Accumulation of Heavy Metals Pb, Cu, Zn in the Water and Sediment in Cirebon and Demak

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Abstract. Industrial activity in the northern coast of Java continues to increase in fulfilling the human needs, along with the increase of the population. The impact of this activity includes heavy metal wastes that flow into the sea. This research aims to explain the heavy metal content of Pb, Cu, Zn in the sediment and water. The research was conducted in January, February, and March 2017 in Cirebon and Demak waters. Examples of water and sediment were taken by purposive sampling method, at three observation points from each location. The water sample was taken directly using a polyethylene bottle at 1-10 cm water deep, meanwhile the sediment sample was taken using a plastic-coated shovel. Heavy metal analysis was performed using AAS (Atomic Absorption Spectrophotometry) with the wavelength of Cu metal is 324.754 nm, Pb = 217.005 (nm) and Zn = 213.857 (nm). The results showed that the heavy metal content of Pb, Cu, Zn in water was below the quality standard. The average of heavy metal content of Pb, Cu, Zn in Cirebon water was 0.21 mg / l, 0.02 mg / l, 0.042 mg / l and in Demak was 0.119 mg / l, 0.02 mg / l, 0.044 mg / l. The average Cu heavy metals in Cirebon and Demak waters had exceeded the ISQG of the CCME water quality index.

1. Introduction
Northern Java coastal waters is one of the waters in Indonesia bordered with the Kalimantan Strait. Northern Java coastal waters, especially in Cirebon and Demak are widely used for shipping, port, tourism, and fishery activities. Fishery is one of the main sectors for coastal communities, but these waters are also used as a place where waste for residents concentrates in the island of Java. Java island is experiencing a fairly rapid industrial growth, as of 2012, 72% of industrial areas in Indonesia are mostly concentrated in Java [1]. These growths have consequences for degradation of aquatic environment. The coastal water of Cirebon has been polluted by the activities of fishery activities, household wastes, garbages, and organic materials [2]. In addition, Cirebon Regency has been polluted by heavy metals Cu, Pb and Zn which exceed the quality standard, allegedly due to mining and agriculture activities [3]. On the other hand, Demak waters has been polluted by heavy metals of Pb,
Cd and Cr in seawater and sediment caused by industrial activities located at the border of Semarang and Demak [4]. Furthermore, Cu and Cd metals existing in water and metals Pb, Cd, Cu, and Cr in sediments are suspected to be derived from volcanic, shipping, and agricultural activities [5].

The heavy metals in the water column will be suspended along with suspended solids at the bottom of the water. Heavy metal will be undegradable, so it will continue to exist in nature [6]. Increasing metals concentration in sediments will have an effect on benthic animals and will increase through bioaccumulation and bio magnification processes, which may endanger the ecosystem [7]. Monitoring activities are should be conducted in coastal area management. Therefore, this research is expected to provide information about the heavy metal content in sediment and water.

2. Data and Methods
This research was conducted in January-March 2017 in the waters of Cirebon and Demak (Figure 1). This research used quantitative descriptive analysis. Location of Cirebon and Demak waters then divided into 3 stations that are considered to represent each region. We used average values from those 3 stations to figure out the condition each month. Water samples and sediments were tested using AAS (Atomic Absorption Spectrophotometry) method at LPPT Laboratory of UGM Yogyakarta with the wavelength of Cu metal was 324,754 nm, Pb’s was 217,005 (nm) and Zn’s was 213,857 (nm). Sedimentary water samples were taken at low tide. Water sampling was taken on surface water with a depth of 0-10 cm using a 250-ml polyethylene bottle (SNI 6989.59, 2008). The samples were then preserved using concentrated HNO₃ solution until reach pH value <2, then stored in a cooling box and subsequently brought to the laboratory for testing heavy metals [8]. Sediment samples were taken using a plastic coated shovel, aiming to avoid metal contamination in sediment with iron on a shovel. The sediment samples of 500 grams were taken with a thickness of ± 10 cm from the base surface and were placed in a plastic bag and stored in an ice box. After that, the sample was dried using an oven at 100°C for two days.
Figure 1. Water and Sediment Sampling Station in Cirebon and Demak waters

As a supporting analysis data, we used monthly average surface current pattern analysis during sampling (January - March 2017) in the northern waters of Java connecting Cirebon waters to Demak. We used the surface current velocity and meridional surface current model data from HyCOM (Hybrid Coordinate Ocean Model) with resolution of 0.08°, which were processed and displayed using GrADS (Grid Analysis and Display System) software. Meridional surface current shows a north-south direction of sea surface current which triggered by surface wind. Table 1 is an overview of the location of the research sample.

Table 1. Research Sampling Location

| Location | Station | Coordinate | Location Information |
|----------|---------|------------|----------------------|
| Cirebon waters | 1 | S06.75350° E108.60440° | Coastal Mundu Village, Mundu District, Cirebon Regency. This location is adjacent to the Mundu and Kaliwaga rivers, especially place for fishing activities. |
| | 2 | S06.73518° E108.58736° | Surrounding coastal waters, Lemahwungkuk District, Cirebon Regency. The location is close to the National Fishery Port Kebawan and place for tourism activity. |
| | 3 | S06.64807° E108.56174° | Mertasinga Village, North Cirebon District, Cirebon Regency. This location is adjacent to PPI Bondet, especially use for many activities of fishermen, agriculture and mining of natural stone. |
| Demak waters | 1 | S06.91758° E110.48329° | Bedono Village, Sayung District, Demak Regency. This location is adjacent to the port of Tanjung Mas Semarang and Kaligawe Industry. |
| | 2 | S06.81476° E110.54371° | Purworejo Village, Bonang District, Demak Regency. This location is adjacent to the Port of Morodemuak resulting in many shipping activities. |
| | 3 | S06.74098° E110.34623° | Bungo Village, Wedung District, Demak Regency. This location are well known as a place for many fishing and agricultural activities. |

3. Results and Discussions
3.1. Heavy Metal Pb, Cu, and Zn in Sea Water

Heavy metal Pb in seawater in the Cirebon waters was higher than that of in Demak waters. The mean concentration of Pb metal in Cirebon was 0.205 ppm and in Demak was 0.119 ppm (Table 2). Both locations have exceeded the Decree of State Minister of Environment [9] quality standard on sea waters for marine biota as well as for marine tourism. Pb metal in these two waters allegedly sourced from shipbuilding activities such as boat painting, boat engine repairs, and diesel fuel. Cu metals in both waters were <0.02 ppm. This value was still below the water quality standard for fish farming based on PP-RI No.82 / 2001 which is 0.02 ppm. Zn metal in Demak waters was higher than in Cirebon, but there was only slight difference. The concentration of Zn metal in Demak was 0.043 ppm and Cirebon was 0.042 ppm. The average value of Zn metal in Cirebon and Demak were below the seawater standard for marine biota, respectively.
Most of the Pb, Cu, and Zn metals in the water are diluted by the river currents. Heavy metals in estuary areas are strongly influenced by river currents and salinity [10]. The small value of metal in water does not mean there is no heavy metal in the waters. This condition was caused by heavy metal content concentrated or trapped in the sediment.

### Table 2. Results of analysis of heavy metals Pb, Cu, and Zn in seawater

| Station | Pb (ppm)        | Cu (ppm)        | Zn (ppm)        |
|---------|-----------------|-----------------|-----------------|
| Cirebon January | 0.392 ± 0.169 | <0.02 ± 0.00 | 0.05 ± 0.018 |
| waters February | <0.096 ± 0.00 | <0.02 ± 0.00 | 0.03 ± 0.013 |
| March | 0.127 ± 0.027 | <0.02 ± 0.00 | 0.047 ± 0.023 |
| Average | 0.205 ± 0.111 | <0.02 ± 0.00 | 0.042 ± 0.014 |
| Demak January | <0.096 ± 0.00 | <0.02 ± 0.00 | 0.057 ± 0.040 |
| waters February | <0.096 ± 0.00 | <0.02 ± 0.00 | 0.057 ± 0.003 |
| March | 0.164 ± 0.059 | <0.02 ± 0.00 | 0.017 ± 0.006 |
| Average | 0.119 ± 0.034 | <0.02 ± 0.00 | 0.043 ± 0.023 |

Decree of State Minister of Environment (2004) 0.008* 0.008* 0.05*

### 3.2. Heavy Metal Pb, Cu, and Zn in the Sediment

The results of sediment conditions analysis in Demak and Cirebon waters were compared with the ANZECC / ARMCANZ sediment guidelines from Australia and New Zealand and the Canadian Council of Ministry of Environment from Canada [11] were presented in Table 2. References to both sediment quality guidelines this is done because Indonesia does not have quality guidelines for sediment. The mean values of Pb, Cu and Zn metal in sediment are below the standard of ANZECC / ARMCANZ. Referring to the CCME quality standard the concentrations of Pb and Zn metals are also below the quality standard, but Cu concentrations in all stations have passed the ISQG. Based on the comparison with the quality standard guidelines, Cu heavy metals begin to be at risk for the quality of the aquatic environment, this should be wary of the heavy metals that can accumulate in the body of marine life, such as shells.

The average heavy metal Pb in sediment in Demak waters is higher than in Cirebon waters. The high content of heavy metal Pb in Demak waters is thought to be derived from activities at the Fishery Seaport (PPP) of Morodemak, Kaligawe Industry, and Tanjung Mas Semarang Port which flows into the waters of Sayung Demak. In Sayung sub-district polluted Pb metal derived from industrial activity in Kaligawe which discharges its waste into marine waters through the flow of the river Sayung and the influence of currents and winds that bring it up to the mouth of the river Sayung [12]. The presence of heavy metal content in sediments in Cirebon waters is allegedly sourced from activities at the Fishery Port of Nusantara (PPN) of Resistance and shipbuilding activities in PPI Bondet.

Cu metal content in Cirebon waters was higher than in Demak. Cu metal content in the waters of Cirebon is allegedly derived from volcanic activity, mining and agriculture in the upstream. This was due to the high suspended materials from the Mundu River and Kalijaga Cirebon, which receive the flow from the Ciremai River Basin and causes the waters to become turbid [13]. Furthermore, it received a watershed flow from the Palimanan area. In Palimanan area there are many limestone mountains used for mining activities of natural stone. The heavy metal content of Cu in Demak waters was caused by natural activities such as erosion and agriculture. The extent of agricultural land in
Wulan Demak river basin was thought to be the source of Cu metal carried by the river [13]. Also suspected in the vicinity of the river, there were many activities of fishing boats and shipbuilding that produce Cu metal waste. In addition, the high Cu metal in the sediments was thought to be caused by volcanic activity [5].

| Table 3. Result of analysis of heavy metals Pb, Cu, Zn in Sediments |
|------------------|------------------|------------------|------------------|
| Station          | Month            | Pb (ppm)         | Cu (ppm)         | Zn (ppm)         |
| Cirebon waters   | January          | 11.86 ± 2.04     | 28.203 ± 9.337   | 58.423 ± 2.63    |
|                  | February         | 13.263 ± 1.28    | 56.643 ± 25.495  | 56.377 ± 2.15    |
|                  | March            | 12.343 ± 1.79    | 21.29 ± 4.51     | 57.137 ± 1.74    |
|                  | Average          | 12.49 ± 1.53     | 35.38 ± 15.97    | 57.31 ± 1.96     |
| Demak waters     | January          | 11.337 ± 2.14    | 5.077 ± 2.36     | 57.587 ± 2.09    |
|                  | February         | 15.54 ± 1.03     | 21.54 ± 2.07     | 56.43 ± 2.015    |
|                  | March            | 14.2 ± 1.41      | 28.203 ± 2.54    | 59.637 ± 0.98    |
|                  | Average          | 14.73 ± 1.92     | 24.21 ± 2.53     | 57.88 ± 1.686    |
| ANZECC/ARMCANZ, 2000 | Low     | 50               | 65               | 200              |
|                  | High             | 220              | 270              | 410              |
| CCME, 1998       | ISQG             | 30.2             | 18.7             | 124              |
|                  | PEL              | 112              | 108              | 271              |

The average concentration of Zn metal in Demak waters was higher than in Cirebon waters, although only 0.5 ppm difference. The high content of heavy metal Zn in Demak waters was due to industrial activity in the Kaligawe river. The high content of heavy metals Zn in Cirebon waters allegedly sourced from volcanic activity, shipping, domestic waste, and industry. In addition, the density of population activity around the two waters resulted in the amount of garbage causing the contamination of heavy metals Zn.

3.3. The Comparison of Heavy Metals Pb, Cu, and Zn in Seawater and Sediment

In general, based on the comparison between the heavy metal content in water (Table 2) and in the sediment (Table 3), it can be seen that the heavy metal content in the sediments was much larger than in water (Figure 2). This was consistent with the statement that heavy metal content in the sediments is much greater than in water due to deposition and sedimentation factors [15]. In addition, heavy metal content in sediments is much more toxic due to accumulation of organic and inorganic substances that are easier to occur in sediments than in water [16].
Figure 2. Comparison of the average content of heavy metals in water and sediments in the waters of Cirebon and Demak

3.4. Surface Current Pattern Analysis
Circulation and surface current due to wind patterns and geometric topography of the sea also play a role in the distribution of heavy metals distribution [17]. Unlike the concentration of surface-heavy metals that tend to be influenced by various factors such as patterns of currents that can disperse heavy metals in water at sea level in all directions [18]. Based on some of these studies, to see more clearly the direction of the distribution of heavy metals in the waters of Cirebon and Demak, then analyzed the current pattern of HyCOM satellite imagery at the time of sampling in the location, from January to March 2017.

Based on Figure 3, from January to March 2017, it can be seen that in general the surface current in Cirebon waters flows to south (negative value), meanwhile in Demak waters, the surface current flows to north (positive value). This was because the movement of surface currents follows the direction of wind movement, which generally parallel to the shoreline. Heavy metal content in Cirebon waters possibly due to the accumulation of current flow from another coastal area which heading to south, to Cirebon waters. On the other hand, heavy metal content in Demak waters was more spread because they were heading to north, leaving Demak waters. This condition caused heavy metal content in Cirebon waters showed higher value than that of in Demak waters.

The highest current velocity occurred in February 2017 and the lowest surface current velocity occurred in March 2017 (Table 4). On the whole month, the overall surface velocity in Cirebon waters was generally lower than the current velocity in Demak Waters. This can lead to higher heavy metal content of Pb in water in Cirebon waters than that of in Demak. In addition, the weak current velocity in Cirebon waters also resulted in higher heavy metal content of Cu in sediments with a significant difference with Demak waters (11.17 ppm). The result of this study was corresponding to research conducted by [18] which stated that the increasing concentration of heavy metals especially Pb in the sediment was caused by weak seawater currents.

| Month       | Cirebon waters (1) | Demak waters (2) |
|-------------|---------------------|------------------|
| January 2017| 0.049 m/s           | 0.138 m/s        |
| February 2017| 0.059 m/s         | 0.168 m/s        |
| March 2017  | 0.030 m/s           | 0.067 m/s        |
4. Conclusions
The content of Pb metal in water in Cirebon was higher than in Demak, but in both waters it has exceeded the Decree of State Minister of Environment [9] quality standard. The content of Cu metal in sediments in Cirebon was higher than in Demak. Metals Pb, Cu and Zn on sediments in Cirebon and Demak under the standard of ANZECC / ARMCANZ, but referring to the CCME quality standard Cu metal concentrations have passed the ISQG, so we need to be aware. In general, the heavy metal content in the sediment is higher than in water. The higher content of heavy metals in Cirebon waters was possibly caused by the accumulation of surface current flow from another coastal area which heading to south, to Cirebon waters and also caused by weaker sea surface current velocity than that of in Demak waters.

Recommendations
It is expected to conduct further research in the Cirebon and Demak waters with longer time scales in order to be able to determine the conditions of heavy metals in water and sediments and able to illustrate the conditions of both waters throughout the year.

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