the high turbidity. In Blanakan river, Eh and turbidity parameters were in one group with Cu (Figure 6). Hence, the Cu was influenced by anthropogenic inputs [12]. These terrestrial inputs from nearby upstreams and river banks have also contributed to the increase of turbidity and Eh in river [13].

![Figure 5](image_url)

**Figure 5.** The box plots of pH, DO (mg/L), temperature (°C) and salinity (ppt) in Blanakan river

However, for such correlation was not observed for Zn. The lack of Zn correlation with Eh has been reported previously. From the samples collected from the river, Eh was not directly correlated
with any types of metals [8]. Nonetheless, Zn has correlation with salinity and temperature parameters (figure 5). Zn is known as a metal that has correlation with temperature and salinity, but not with Eh and DO [9,10]. At high temperature, the release rates of metals were increased more rapidly than at low temperature. The release of Zn, Cu, Cr, and Pb appeared to increase [11]. For example, when the water temperature increasing from 30 to 35 °C, the Zn increased from 0.48 to 0.49 mg/L [15]. In this research, the temperature increase was followed by increase of Zn value. Increase of temperature from 25 to 29 °C influenced the increased of the Zn up to 2.1 mg/L.

**Figure 6.** The graphical plots of Cu, Zn, Eh and physico-chemical parameters in Blanakan river

**Table 1.** The factor analysis of Zn, Cu, Eh and physico-chemical parameters

| Physico-chemical parameters | Factor 1 | Factor 2 |
|-----------------------------|----------|----------|
| Salinity                    | 0.709    | -0.538   |
| Turbidity                   | -0.731   | 0.588    |
| pH                          | -0.379   | 0.723    |
| Temp.                       | 0.051    | -0.579   |
| DO                          | 0.114    | 0.952    |
| Eh                          | -0.756   | -0.600   |
| Zn                          | 0.553    | -0.044   |
| Cu                          | -0.875   | -0.203   |

4. **Conclusions**
Cu and Zn contents were still below permissible limits of WHO. The Cu content in Blanakan river was influenced by the redox gradients. Conversely, the Zn content in Blanakan river was more influenced by the temperature gradients rather than Eh. Positive correlation of Cu with Eh indicating that terrestrial inputs strongly contributed to the distributions of Cu.

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