Potential of heavy metal contamination in cultivated red seaweed (*Gracilaria* sp. and *Eucheuma cottonii*) from coastal area of Java, Indonesia

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Abstract. Heavy metal is one of the widespread environmental contaminants in Indonesian coastal waters. These heavy metals have a potential negative impact on the aquatic organism and the people who consumed it. Most seaweed cultivation in Indonesia is located in urbanized estuaries, cultivated seaweed can accumulate contaminants such as heavy metals. This study focuses on the analysis of heavy metals such as lead (Pb) and cadmium (Cd) in *Gracilaria* sp. and *Eucheuma cottonii* from various cultivation areas in Java, Indonesia. The purpose of this study is to find out whether seaweed can pose a potential risk to consumers and know the source of heavy metal contamination. The Atomic Absorption Spectrometry (AAS) method was used to determine the heavy metal level in seaweed. These results indicate generally that heavy metal contents of seaweeds cultivated urbanized estuaries should be monitored since accumulation appears to be site-dependent. Seaweed that cultivated in locations around the industry with poor waste management has an impact on higher levels of heavy metal.

1. Introduction

Indonesia is the world’s largest archipelagic state with some 17,508 islands and 54,716 km of coastline, and the world’s fourth most populous nation (247.5 million). In 2012, Indonesia’s fishery production reached approximately 8.9 million tonnes, of which inland and marine catch accounted for about 5.8 million tonnes and aquaculture 3.1 million tonnes in addition to 6.5 million tonnes of seaweeds [1]. Seaweed is increasingly consumed as one of the dietary foods due to its abundance of natural vitamins, minerals, and plant-based protein [2]. For pacific countries, especially developing countries like Indonesia, large amounts of seaweeds are not only foods but also represent an important economic resource. The Food and Agriculture Organization (FAO) shows for 2015, Indonesia has emerged as the second largest aquaculture producer in the world after China [3,4], and the main cultured seaweeds were *Gracilaria* sp. and *Eucheuma cottonii*.

Recently, concern has been raised about possible heavy metals contamination in seaweeds. Population growth and industrial development along the coast have greatly influenced pollution loads into the coastal marine environment. Toxic heavy metals are one of the widespread environmental contaminants in Indonesian coastal waters. Based on several studies conducted in coastal areas, heavy metal contaminations are among the persistent issues in Indonesia [5]. Land-based activities are a major source of pollution in the coastal waters of Indonesia i.e. sources of metals derived from mining, petrochemical industry, printing, electronic industry, and municipal waste are ultimately discharged.
into the marine environment [6]. Elevated heavy metal contamination has been mostly recorded on the northern coast of Java Island [5].

Seaweeds can rapidly accumulate elevated concentrations of metals, such as lead (Pb) and Cadmium (Cd). In some conditions, seaweeds have been used as bioindicato"rs of metal pollution in estuarine and coastal waters [7–10]. Accordingly, these elements can be very damaging even at low levels when ingested over a long period of time and have a potential negative impact on the health of people who consume these seaweed products. Heavy metals accumulate in the fatty tissues and internal organs of human body, which may affect the central nervous system. The level of metal contaminants is an important determinant for the safety of edible seaweeds [11]. So, heavy metal evaluation is needed to find out more about the distribution of heavy metals in seaweed, especially seaweed in Java as the island with the largest population and industry in Indonesia.

2. Materials and methods

2.1. Study Sample

The types of seaweed samples used in this study were *Gracilaria* sp. and *Eucheuma cottonii*. These species are the main cultured seaweed in Indonesia and can be found at sites throughout the year. Both of these seaweeds have several advantages for fish farmers, i.e. having high economic value, large market opportunities and not requiring special treatment and costs. The differences between these seaweeds are place for cultivation. The cultivation of *Gracilaria* sp. can be cultivated along with shrimp and milkfish and can further optimize the use of pond. Generally, *Gracilaria* sp. is cultivated in the brackish pond area with a water base that has a type of sandy clay substrate [12], and for *Eucheuma cottonii*, it's cultivated grows most rapidly in areas of strong tidal currents, higher salinity (away from estuaries), bright light, with water base of sand, coral and rock [13].

Samples of *Gracilaria* sp. and *Eucheuma cottonii* were collected in the same ages, size and healthy in appearance. These samples were taken using the quadrant transect method. Transects are randomly placed at the specified station. Examples of seaweed taken as many as 3 replications and mixed into one. Seaweeds were rinsed thoroughly with water on-site and placed in plastic bags and transferred to the laboratory as soon as possible. Before further processing, samples were initially washed under a jet tap water and rinsed in distilled water to remove any particle.

2.2. Sampling area

All sampling sites have been selected based on level productivity. Sampling of seaweed was conducted from April – Mei 2019 and they were collected from 6 different stations along the coastline of the north Java Island. All sampling sites were to cover regions of Java Island including East Java, Central Java, and West Java (figure 1 and figure 2).

Figure 1. Location of seaweed sampling area. The square in the left map indicates the regional location of Java Island within the Indonesian archipelago.
For further details, *Gracilaria* sp. was taken from Muara Gembong, Bekasi District, West Java (b); Randusanga Kulon, Brebes District, Central Java (c); and Jabon, Sidoarjo District, East Java (e). For *Eucheuma cottonii* was taken from Tirtayasa, Serang District, Banten (a); Karimunjawa, Jepara District, Central Java (d); and Pademawu, Pamekasan District, East Java (f) (figure 2).

2.3. Determination of metal concentration

Seaweed is certainly clean of epiphytes, sand and mud particles. They were allowed to dry and then will be determined for heavy metal concentration. The response of this experiment is the level of 2 types heavy metal (Pb and Cd) that was measured by using Atomic Absorption Spectofotometry (AAS), which has a limit detection of 0.001 ppm. Flame atomic absorption spectroscopy, FAAS, is a well-known quantitative elemental analysis method for a wide range of samples. It is simple, inexpensive, rapid, and applicable to wide range of samples [14].

2.4. Data Analysis

Data analysis for this study was carried out statistically and descriptively. Statistical analysis was performed by SPSS with significant at p-value < 0.05. The mean values of three replicates were calculated. Descriptive analysis was performed by comparing observational data with natural conditions and previous research.

3. Results and discussion

3.1. Seaweed metal analysis

The results of heavy metal concentrations in *Gracilaria* sp. and *Eucheuma cottonii* samples that collected from Java Island region are shown in table 1 and table 2 for 3 stations each type. Lead (Pb) element concentrations in seaweed are higher than the cadmium (Cd) elements for each station whether in *Gracilaria* sp. or in *Eucheuma cottonii*.

Pb concentration of seaweed that cultivated in Java ranged from 0.230±0.035 mg/L to 0.794±0.013 mg/L. The lowest average Pb concentration was found in *Eucheuma cottonii*, from Karimun Jawa (substrate of sand and mixed coral) and the highest was in *Gracilaria* sp., from Sidoarjo (muddy sand substrate).
Table 1. Pb concentration for Gracilaria sp. and Eucheuma cottonii

| Type            | Origin                  | Concentration (mg/L) | Pb      | Cd      |
|-----------------|-------------------------|----------------------|---------|---------|
|                 |                         |                      | I       | II      | III     |
| Gracilaria sp.  | Sidoarjo, East Java     | 0.806                | 0.795   | 0.780   | 0.794±0.013 |
|                 | Brebes, Central Java    | 0.463                | 0.501   | 0.483   | 0.482±0.019 |
|                 | Bekasi, West Java       | 0.558                | 0.508   | 0.478   | 0.515±0.040 |
|                 |                         |                      |         |         |         |
| Eucheuma cottonii | Pamekasan, East Java  | 0.681                | 0.720   | 0.690   | 0.697±0.020 |
|                 | Karimun Jawa, Central   | 0.268                | 0.198   | 0.224   | 0.230±0.035 |
|                 | Java                    |                      |         |         |         |
|                 | Serang, Banten          | 0.453                | 0.498   | 0.462   | 0.471±0.024 |

The different result was found in Cd concentration. The concentration of Cd was found in 6 stations is not detected or in the lowest concentration. The highest Cd concentration in Gracilaria sp. is from Bekasi with 0.121 mg/L and 0.223 mg/L in Eucheuma cottonii from Pamekasan. This was due to some activities on the cultivation area estimated to contain more lead content than cadmium such as waste from the power stations, runoff from land, settlement, and boat transportation routes [15].

Table 2. Cd concentration for Gracilaria sp. and Eucheuma cottonii

| Type            | Origin                  | Concentration (mg/L) | Cd      | Pb      |
|-----------------|-------------------------|----------------------|---------|---------|
|                 |                         |                      | I       | II      | III     |
| Gracilaria sp.  | Sidoarjo, East Java     | 0.114                | 0.118   | 0.118   | 0.117±0.002 |
|                 | Brebes, Central Java    | 0.020                | 0.020   | 0.023   | 0.021±0.002 |
|                 | Bekasi, West Java       | 0.125                | 0.120   | 0.119   | 0.121±0.003 |
|                 |                         |                      |         |         |         |
| Eucheuma cottonii | Pamekasan, East Java  | 0.218                | 0.226   | 0.225   | 0.223±0.004 |
|                 | Karimun Jawa, Central   | 0.014                | <0.010  | <0.010  | 0.011±0.002 |
|                 | Serang, Banten          | 0.020                | 0.023   | 0.019   | 0.021±0.002 |

3.2. Potential risk of seaweed

Gracilaria sp. and Eucheuma cottonii are not only a valuable source of natural products for commercial importance but also the source of food for daily consumption. Seaweed is proved to be the rich source of minerals elements and recommended as food supplements to help meet the daily intake of essential mineral and trace elements [2]. Because of these benefits, in Indonesia, seaweeds are increasingly used for cuisines and can be eaten raw, cooked or processed.

Table 3. Pb and Cd concentration for seaweed in Indonesia

| Type            | Origin                  | Concentration (mg/L) |
|-----------------|-------------------------|----------------------|
|                 |                         |                      |
| Gracilaria verrucosa | Tegal, Central Java  | 0.209 – 0.326       | -        |
| Gracilaria sp.   | Sidoarjo, East Java     | 0.725                | -        |
| Eucheuma cottonii | Takalar, South Sulawesi | -                   | 1.980 – 2.419 |
| Eucheuma sp.     | Sumenep, East Java      | 0.018 – 0.027       | 0.129 – 0.131 |
| Eucheuma cottonii | Bantaeng, South Sulawesi | -                  | 0.182 – 0.292 |
| Caulerpa spp.    | Laikalang, South Sulawesi | 0.350             | <0.001   |
| Sargassum sp.    | Jepara, Central Java    | 0.220 – 0.790      | -        |

In some previous research, concentrations of Pb and Cd were shown in table 3 from several seaweeds such as Gracilaria sp., Eucheuma cottonii, Caulerpa spp., and Sargassum sp. which were collected from some locations in Indonesia whether cultivation or wild [16–23].
This study concerned with the potential risk seaweed to consumers. The appropriate limits for heavy metals in ‘fruits, vegetables, seaweed and cereals’ in Indonesia are set out in Badan Standarisasi Nasional (the National Standards Agency from Indonesia) 7387:2009 document ICS 67.220.20 governing about maximum limits for heavy metals contamination in food. In addition, other heavy metal limits have also been determined by other world authorized standards (table 4) [24]. There are five major heavy metals which have been determined the allowable limit, lead (Pb) and cadmium (Cd) are include. The national limit allowed in food stipulated by Indonesian law is 0.5 mgkg\(^{-1}\) for Pb and 0.2 mgkg\(^{-1}\) for Cd [24,25].

|                  | FDA (Total Daily Intake (TDI) mcg/day) | WHO/FAO (Provosional Tolerable Weekly Intake (PTWI) µg/kg body weight) | EU (mg/kg wet weight) | CA PROP 65 (mcg daily intake) | SNI (mg/kg) |
|------------------|----------------------------------------|-----------------------------------------------------------------------|------------------------|-------------------------------|-------------|
| Arsenic (As)     | -                                      | 15                                                                    | -                      | 10                            | 0.1         |
| Cadmium (Cd)     | -                                      | 25                                                                   | 0.05                   | 4.1                           | 0.2         |
| Lead (Pb)        | 75                                     | -                                                                    | 0.2                    | 0.5                           | 0.5         |
| Mercury (Hg)     | -                                      | 1.6                                                                   | 0.1                    | 0.3                           | 0.03        |
| Tin (Sn)         | -                                      | 14                                                                   | 50                     | -                             | 40          |

Figure 4 shown over all Pb and Cd concentration from *Gracilaria* sp. and *Eucheuma cottonii* in Java comparasion with other study. For the results, Cd that are covered in the Indonesian (BSN) limits concentrations found in this study were below the limits of detection (figure 3) both in *Gracilaria* sp. or in *Eucheuma cottonii*. Otherwise Pb is detected in some samples above the detection limit (figure 3).
Figure 3. Comparison of Pb and Cd concentration in *Gracilaria* sp. (a) (b) and *Eucheuma cottonii* (c) (d) in Java Island, Indonesia with the maximum limit by BSN

It is estimated that the normal consumption of the population will be less than 500 g of wet weight per household per day, although no accurate consumption measurements have been made. So, based on this estimated consumption pattern, there is a low level of heavy metals in this study, consumption of *Gracilaria* sp. or *Eucheuma cottonii* from aquaculture activities in Java does not pose a human health hazard. However, *Gracilaria* sp. which is cultivated in ponds that are directly adjacent to the source of waste or contaminants will contain more metal. Therefore, we propose that the location of the pond as a place for seaweed cultivation needs to be considered when cultivating *Gracilaria* sp.

3.3. Source of heavy metal in seaweed

Based on the results shown in the graph, only a few areas have detected a Pb concentration above the detection limit (figure 3). Based on several previous studies that explain the heavy metal contamination, waste effluents that directly flow into the waters will cause heavy metals to be carried towards the estuary and affect the quality of water used as a source of water from aquaculture activities.

The results of the highest Pb shown in the *Gracilaria* sp. that cultivated in Sidoarjo, East Java. Disposal of factory waste into the river causes changes in water quality. Pollution in the waters of Sidoarjo is increasingly alarming because of the discharge of waste from the Lapindo mudflow. One of the rivers affected by industrial waste and Lapindo mud discharge is the Porong river [26,27]. Seaweed Ponds in Sidoarjo received water from the Porong River which contained industrial waste and Lapindo mud which resulted in the transport of sediments carried to the sea. Lead levels are estimated to be different in each farm that receives water from the Porong River and from the sea which is included in one of these streams.

On the other hand, there is also a high Pb metal content in *Eucheuma cottonii* which is cultivated in Sumenep. This is related to the circumstances surrounding cultivation. The environment of seaweed cultivation which is far from contaminant sources will not pollute the cultivation location and will make seaweed not contaminated by heavy metals. Weather also affects the condition of heavy metals in seaweed cultivation. Heavy metals tend to follow the flow of water and the effect of dilution when there is incoming water, such as rainwater, also results in a decrease in the concentration of heavy metals in water. The concentration of heavy metals in water will also influence the concentration of heavy metals present in sediments. The tendency of increasing concentrations of heavy metals in sediments is caused by high concentrations of heavy metals in water [28,29].

4. Conclusion

The results show that the average Pb and Cd in Java for *Gracilaria* sp. is 0.482 - 0.794 and 0.021 - 0.121 ppm and for *Eucheuma cottonii* 0.230 – 0.697 ppm and 0.011 – 0.223 ppm. It showed that the highest heavy metal concentrations detected in *Gracilaria* sp. from Sidoarjo with lead (Pb) 0.794±0.013 ppm and *Eucheuma cottonii* from Pamekasan with lead 0.697±0.020 ppm. In general, lead is found in seaweed because of its living habitat. These results indicate generally that heavy metal contents of seaweeds cultivated urbanized estuaries or others should be monitored since accumulation appears to be site dependent. Some seaweed tends to accumulate moderate amounts of Pb and some of the other seaweed has a level of heavy metals that have exceeded the limits determined by SNI. Based on research that has been done, it is recommended to evaluate the level of other heavy metals using more types of seaweed in various other places. In addition, traceability for metal contamination in seaweed can be carried out for further research.

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