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Abstract. *Eucheuma spinosum* is a species of seaweed widely cultivated in Indonesia. This seaweed contains high carrageenan, ranging between 65-67 percent. Carrageenan plays a very important role as a stabilizer, thickener, gel maker, emulsifier and others. This property is widely used in the food industry, medicine, cosmetics, textiles, paints, toothpaste and other industries. This very important benefit requires that *E. spinosum* must be safe from harmful metal content. This study aims to analyze whether *E. spinosum* is a bioaccumulator of harmful metals. This research was conducted in three sea areas around South Sulawesi, namely the Gulf of Bone, the Flores Sea and the Makassar Strait. Seaweed samples were taken from seaweed cultivation locations in these three areas. The metal concentrations analyzed were Copper (Cu), Cadmium (Cd), and Lead (Pb). This study indicated that *E. spinosum* was a bioaccumulator because at each sampling location the concentrations of Cu, Cd, and Pb at *E. spinosum* were generally greater than those in ambient seawater. *E. spinosum* was non-permanent or non-consistent bioaccumulator because the concentrations of Cu, Cd, and Pb in *E. spinosum* tissue are not directly proportional to the concentrations of Cu, Cd, and Pb in seawater.

1. Introduction
Eucheuma spinosum is edible red seaweed. In general, seaweed is a healthy food variant that is low in calories, but rich in vitamins, minerals and fiber [1]. *E. spinosum* is a raw material for carrageenan powder [2]. Carrageenan is widely used in the textile, cosmetics, and other industries. Its main function is as a stabilizer, emulsifier, thickener, filler and gel maker. In the food industry, these three products (gelatin, carrageenan and alginate) are widely used for the manufacture of bread, soup, sauce, ice cream, jelly, candy, cheese, pudding, jam, beer, wine, coffee and chocolate. In the pharmaceutical industry it is useful as a laxative or dissolving drug, as an additive in the manufacture of medicines and toothpaste as well as a mixture for forming dental samples. In the textile industry it can be used to protect silk sheen. In the cosmetic industry, it is useful in the manufacture of ointments, creams, lotions, lipsticks, shampoos, hair dyes and soaps [3]. Seaweed is used as animal feed, fertilizer and raw material for various industrial applications [4-7].

E. spinosum contains iota of keratin and other nutrients, including carbohydrates (69.07-69.66% of dry weight), fiber content (15.12-19.89%), protein (6.04-7.33%), ash (23.35-24.66%), fat content (0.012-0.032%). Macro minerals contained in *E. spinosum* are Ca (0.0455-0.796%), Cl (0.12-0.133%), K (2.881-3.539%), Mg (0.395-0.582%) and Na (0.0455-0.796%). and micro minerals are Zn (4.68-26.37 ppm) and Cu (0.036-0.175 ppm) [8].

Several studies have shown that seaweed was a great source of protein, fat, essential vitamins and minerals [4, 5, 9, 10]. The seaweed nutrients composition is determined by environmental conditions such as habitat, light, water temperature and salinity [9, 11]. Seaweed also contains essential minerals such as Ca, Mg, Se, and Fe [11].

This very important nutritional content makes the food safety aspect of *E. spinosum* very important. Metal content that is harmful to health is widely used in determining food safety. Until now, the content of dangerous metals in *E. spinosum* cultived in the cultivation center of South Sulawesi, Indonesia has never been studied. Therefore, it is necessary to analyze the potential accumulation of hazardous metals in *E. spinosum*. The results of this study are needed to ensure that the *E. spinosum* produced in South Sulawesi, Indonesia is safe for health. This study aims to analyze whether *E. spinosum* is a bioaccumulator of harmful metals.

2. Materials and Methods

This study was conducted in three sea areas around South Sulawesi, namely Gulf of Bone, Flores Sea and Makassar Strait. Seaweed samples were taken from four seaweed cultivation areas (Bone, Sinjai, Bantaeng, and Pangkep Regency) (Figure 1). Samples were taken at the *E. spinosum* cultivation location in the coastal area.

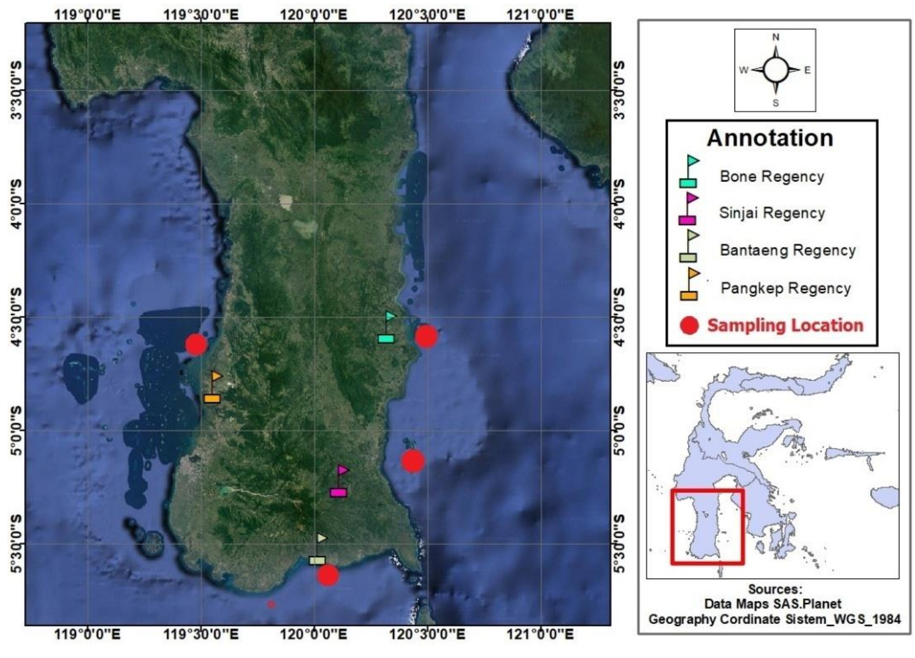

Figure 1. Sampling location of *Eucheuma spinosum* at Bone, Sinjai, Bantaeng and Pangkep Regency.

In the laboratory, the seaweed was washed and dried. The drying was carried out in two stages, namely air drying and oven drying. Air drying was carried out at room temperature (32-33ºC) for two days. Oven drying was carried out at 50ºC for 48 hours. After drying, the sample was mashed and then analyzed for its heavy metal content. The heavy metal concentrations analyzed were Copper (Cu), Cadmium (Cd), and Lead (Pb). The quantitative content of Cu, Cd and Pb metals was analyzed using Atomic Absorption Spectrophotometer techniques [12, 13].

3. Results

3.1. Copper (Cu)

Cu concentration in seawater was <0.001-1.618 with an average of 0.258 ± 0.443. While the Cu concentration in E. spinosum was <0.001-3.610 with an average of 0.916 ± 1.542. This study indicates that Cu concentrations in the seaweed *E. spinosum* was generally greater than in the sea water, but not significantly different (P> 0.05), except in Pangkep Regency, Cu concentrations in the seaweed *E. spinosum* was greater than in the sea water, and significantly different (P <0.05). The concentration of Cu in *E. spinosum* was inconsistent; at certain stations the concentration was higher than sea water (accumulation), namely Bantaeng and Pangkep Regency, while at other stations the concentration was lower than sea water, namely Bone and Sinjai Regency (Table 1). The correlation curve of the Cu concentration in seawater and *E. spinosum* shows that the Cu concentration in *E. spinosum* did not increase consistently with the increase in Cu concentration in seawater (Figure 2). All correlation curves of Cu concentrations between sea water and *E. spinosum* did not show any progressive accumulation. The Cu concentrations of *E. spinosum* at the four-sampling location were still below the safe limit for health (30 ppm) (Indonesian National Standard, SNI: 01-2802-1995).

Table 1. Concentration of Copper (Cu) *Eucheuma spinosum* at Bone, Sinjai, Bantaeng and Pangkep Regency.

Regency	Cu Sea Water (CuSw)	Cu *E. spinosum* (CuEs)	Δ (CuEs-CuSw)	Annotation
Bone	0.136	0.030	-0.106	Non accumulation
Bone	0.135	0.030	-0.105	Non accumulation
Bone	0.100	0.060	-0.040	Non accumulation
Mean± STD	0.123±0.021	0.040±0.017	-0.083±0.038	Non accumulation
Sinjai	0.283	0.010	-0.273	Non accumulation
Sinjai	1.618	0.000	-1.618	Non accumulation
Sinjai	0.388	0.000	-0.388	Non accumulation
Mean± STD	0.763±0.742	0.003±0.006	-0.760±0.746	Non accumulation
Bantaeng	0.155	0.140	-0.015	Accumulation
Bantaeng	0.174	0.130	-0.044	Non accumulation
Bantaeng	0.100	0.180	0.081	Accumulation
Mean± STD	0.143±0.039	0.150±0.026	0.007±0.065	Accumulation
Pangkep	<0.001	3.610	3.609	Accumulation
Pangkep	<0.001	3.440	3.439	Accumulation
Pangkep	<0.001	3.360	3.359	Accumulation
Mean± STD	<0.001±0.000	3.470±0.128	3.469±0.128	Accumulation

3.2. Cadmium (Cd)

Generally, there was an accumulation of Cd. The Cd concentration of sea water was <0.001-0.262 with an average of 0.175 ± 0.106. While the concentration of Cd *E. spinosum* is 0.040-1.860 with an average of 0.901 ± 0.582. This study indicates that Cd concentrations in the seaweed *E. spinosum* was greater than in the sea water, and significantly different (P<0.05). All stations indicated an accumulation of Cd in *E. spinosum*, except for one replication at the station in Bantaeng Regency (Table 2). Although there was an accumulation, the correlation curve of Cd concentrations in seawater and *E. spinosum* indicated that the Cd concentration in *E. spinosum* did not increase consistently with the increase in Cd concentration in seawater (Figure 3). All correlation curves of Cd concentrations between sea water and *E. spinosum* did not show any progressive accumulation. The Cd concentrations of *E. spinosum* at the four-sampling location were exceed the safe limit for health (0.2 ppm) (SNI 7383: 2009).

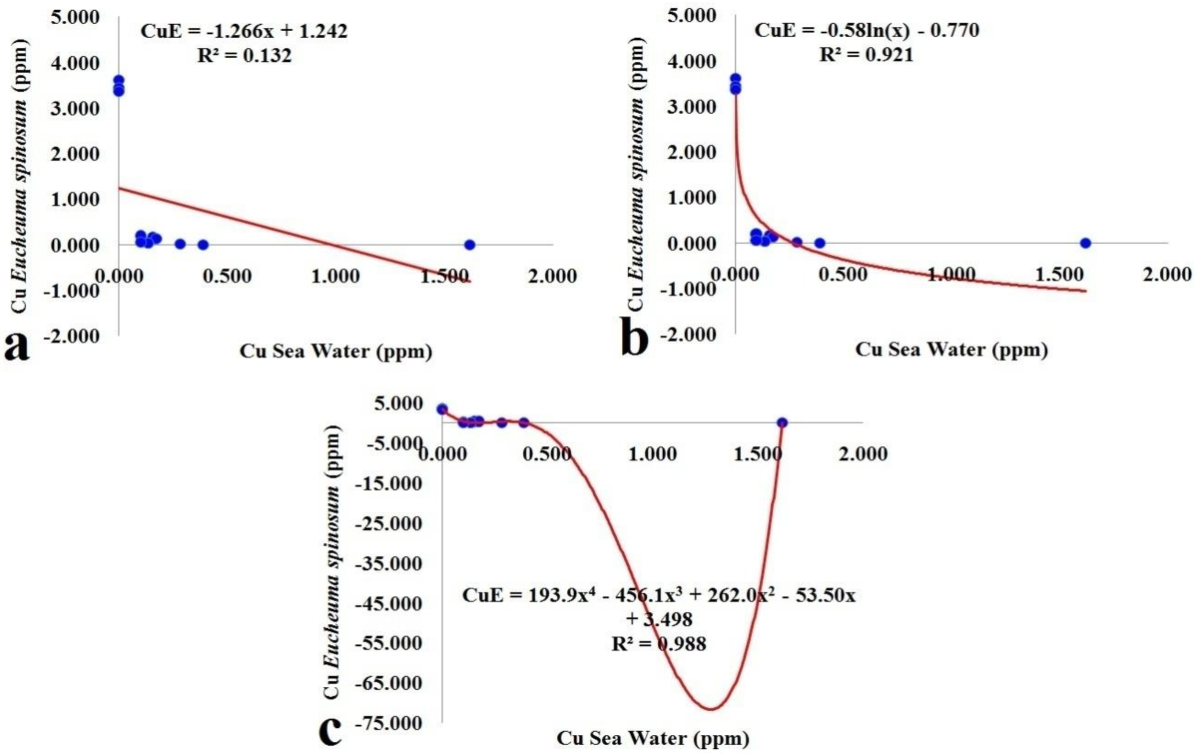

Figure 2. Relationship curve of Cu concentrations in sea water and *Eucheuma spinosum* in Bone, Sinjai, Bantaeng and Pangkep Regency. Linear Equation (a), Power Equation (b), and Polynomial Equation (c).

Table 2. Concentration of Cadmium (Cd) *Eucheuma spinosum* at Bone, Sinjai, Bantaeng and Pangkep Regency.

Regency	Cd Sea Water (CdSw)	Cd *E. spinosum* (CdEs)	Δ (CdEs-CdSw)	Annotation
Bone	0.250	0.550	0.300	Accumulation
Bone	0.236	0.480	0.245	Accumulation
Bone	0.218	0.440	0.222	Accumulation
Mean± STD STD	0.235±0.016	0.490±0.056	0.256±0.040	Accumulation
Sinjai	0.262	1.010	0.749	Accumulation
Sinjai	0.215	0.710	0.495	Accumulation
Sinjai	0.228	0.850	0.622	Accumulation
Mean± STD	0.235±0.024	0.857±0.150	0.622±0.127	Accumulation
Bantaeng	0.233	0.040	-0.193	Non accumulation
Bantaeng	0.246	0.650	0.404	Accumulation
Bantaeng	0.214	0.740	0.527	Accumulation
Mean± STD	0.231±0.016	0.477±0.381	0.246±0.385	Accumulation
Pangkep	0.001	1.670	1.669	Accumulation
Pangkep	0.001	1.860	1.859	Accumulation
Pangkep	0.001	1.810	1.809	Accumulation
Mean± STD	0.001±0.000	1.780±0.098	1.779±0.098	Accumulation

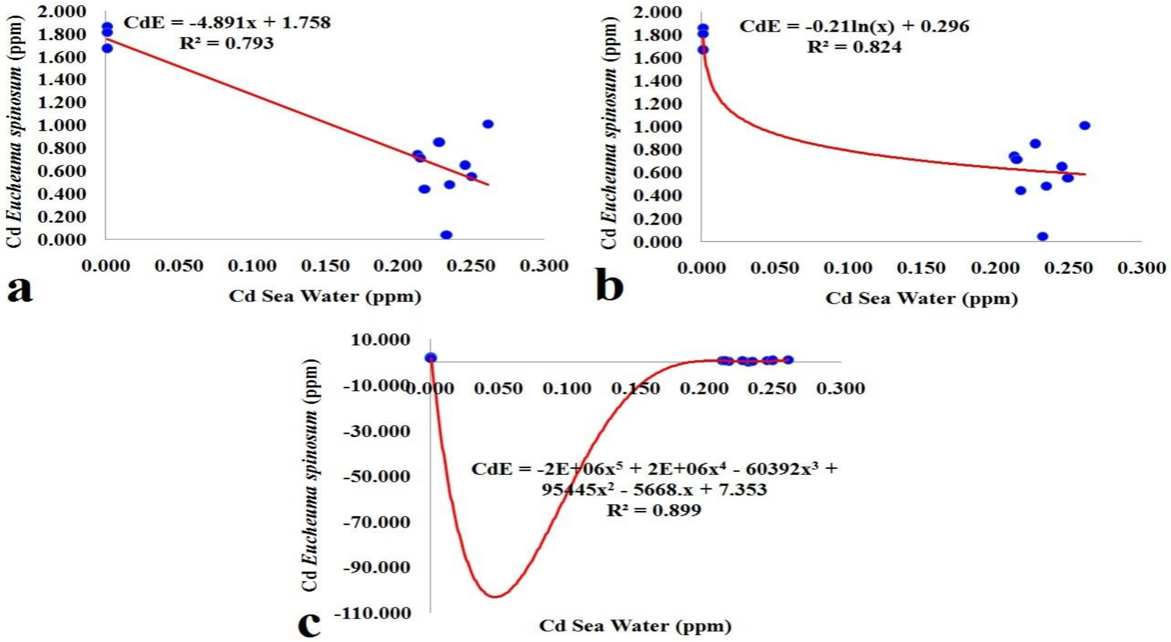

Figure 3. Relation curve of Cd concentration in sea water and *Eucheuma spinosum* in Bone, Sinjai, Bantaeng and Pangkep Regency. Linear equation (a), power equation (b), and polynomial equation (c).

3.3. *Lead (Pb)*

Generally, there was no Pb accumulation. The Pb content in seawater was <0.001-3.009 with an average of 1.208 ± 1.052. While the Pb content in *E. spinosum* was <0.001-1.590 with an average of 0.680 ± 0.532. This study indicates that Pb concentrations in the seaweed *E. spinosum* were less than in the sea water, but not significantly different (P> 0.05). All stations showed no Pb accumulation in *E. spinosum*, except for two replications in Bantaeng Regency and one replication in Sinjai Regency (Table 3).

Table 3. Concentration of Lead (Pb) *Eucheuma spinosum* at Bone, Sinjai, Bantaeng and Pangkep Regency.

Regency	Pb Sea Water (PbSw)	Pb *E. spinosum* (PbEs)	Δ (PbEs-PbSw)	Annotation
Bone	1.891	0.430	-1.461	Non accumulation
Bone	1.339	0.610	-0.729	Non accumulation
Bone	2.748	0.400	-2.348	Non accumulation
Mean± STD	1.992±0.710	0.480±0.114	-1.512±0.811	Non accumulation
Sinjai	1.456	1.280	-0.176	Non accumulation
Sinjai	1.684	0.820	-0.864	Non accumulation
Sinjai	1.554	1.590	0.036	Accumulation
Mean± STD	1.565±0.114	1.230±0.387	-0.335±0.470	Non accumulation
Bantaeng	3.009	1.070	-1.939	Non accumulation
Bantaeng	0.288	0.830	0.542	Accumulation
Bantaeng	0.529	1.130	0.602	Accumulation
Mean± STD	1.275±1.506	1.010±0.159	-0.265±1.450	Non accumulation
Pangkep	<0.001	<0.001	0.000	Non accumulation
Pangkep	<0.001	<0.001	0.000	Non accumulation
Pangkep	<0.001	<0.001	0.000	Non accumulation
Mean± STD	<0.001±0.000	<0.001±0.000	0.000±0.000	Non accumulation

The correlation curve of Pb concentrations in seawater and *E. spinosum* indicated that the Pb concentration in *E. spinosum* did not increase consistently with the increase in the Pb concentration in seawater (Figure 4). All correlation curves of Pb concentrations between sea water and *E. spinosum* did show non consistent progressive accumulation. The mean Pb concentrations of *E. spinosum* was not exceeding the safety limit for the health at Bone and Pangkep Regency, and exceed the safe limit for health (0.5 ppm) (SNI 7383: 2009) at Takalar and Sinjai Regency.

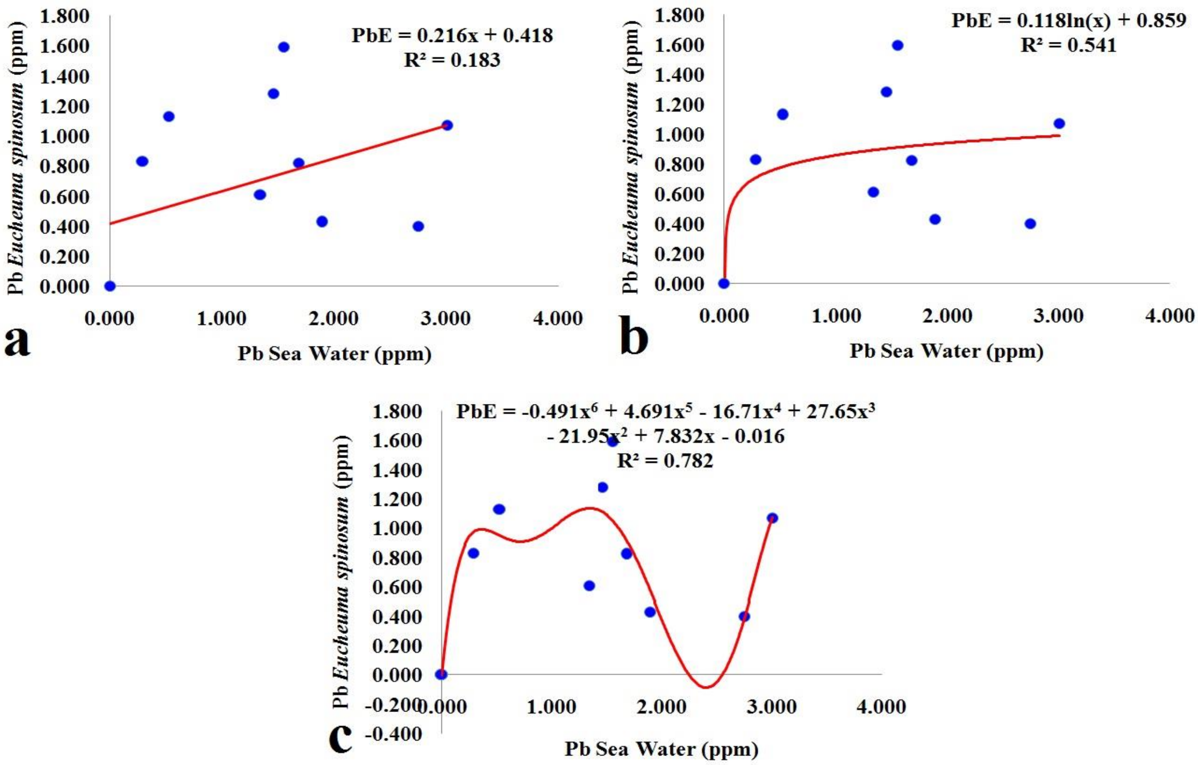

Figure 4. Relation curve of Pb concentration in sea water and *Eucheuma spinosum* in Bone, Sinjai, Bantaeng and Pangkep Regency. Linear equation (a), power equation (b), and polynomial equation (c).

4. Discussion

One of the environmental pollutions is the presence of heavy metal in the sea water. The metals Cu, Cd and Pb are three of the seven metals which are categorized as heavy metals [14]. The content of Cu, Cd and Pb in *E. spinosum* which was higher than the content of Cu, Cd and Pb in seawater indicates that *E. spinosum* has the potential as a heavy metal bioacumulator. The presence of heavy metals in the waters is not good for macroalgae life because it can cause disruption in the photosynthetic process in macroalgae, namely a decrease in the ability to absorb solar energy [15]. The heavy metals can be very reactive and toxic to organisms. In high or acute metal content, it can cause damage to macro algae cells. Whereas at a lower level, or chronically, macro algae accumulates heavy metals and can spread them to organisms at higher trophic levels, such as molluscs, crustaceans and fish [16]. The accumulation of metals in the tissues of organisms can permanently harm life in the higher food chains, including humans because molluscs, crustaceans and fish are great sources of animal protein for humans.

The inconsistent bioaccumulation of metals at *E. spinosum* indicates that there were other factors besides the metal concentration in the sea water. In certain seaweed species, such as *Sargassum fillipendula*, metal content was significantly affected by pH [17]. However, pH may not be a single factor, and water quality parameters such as temperature and salinity are likely to have an effect [18].

The influence of water conditions on a spatio-temporal scale also seems to have an effect on metal bioaccumulation in seaweed. Previous research results show that, algae has the potential for accumulation of heavy metals with concentrations that fluctuate according to space and period, *Enteromorpha linza* that lived on Sinop station in 1998 and 2000 on the Turkish Coast of the Black Sea shows the potential for accumulation with varying concentration [19].

The ability of seaweed to absorb and release metals, both alive or dry, makes seaweed available as biosorbent agents [20]. This can happen because the thallus of the seaweed has the ability to selectively form bonds with metal cations Cu, Cd, and Pb [21]. Seaweed cell wall which is rich in polysaccharides and has a functional carboxylic acid group can play an active role in metal binding [22].

Previous studies have reported cases of the accumulation of metals, for example Cu, which are inconsistent, sometimes high and sometimes low, at *E. spinosum* [18]. Previous studies have also reported inconsistent accumulations in *Gracilaria* sp, where Pb accumulation decreased during the cultivation period, from 3.38 ± 0.23 ppm before planting (age 0 days) to 0.84 ± 0.00 at harvest (age 40 days) [23]. This decrease in heavy metal concentration was thought to also occur in *E. spinosum*. The results of these previous studies reinforce the notion that there was an accumulation of Cu, Cd, and Pb at seaweed *E. spinosum*, but the accumulation was not consistent.

Inconsistent or inconsistent accumulation of metals in seaweed is likely due to the simple cell structure [24], so the metal can be accumulated or released back easily [20]. The non-permanent accumulation was thought to make seaweed more resistant to heavy metal concentration than animals, such as the blue spotted ray *Dasyatis kuhlii* which can cause hypertrophy if the Pb accumulates in the gills reaches 0.2 ppm [25].

The ability of seaweed to absorb and release metals makes seaweed derivative products, especially E. spinosum, to remain safe, even though the metal concentration is higher than other aquatic organisms, because the metal content in seaweed can be released during washing or during the processing into carrageenan. The metal content found in *E. spinosum* at all research sampling stations is higher than other marine organisms, such as *Holothuria scabra* [26] and *Bohadschia vitiensis* [27]. When compared with other macroalgae species, such as *Sargassum*, the Pb content of *E. spinosum* was much lower than Sargassum [20].

The results of this study indicate that *E. spinosum* was a bioaccumulator, but not a permanent bioaccumulator, metals can be accumulated or excreted. From a food safety aspect, this was a good thing because even though there was metal accumulation, the metal can be released during the *E. spinosum* processing and the product become save as food or feed.

5. Conclusion

This study indicated that *E. spinosum* was a bioaccumulator because at each sampling location the concentrations of Cu, Cd, and Pb at *E. spinosum* were generally greater than those in ambient seawater. *E. spinosum* was non-permanent or non-consistent bioaccumulator because the concentrations of Cu, Cd, and Pb in *E. spinosum* tissue are not directly proportional to the concentrations of Cu, Cd, and Pb in seawater.

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