Analysis of Pb residues on seaweed *gracillaria* spp in Randusangan District, Brebes, Central Java, Indonesia

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Abstract. Heavy metal content in water always changes depending on lithology and disposal of contaminated waste. Heavy metals are difficult to decompose in water and are easily bound in sediment so that the more sediment accumulation, the greater the heavy metal content. Heavy metals have toxic effects on humans and other livings, accumulate in the body of an organism and stay for a long period. This compound can lead to a decrease in water quality which will affect the fishery and in pond cultivation. One of the important heavy metal pollutants is lead (Pb), which is usually came from many sources. The purpose of this study was to determine the concentration of lead in seaweed, pond water, and sediment. This research was conducted in March 2018 from 6 pond stations. This research was conducted using descriptive and statistic analysis. Analysis of Pb compound is done using AAS (Atomic Absorption Spectrophotometry). The results of the analysis of Pb content in seaweed ranged between 0.0163-0.1377 mg/ kg. Pb content in pond water range from 0.0087 -0.0137 mg / lt and the Pb content in sediment range between 1.2703-2.3594 mg/ lt. Based on the analysis, the Pb content is most abundant in sediments where the Pb content has exceeded the threshold value (SNI) of 0.3 mg/kg. Pb content on seaweed and pond water are still within the standard value of Pb metal contamination (BPOMRI No. 23 of 2013) which is 0.20 mg/kg. The relationship between Pb content in seaweed to the water is categorized as a weak (R = 0.073), it is similar to the seaweed with sediment (R = 0,28).

1. Introduction
The increase in industrialization, population and cultivation will result in increased pollution. Heavy metal content in water always changes depending on the time of disposal of waste. Heavy metals are bound in sediment and relatively difficult to decompose in water so that the more sediment, the greater the heavy metal content [1,2]. One of potential pollutant is heavy metal Pb. Heavy metals have toxic effects on humans and other livings. This compound can accumulate in the body of the organism and stay for a long period of time [3]. This waste can lead to a decrease in water quality which has an impact on the decline in the quality of pond commodities [2]. The concentration of Pb in the environment affected by the level of human activities, for example in industrial areas, on highways, cultivation and in landfills. Pb is widely used by human life as an ingredient in making ammunition batteries, metal products (sheet metal, solder and pipes), medical equipment (radiation detectors, and surgical instruments) paints, ceramics, practical scientific activity equipment for oil mixtures of ingredients to increase value octane [4]. Brebes Regency is one of the coastal areas which has wide pond areas, one of which is in the Randusanga District. Here, the main commodity of cultures is not only fish and shrimp but also seaweed. Besides aquaculture activities, this area is also used for industries, agriculture (paddy and onion) and settlement. Moreover, there is another land use in this...
wet area, namely Onion culture. This valuable commodity receives artificial compound in high number during farming practice, especially pesticides [5]. Transportation, farming practice and industries are the most likely activities contribute to the Pb sources of Pb in Brebes. The purpose of this study is to determine the concentration and relationship of lead metal in seaweed, pond water, and sediment.

2. Materials and Methods
This research was conducted in by March 2018. Seaweed, water and sediment samples were taken from the aquaculture area of Randusanga District, Brebes, Indonesia. The stations of the study were selected to represent the condition and land usage of the body water which are also considered the possibility of high heavy metal contamination. The sample is taken by purposive sampling. Samples of water, seaweed, and sediment were taken directly from six ponds in the Randusanga sub-district of Brebes Regency from landward direction to the coastal area. Many farmers apply polyculture technique in which fish is cultured together with seaweed, whereas others apply monoculture both fish, shrimp, and seaweed separately. The Station took as follows:

| NO | Station | Condition and land usage               |
|----|---------|---------------------------------------|
| 1  | St 1    | Pond close to the settlement           |
| 2  | St 2    | Polyculture pond with shrimp-seaweed   |
| 3  | St 3    | Polyculture Pond of milkfish-seaweed   |
| 4  | St 4    | Pond of seaweed (monoculture)          |
| 5  | St 5    | Pond with mangrove stand               |
| 6  | St 6    | Pond around coastline                  |

Analysis of Pb levels in water, sediment and seaweed were analyzed by using AAS (Atomic Absorption Spectrophotometry) at the Wahana Laboratorium Semarang. This research uses descriptive and statistic analysis. Descriptive analysis is chosen to identify the Pb values based on spatial and standard values. Statistic analysis is done to identify the relationship between Pb values to other parameters [6].

3. Results and Discussion
The concentration of Pb in water, sediment and seaweed are very respectively 0.0163-0.0,1377 mg/kg; 0.0087- 0.0137 ppm and 1.2703-2,3594 mg/kg. The highest value of Pb is found in sediment. This is consistent with the Kariada [7] finding, in which heavy metal concentration is highest in sediment compare to the plant tissue and waterbody. This can be explained that Pb content is fixed onto the substrate, mainly silt and loam through adsorption mechanism, as stated by Kumar [2]. This is similar to the finding of several researcher i.e. Saputra et al. [8] and Mulyadi et al. [9]. The second highest value is found in seaweed, which is in this case, grow in the floor of waterbody close to the deposited clay. This high value is also related to the capability of the seaweed to absorb and accumulate such toxic material within their body, as mention by Kumar et al. [2] and Mulyadi et al. [9]. The least content is observed from water regime, since its mobility and dilution mechanism working therein.

Data of the Pb content as mentioned in Table 1.

| No | Station | St 1 | St 2 | St 3 | St 4 | St 5 | St 6 | Standard |
|----|---------|------|------|------|------|------|------|----------|
|    | Pb Concentration (mg/kg) | 0.0163 | 0.0265 | 0.0538 | 0.0164 | 0.1377 | 0.0332 | 0.300     |
In term of spatial concentration, the highest value of Pb in seaweed is found in Station 5 as high as 0.1377 mg/kg, whereas the lowest is Station 2 as low as 0.0087 mg/kg (Table 2). Such a high number, however, is still under the government standard value i.e. 0.300 mg/kg. The highest content in Station 5 can explain that it is believed related to the higher mud substrate content. The occurrence of mangrove surrounding the pond can promote the accumulation of silt and clay in the floor [10]. Besides, isolated body water of the pond tends to reduce the weave and water current actions and so promote to the settlement of silt [7]. Darmono [1] and Kumar et al., [2] mentioned that the higher the mud accumulation, the higher the metal content. These will provoke sedimentation and so do the Pb accumulation. The least value of Pb is observed from Station 1 about 0.0163 mg/l. This can be explained that this pond is densely populated with seaweed and therefore the distribution of absorption is wider (effectively low in Pb accumulation) Seaweed take Pb compound from the substrate and therefore low in the Pb number [11]. Station 4 which apply monoculture with seaweed is similar to Station 1. Station 2, 3 and 6 tend to similar to Station 5.

In the body water, the highest number is consistent to the one in seaweed tissue; measured in Station 5; as high as 0.0137 ppm followed by Station 2 and Station 6 (0.012 ppm). This value is a little higher to the standard in water namely 0.01 ppm. Such higher values are related to the absence or least in seaweed population on these three stations. This is a response to the high Pb value in seaweed above. The least number occurs in Station 2 (0.0087 ppm) followed by Station 3 (0.0097 ppm). The pond on these stations used to culture fishes in a polyculture system and likely effective to absorb the Pb content.

**Table 3.** Average Pb concentration in water in the Randusanga pond in Brebes Regency

| No | Stations                              | St 1 | St 2 | St 3 | St 4 | St 5 | St 6 | Standard |
|----|--------------------------------------|------|------|------|------|------|------|----------|
|    | Pb Concentration (ppm)               | 0.0107 | 0.0087 | 0.0097 | 0.0123 | 0.0137 | 0.0120 | 0.01      |

Notes:
- Station 1. Pond close to the settlement
- Station 2. Polyculture pond with shrimp-seaweed
- Station 3. Polyculture Pond with Milkfish-seaweed
- Station 4. Pond of seaweed (monoculture)
- Station 5. Pond with mangrove stand
- Station 6. Pond around coastline

In table 3 shows that the highest Pb heavy metal content in sediment is found in station one as high as 2.3594mg/ l, then followed respectively by Station 3 and Station 5 (2.3320 and 2.2519 mg/kg). These numbers are lower than the standard (Government regulation no. 82 the year 2001) about water liability for fish culture. This high number is possible because the pollution of Pb mostly comes from the land areas such as industry and agriculture. Station 5 is high which is related to the present of mangrove stand which enables to trap sediment, as explain before Stations 1 and three are close to the river while station 5 goes forward to the coastal and estuary. To reduce such a higher number can be reduced by applying re-vegetation, especially mangrove as stated by Kariada [7]. Station 6 is the least
in Pb content which is related to the dilution from the sea water. Besides, the presence of current on the coastline reduce settlement of the sediment, a potential deposit of Pb compound.

**Table 4.** Average heavy metals in sediments in the Randusanga pond in Brebes Regency

| No | Stations                     | St 1    | St 2    | St 3    | St 4    | St 5    | St 6    | Standard |
|----|------------------------------|---------|---------|---------|---------|---------|---------|----------|
| 1  | Pb Concentration (mg/kg)     | 2.3594  | 1.8203  | 2.3320  | 1.8858  | 2.2519  | 1.2703  | 0.300    |

Note:
Station 1. Pond close to the settlement
Station 2. Polyculture pond with shrimp-seaweed
Station 3. Polyculture Pond with Milkfish-seaweed
Station 4. Pond of seaweed (monoculture)
Station 5. Pond with mangrove stand
Station 6. Pond around coastline

Figure 1. shows that the highest Pb heavy metal content is found in sediments, this is because the heavy metals that enter the environment will partly be absorbed into the substrate (sediment) and some will enter the river water flow system which will then be carried into the sea. Heavy metals carried by these streams will settle into the bottom of the water through sedimentation. This will cause aquatic biota feed in the waters will have a very large chance to be contaminated by heavy metals. The presence of Pb heavy metal concentrations detected in sediments indicates that the Pb heavy metal adsorption process has occurred, the higher the concentration of Pb heavy metals in sediment, the higher the absorption of Pb heavy metals in seaweed [11]

![Figure 1. The concentration of Pb in sediment, water, and seaweed](image-url)

The low heavy metal content is measured in the water which is possible because the water, especially in the pond dilutes and flows, so that the Pb heavy metal is not much concentrated. Heavy metal Pb is a toxic heavy metal that is accumulative so that its toxicity mechanism is divided into several organs that are affected, namely as follows: hemopoietic system; Pb inhibits hemoglobin
formation, causing anemia; central nervous system and edge; can cause peripheral nerve disorders; kidney system; can cause glucosuria, fibrosis, glomerular atrophy and so on [1, 9]. Pb can accumulate in living body tissues in water contaminated with Pb [13]. This is possible for Pb to contaminate more aquatic organisms such as fish, shellfish, shrimp, and crabs, but less contaminate the grass because the structure of the seaweed tissue is different from aquatic organisms. Based on the results of the analysis, the Pb content is most abundant in sediments where the Pb content has exceeded the threshold (SNI) of 0.3 mg/kg. Pb content on seaweed and pond water is still within the threshold of Pb metal contamination by BPOMRI No. 23 of the year 2013 which is 0.20 mg/kg. Pb content in water is also below the standard based on PP RI No. 82 of 2001 concerning Management of Water Quality and Water Pollution Control.
Physical and chemical factors are mention in Table 5. This showed of all factor are most suitable to the standard, except turbidity which is very high varies between 45.7 – 239.0. Turbid water can be trigger by current such as Station 6, and also drive by fish motion as in Station 2. The pH value, in general, is still under standard criteria, except Station 4. This is likely related to the domestic wastes from public facilities, i.e. school, which discharged quite a lot into the inlet. Inaccurate measurement likely happens in this peculiar pH data and should be re-check.

| Table 5. Physico-Chemical factors measured from the study areas |
| No | Physico-chemical factors | Station 1 | Station 2 | Station 3 | Station 4 | Station 5 | Station 6 | Standard |
|----|--------------------------|-----------|-----------|-----------|-----------|-----------|-----------|----------|
| 1  | Salinity (ppt)           | 22        | 23        | 25        | 24        | 27        | 28        | <20      |
| 2  | pH                       | 6,70      | 6,7       | 6,2       | 9,57      | 7,30      | 7,54      | 6-9      |
| 3  | Desolved Oxigen (ppm)    | 6,4       | 6,50      | 7,50      | 7,82      | 7,5       | 7,58      | >4       |
| 4  | Turbidity (NTU)          | 78,5      | 239,0     | 45,7      | 172,0     | 187       | 315       | <5       |
| 5  | Temperature (°C)         | 28,5      | 29,85     | 30,4      | 29-32     | 29,6      | 29        | Dev. 3   |

In term to the mathematical relationship between heavy metal content of Pb in water and seaweed showed there is an interaction between them. This can be explained that Pb in water is least taken by seaweed and likely tend to be adsorbed by sediment; as stated by Siahaan et al., [11]. Based on the results of statistical regression tests shows the correlation coefficient / R value is 0.073. This can be categorised as a weak correlation among Pb in water and Pb in seaweed. The value of R is 5% which indicates the effect of Pb on the water with Pb on seaweed is not fully influential. Meanwhile, the relationship between the heavy metal content of Pb in sediment with Seaweed is not related strongly. Regression statistical test between Pb heavy metals in sediment to the seaweed shows the correlation coefficient / R is 0.28. It can also be concluded that the correlation between Pb in water and Pb in seaweed is not strong based on R-square (0.08). It is mean that an R-value of 8% shows the effect of Pb on sediment with Pb on seaweed is not very influential. This is caused by the way seaweed take nutrient which is from water column rather than the substrate.

| Regression Statistics |
|-----------------------|
| Multiple R            | 0.27924     |
| R Square              | 0.077975    |
| Adjusted R Square     | 0.020348    |
| Standard Error        | 13.52489    |
| Observations          | 18          |

4. Conclusion
The Pb concentration of seaweed in Brebes is varied between 0,0163- 0,1377 mg/ kg which is still under the threshold value and is still liable as a food commodity, even though its concentration within
sediment and water are high. There is a weak relationship between Pb content in seaweed to the water (R = 0.073) and sediment (R = 0.28) which can be subjected to manage for fishes culture.

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