Traceability of Seaweed *Gracilaria* sp. Contaminated by Heavy Metal

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Abstract. *Gracilaria* sp as a seaweed that abundant in Indonesia is increasingly being used as a food product because it contains carbohydrates, proteins, fats, vitamins, amino acids, and minerals. However, *Gracilaria* sp that is cultivated in Sidoarjo, East Java, Indonesia is known to contain some dangerous heavy metals. The primary aim of food traceability is to increase food safety. Traceability minimizes disruption to trade and potential public health risks. The purpose of this study was to find out the source of heavy metal contamination on *Gracilaria* sp that cultivated in Sidoarjo. This research uses a descriptive and quantitative method. Atomic Absorption Spectrometry (AAS) method also used to determine the level of heavy metals. These results indicate generally that the source of heavy metal content in seaweed comes from the waste that is around and taken to the cultivation location. In all the samples, the farther the distance from the waste location, the less content-heavy metals were observed. The heavy metal content has been identified the majority of the area has exceeded the seaweed and water quality standard.

Keywords: Heavy metal · Traceability seaweeds · Contamination

1 Introduction

The increasing amount of waste in solid, liquid or gas is caused by the effects of urbanization and industrialization. One of the wastes that need to be considered is heavy metal. These metals are introduced into the environment through various routes, such as transportation vehicles, corrosion of underground pipes, smelting processes, fuel combustion, and municipal wastes. This wastes that get into the water can reduce water quality and cause pollution. Thus, environmental pollution caused by heavy metals is a widespread concern in developing countries such as Indonesia [1, 2]. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of chemicals over time continuously. Therefore, heavy metals that get into the waters will precipitate with sediments and can cause the transfer of toxic chemicals from sediments to organisms. Furthermore, heavy metals pollution have harmful health effects on the life of plants, animals and even humans [2, 3].

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Seaweed is an aquatic organism that can be consumed by humans. Various types of seaweed can be found in Indonesian waters and *Gracilaria* sp. is one type of seaweed that has a high absorption ability of heavy metals because its cell walls contain polysaccharides [4]. This species is widely distributed in most of the Indonesian coastal areas, and one of them is cultivated in Sidoarjo. Previous studies showed that *Gracilaria* sp. That was cultivated in Sidoarjo was contaminated by heavy metals [5]. Concentrations of heavy metal content in *Gracilaria* sp. Show varied results and some of them are above the threshold determined by the BSN (National Standardization Agency of Indonesia) (731: 2009) ICS document 67.220.20 which sets the maximum limit for heavy metal contamination in food [6].

Traceability is a tool to comply with legislation and to meet food safety and quality requirements. It is considered to be an effective safety and quality monitoring system with the potential to improve safety within food chains, as well as to increase consumer confidence and to connect producers and consumers [7]. Monitoring the concentration of heavy metals in water, sediment and aquatic organisms is important as levels of heavy metals in these matrices especially sediment. Sediment gives vital information regarding the degree of pollution, sources of contamination and their distribution. All metals are almost poisonous if present at a level higher than the tolerance limit [8]. So, traceability for heavy metals in *Gracilaria* sp that cultivated in Sidoarjo is needed. This study was to monitor the levels of lead (Pb) and cadmium (Cd) in water and sediment samples collected from Sidoarjo in *Gracilaria* sp pond and to evaluate the source contaminant of heavy metals in the *Gracilaria* sp.

2 Materials and Methods

2.1 Study Area

Sidoarjo is a small town in East Java in Java Island, Indonesia. It is 22 km far away from Surabaya city, the capital of East Java. Sidoarjo is an industrial estate having many industries with many kinds of wastes in there [9]. For the present investigation, water and sediment samples were collected from the *Gracilaria* sp. Pond in Kupang village, Sidoarjo. It is located at the latitude of 7°3' N and longitude of 112°5' E (Fig. 1).

2.2 Sediment and Water Sampling

Sampling locations are carried out around the pond of *Gracilaria* sp., where these ponds are brackish because the water sources come from the Madura Strait (saltwater) and the Porong River (freshwater). Water and sediment samples were collected from six different areas, where this area is located near the predicted location of the arrival of metal contamination, like water inlet from the sea, rivers, and landfills of local residents. These 6 areas are spread across the Kupang Village area including Tanjungsari Hamlet, Kalialo Hamlet, and Tegalsari Hamlet (Fig. 2).

Three random sediment samples (0–10 cm) were collected within each pond, yielding 18 sediment samples in total (3 samples 6 ponds) and three replicates for each sample. 3 water samples including also collected from each pond. Sediment and water samples were placed in a glass bottle during transportation and stored at 20ºC in the laboratory for subsequent analyses.

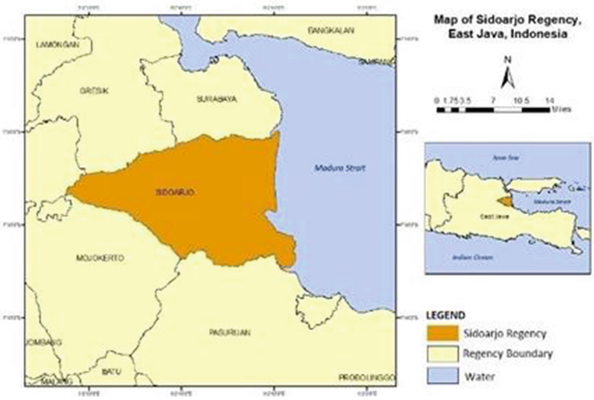

Fig. 1. Location of sampling sites. The orange colour in the left indicates the regional location of Sidoarjo, East Java, Indonesia.

Fig. 2. Sources of water and sediments samples used in this study.

2.3 Determination of 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 Spectrophotometry (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 [10].

2.4 Data Analysis

One-way ANOVA was used to evaluate the effect of heavy metal concentration in water and sediment. The correlation coefficient of variation was used to measure the strength of a linear relationship between heavy metal concentration in water and sediment were considered significant at p- value < 0.05 and < 0.01. Statistical analysis was carried out with SPSS 21.

3 Result and Discussion

3.1 Heavy Metal in Water

Metal concentration in water from the pond of *Gracilaria* sp. in Kupang village, Sidoarjo was illustrated in Table 1. The concentration of the analyzed heavy metals in water was in the order of Pb not detected until 0,085 ± 0,009 mg/L and Cd not detected until 0,014 ± 0,003 mg/L. The statistical analysis performed by one-way ANOVA showed has a significant concentration variation ($p > 0.05$) among Pb and Cd in P1, P2, P2, P4, P5, and P6. However, the concentration of Pb and Cd showed a statistically significant area variation ($p < 0.05$). The highest concentrations of all the detected heavy metals were recorded in the water near the landfills and the lowest one was recorded in the water were near with sea. The lowest concentration of Pb was recorded in the sea. Before entering the pond, the source of water from the sea will pass through the mangroves. The mangrove is predicted to reduce levels of heavy metals from seawater. This is in accordance with the statement that said mangrove is a natural bioremediation agent that can naturally absorb heavy metal content in nature and this function is referred to as biosorption. In addition, mangroves also have a capability called biofilter that is the ability to filter, bind, and trap pollution in the form of free excess sediment, garbage, and other household waste disposal in which this function plays a role in improving water quality [11].

Heavy metals pollution generated by landfills has become increasingly concerned due to its potential impact on human health [12]. In this study, the highest concentrations of all the detected heavy metals were recorded in the water near the landfills. Similar findings have been reported from the previous study which concluded that the high concentration of metals in a pond comes from the landfill sites. The open dumping management system that is used in a landfill site could cause the exposure of toxicant heavy metal, like Pb and Cd, through the leachate to the ponds. A study conducted by Mahardika and Indah shows that the presence of landfills that emit leachate into water bodies causes an increase in heavy metals of the Pb, Cu, and Cr. Concentration of heavy metals that have been analyzed get results passing the quality standard of Government Regulation No. 82 of 2001 [13].

Heavy metals from landfills pose a serious threat to public health since they can cause several physiological effects on human health, as well as ecotoxicological impacts on terrestrial and aquatic ecosystems. This issue also even deteriorated with the improper disposal of electronic products, leading to the release of high levels of heavy metals [12]. The quantity and quality of leachate are influenced by several factors, such as the composition of the waste, biochemical processes that occur in the degradation stages of the waste, amount of moisture, and the local parameters [14]. The composition of leachate formed varied significantly based on the biological and chemical reactions on solid waste, the age of the landfill, waste compositions, landfilling technology, and climatic conditions.

Table 1. Heavy metal contents in water for Pb dan Cd (mean ± SE, mg/L).

	Sample Site	Concentration (mg/L)							
		Pb				Cd			
		(i)	(ii)	(iii)	x̄	(i)	(ii)	(iii)	x̄
River	P1	0,025	0,021	0,019	0,022	0,014	0,015	0,011	0,013
	P2	0,022	0,028	0,022	0,024	0,009	0,011	0,011	0,010
Landfills	P3	0,076	0,093	0,087	0,085	0,014	0,016	0,011	0,014
	P4	0,089	0,064	0,076	0,076	0,012	0,011	0,017	0,013
Sea	P5	< 0,008	< 0,008	nd	< 0,008	nd	nd	nd	Nd
	P6	< 0,000	< 0,008	nd	< 0,008	nd	0,008	0,008	0,008

3.2 Heavy Metal in Sediment

Mean of metal concentration for sediment were found 2,136 ± 0,031 mg/kg until 28,267 ± 0,877 mg/kg for Pb and 0,056 ± 0,005 mg/kg until 0,188 ± 0,021 mg/kg for Cd. Table 2 shows more detail about the concentration of metal in sediment from the pond of *Gracilaria* sp. in Kupang village, Sidoarjo. Both Pb and Cd showed a statistically significant area variation (ANOVA, $p < 0.05$). When compared to water, sediment contained more concentration of metals. Similar findings were reported by other authors. A study that conduct by Jiao shows that the concentrations of heavy metals in the sediment were 1000–100,000 times higher than those in the water. The study showed that the concentrations of heavy metals in sediments such as Zn, Cr, Cu, Pb, Ni, Co, Cd, and Tl are higher than the concentration of heavy metals in water [15]. Sediment act as a reservoir for all contaminants and dead organic matter descending from the ecosystem above Heavy metals entering the water body would be absorbed in sediments, and subsequently might migrate as a result of exchanges between water, sediment, and biota, through biological and chemical process. Heavy metals do not degrade in water but are generally not found in high concentrations, primarily due to deposition in sediments but also because of uptake by plant and animals [16].

The variation of metal concentrations in the sediments of accumulation in each zona is big. Metal concentrations in the sediments of sea zones are apparently lower. According to the previous study, differing sediment heavy metal contents do not necessarily indicate varying degrees of pollution, but rather reflect dissimilarities in grain size. A variety of approaches exist for normalization of concentrations allowing to distinguish anthropogenic pollution effects from natural variability [17]. Metal concentrations in sediments may not increase with decreasing sediment particles as high concentrations of metals have also been found in larger size fractions of sediment. These exceptions probably demonstrate that metal concentrations in sediment are not controlled exclusively by particle size. There are several other factors such as quality and quantity of organic matter, distribution of different mineral phases and metal loading that may also

Table 2. Heavy metal contents in sediment for Pb dan Cd (mean ± SE, mg/kg).

	Sample Site	Concentration (mg/ kg)							
		Pb				Cd			
		(i)	(ii)	(iii)	x̄	(i)	(ii)	(iii)	x̄
River	P1	8,675	8,866	9,083	8,875	0,146	0,168	0,172	0,162
	P2	6,472	6,266	6,583	6,440	0,158	0,122	0,153	0,144
Landfills	P3	28,550	27,283	28,967	28,267	0,177	0,187	0,165	0,176
	P4	25,830	24,036	25,432	25,099	0,201	0,164	0,198	0,188
Sea	P5	2,118	2,118	2,172	2,136	0,068	0,068	0,052	0,063
	P6	2,346	2,290	2,208	2,281	0,061	0,058	0,050	0,056

control metal speciation, distribution, accumulation and bioavailability in coastal sediments. Most contaminants, notably metallic compounds, were found to be accumulated in the sediment through complex physical and chemical adsorption mechanisms Understanding the sources of pollutants in aquatic sediments is important for pollution control. Statistical approaches, such as Pearson correlation analysis, principal components analysis (PCA), and cluster analysis, are considered to be effective tools for uncovering pollution sources and have been used successfully in many studies of heavy metal pollution in sediments [18].

3.3 Comparison of Heavy Metal in Water and Sediment

As heavy metal pollution is dangerous for both aquatic and human health, so the standard of heavy metal content has been determined by the authorized body. Government Regulation No. 82 of 2001 concerning the management of water quality and the control of water pollution regulate the permissible lead content of heavy metals (Pb) in the amount of 0.03 mg/L and cadmium (Cd) of 0.01 mg/L. Whereas for sediment, the standard quality standard for heavy metal content in sediments in Indonesia has not yet been set, so in this study, the quality standard refers to standards set by other countries. Swedish Environmental Protection Agency (SEPA, 2000) is a standard for the Quality of Heavy Metals in Sediments. SEPA regulates the permissible lead content of heavy metals (Pb) in the amount of 25 mg/kg and cadmium (Cd) of 0.2 mg/kg. When water and sediment samples were collected and analyzed for the heavy metal's level, it was found that some samples had heavy metal concentrations above the maximum standard allowed and set by the authorized body. Figure 3 and Fig. 4 shows more detail about the concentration of heavy metals in water and sediment when compared to the standard.

A number of studies have reported a similar phenomenon. A study conducted by Nugraha shows that the heavy metal content of Cd, Cu, Pb, and Hg in Socah and Kwanyar waters is still below the seawater quality standard, while the heavy metal content in

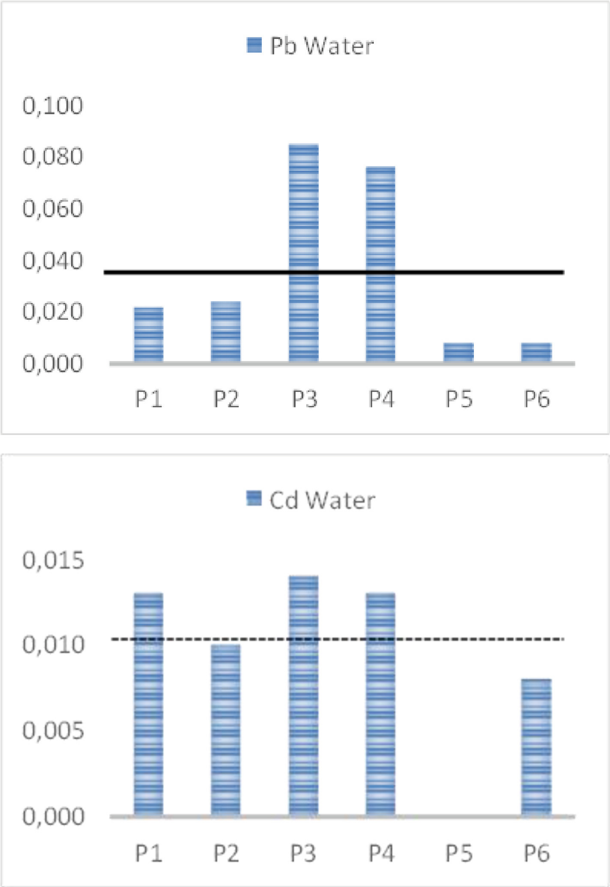

Fig. 3. Comparison of mean concentrations (mg/L) of heavy metal in water

sediments exceeds the seawater quality standard for marine biota. In general, the result shows that heavy metal content in sediments is higher than heavy metal content in water. This is because heavy metals have properties that are easy to bind and settle to the bottom of the water and unite with sediment, therefore heavy metal content in sediments is higher than in water. Precipitation of heavy metals in water occurs because of the presence of hydroxyl and chloride carbonate anions. Heavy metals have properties that easily bind organic material and settle to the bottom of the water and unite with sediment so that the content of heavy metals in sediments is higher than in water [19].

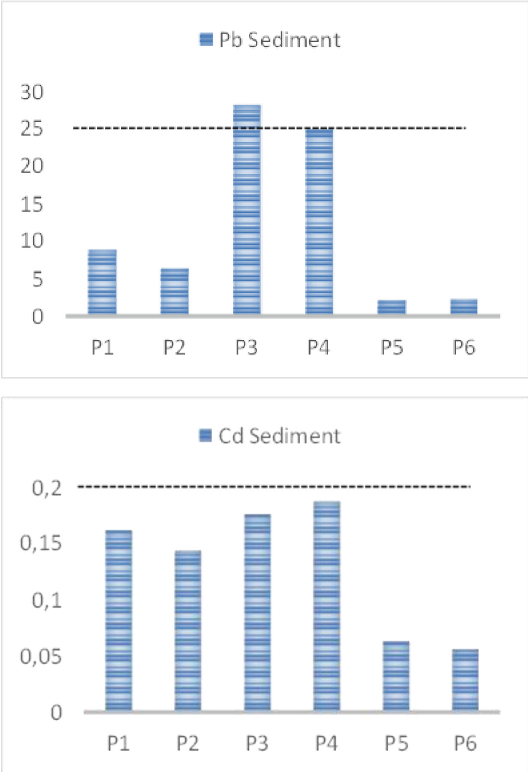

Fig. 4. Comparison of mean concentrations (mg/kg) of heavy metal in sediment

4 Conclusion

The heavy metal concentrations in sediment and water from the brackish pond in Kupang Village, Sidoarjo were investigated in this study. The highest total metal concentrations of water and sediment in ponds og *Gracilaria* sp were observed in ponds near landfill > river > sea. The Cd concentration of the water approached or exceeded the permissible limit of Government Regulation No. 82 of 2001 except for Cd in the sea zone. The concentrations of Pb in sediment in the pond near the landfill were higher than the limit of the SEPA. This pollution level has its bad effect on both *Gracilaria* sp in the area and it can explain the poor quality of the pond *Gracilaria* sp species, so it is strongly recommended that strict vigilance and constant monitoring are needed to maintain the water quality of the pond.

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