HEAVY METALS IN EDIBLE SEAWEEDS FROM COASTAL AREAS OF MANILA BAY AND ROXAS CITY, PHILIPPINES.

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Abstract

Seaweeds, which are widely accepted as a health food, have become a popular ingredient in many seafood delicacies. Nevertheless, similar to the consumption of other marine products, there is the risk of heavy metal exposure. This study focuses on determining the concentration of heavy metals Cd, Pb, and Zn in edible seaweeds found in the Philippines: Caulerpa racemosa (Forskl.) J.Ag, Hypnea nidulans Setchell, and Gracilaria tenuistipitata. Results have shown that Caulerpa racemosa accumulated the least amount of heavy metals and consumption of this seaweed present little risk. On the hand, the heavy metal content of Gracilaria is of main concern to consumers.

Introduction:-
Seaweeds have been used for a wide variety of application: as ingredient in salads and certain exotic dishes; as thickening and gelling agent; as herbal product, as material in waste water treatment; as animal feed; as fertilizer; as component of personal care products, and many more. Edible seaweeds are popularly accepted as a health food. Such claim is supported by studies which have demonstrated that seaweeds are rich in fiber, vitamins and minerals, phytochemicals and antioxidants, and low in fat but rich in essential fatty acids. (Boonchum, et al. 2011; Brownlee, et al. 2012; Downtenski, et al. 2007; Lou, et al. 2010; Manivannan, et al. 2008; Matanjun et al., 2009; Mohammad, et al. 2013; Norziah and Ching, 2000; Ortiz, et. al 2006; Ratana-Arporn and Chiraprart, 2006; Seenivasan et al. 2012; Suresh, et al. 2012). Nevertheless, there are health risks in seaweed consumption due to the possible bioaccumulation of heavy metals reported to be present in the oceans, seas, rivers, and lakes (Alkhalifa, et al. 2012; Besada, et. al. 2009; Dadolahi-Sohrab, et al. 2011; Guiteouni, et al. 2016; Rybak, et al. 2012). Cadmium, for example, is a heavy metal that affects a number or organs in humans particularly the kidney resulting in renal problems (ATSDR 2012; Goyer 2001), while Pb accumulation in the body may cause major damage to the nervous, hematological, cardiovascular systems and the kidney (Goyer, 2001; Jarup, 2003). On the other hand, Zn is a trace element used by as metal cofactor by several enzymes in the body and therefore considered as an essential element. In this study the concentration of Cd, Pb, and Zn in popular edible seaweeds in two locations in the Philippines were determined and compared.

Materials and Methods:-
Seaweeds samples were purchased from local markets from two locations during the months of June (Batch 1) and October (Batch 2): Caulerpa racemosa (Forskl.) J.Ag., and Hypnea nidulans Setchell from Roxas City, Capiz, Central Philippines (Visayas); and Caulerpa racemosa (Forskl.) J.Ag., and Gracilaria tenuistipitata from local...
markets along the Manila Bay area (Luzon). The samples were washed repeatedly with tap water and three times with distilled water. The samples were freeze-dried, grounded, and stored at -20ºC.

The cadmium, lead, and zinc content of the freeze-dried samples were subjected to acid digestion and analyzed via atomic absorption spectroscopy (Shimadzu AA-6300 model). All analysis was done in triplicate.

**Identification of Seaweeds:**
The seaweeds were identified and authenticated by the Botany Division of the Philippine National Museum.

**Results:**
The Cd, Pb, and Zn content in the freeze-dried seaweeds are summarized in Table 1. Results show that there is not much difference in the Cd content among the samples with values ranging from 0.1672 – 0.2047 mg/kg. The amount of Pb is relatively lower in the *C. racemosa* samples collected from both locations (2.612 – 2.709 mg/kg range). Pb content is significantly higher in the *G. tenuistipitata* sample collected during the month of June. Similar pattern as the Pb content was observed in the amount of Zn in the samples.

**Table 1:** Heavy Metal Content in Seaweeds (mg/kg dry weight)

<table>
<thead>
<tr>
<th>Species</th>
<th>Batch 1 Cadmium</th>
<th>Batch 2 Cadmium</th>
<th>Batch 1 Lead</th>
<th>Batch 2 Lead</th>
<th>Batch 1 Zinc</th>
<th>Batch 2 Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>C. racemosa</em> (Visayas)</td>
<td>0.2143</td>
<td>0.2947</td>
<td>2.270</td>
<td>2.540</td>
<td>9.741</td>
<td>12.09</td>
</tr>
<tr>
<td><em>H. nidulans</em> (Visayas)</td>
<td>0.1792</td>
<td>0.1672</td>
<td>2.903</td>
<td>4.983</td>
<td>17.04</td>
<td>38.42</td>
</tr>
<tr>
<td><em>C. racemosa</em> (Luzon)</td>
<td>0.2129</td>
<td>0.2947</td>
<td>2.612</td>
<td>2.709</td>
<td>7.233</td>
<td>6.031</td>
</tr>
<tr>
<td><em>G. tenuistipitata</em> (Luzon)</td>
<td>0.2036</td>
<td>0.1835</td>
<td>9.767</td>
<td>3.441</td>
<td>210.9</td>
<td>23.00</td>
</tr>
</tbody>
</table>

![Cadmium graph](image-url)
A comparison of the average Cd, Pb, and Zn content (in mg/kg dry weight) are presented in Table 2. Results show the *C. racemosa* accumulated the least amount of heavy metal. Moreover, the Cd content is lower as compared to Pb in all the samples. Once more, data demonstrate that *G. tenuistipitata* accumulated a substantial amount of Zn as compared to the rest of the samples.

### Table 2: Heavy Content in Seaweeds (average, mg/kg dry weight)

<table>
<thead>
<tr>
<th>Species</th>
<th>Cadmium</th>
<th>Lead</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>C. racemosa</em> (Visayas)</td>
<td>0.2545</td>
<td>2.405</td>
<td>10.92</td>
</tr>
<tr>
<td><em>H. nidulans</em> (Visayas)</td>
<td>0.1732</td>
<td>3.943</td>
<td>27.73</td>
</tr>
<tr>
<td><em>C. racemosa</em> (Luzon)</td>
<td>0.2538</td>
<td>2.661</td>
<td>6.632</td>
</tr>
<tr>
<td><em>G. tenuistipitata</em> (Luzon)</td>
<td>0.1935</td>
<td>6.604</td>
<td>117.0</td>
</tr>
</tbody>
</table>
Discussion:
Several studies have shown that many factors influence the heavy metal content in seaweeds. This includes the species itself, geographical and geochemical properties of the habitat, the level of pollution, and time of harvesting (Alkhalifa et al. 2012; Dadolahi-Sohrab, et al., 2011; Guitouni, et al. 2016; Khristoforoba, et al. 1980; Lenin Raj 2009; Rao, et. al. 1995; Rybak, et al., 2012). The amount of Cd is relatively lower as compared to the amount of Pb in all the samples. Data also show that Hypnea nidulans and Gracilaria tenuistipitata have a higher capacity to bioaccumulate Pb as compared to that of Caulerpa racemosa. It is noteworthy that Caulerpa species are a more popular ingredient in salads as compared to Hypnea and Gracilaria, however the latter are used as raw materials for making gelatin, thickening agents, and animal feed. Lenin Raj (2009) has presented data showing the relatively high capacity of a Hypnea species to accumulate heavy metals. Results are also consistent with the study of Mouradi et al. (2014) showing that the genus Gracilaria has a high ability to accumulate heavy metal. Gracilaria species is very common in the Manila Bay area, a highly urbanized area and relatively more polluted due to domestic and industrial wastes. This should explain the much higher concentrations of Pb and Zn. The amount of Zn between two batches of harvesting in Gracilaria is strikingly different. A possible explanation is that during the time of the second harvesting, there must have been a waste dumped in the Manila Bay area containing large amounts of Zn.

In France (CEVA, 2014), where seaweeds are considered as a novel food, the tolerable limit of Cd and Pb in dried seaweeds for human consumption has been set to 0.5 and 5 mg/kg dry weight, respectively. In the Philippines, the Food and Drug Administration has categorized dried seaweeds as processed food and has set a limit for adults of 0.3 and 10 mg/kg for Cd and Pb respectively. Therefore, based on these values, the amounts of Cd and Pb are generally still below the maximum limit. However caution must be considered with G. tenuistiptata which is a little above the limit set by France (CEVA, 2014).

The Joint FAO/WHO Expert Committee on Food Additives Meeting in 2010 and the Joint FAO/WHO Codex Alimentarius Commission 2011 have established the Provisional Tolerable Daily Maximum Intake for Zn, an essential mineral used by many metalloenzymes, to be in the range 0.3-1 mg/kg bw. The values presented in the data are in terms of mg/kg dry weight of the samples. Caulerpa, Gracilaria, and Hypnea are usually consumed as
fresh samples, with approximate water content in the range of 85-95% (Ahmad, 2012; McDermid, 2007; Nor Salmi, et al. 2012; Sanjaya, et al., 2016). Therefore results imply that generally, seaweeds, like marine products, can be a possible dietary source of Zn. Nevertheless, consumers must be aware of the Zn content in Gracilaria harvested from the Manila Bay area, which is beyond the limit set by FAO/WHO.

**Conclusion:**
This study has shown that values of Cd, Pb, and Zn in Caulerpa racemosa, a popular ingredient used in seafood salads, is well below the limit indicating very little risk posed by consumption of this seaweed. Although, still below the limit, consumers must be aware of the relatively higher heavy metal content in Hypnea. Moreover, consumption of Gracilaria is of main concern, considering that among the three species, it is the one with the highest heavy metal content. Regular monitoring is necessary to protect consumers from deleterious effects of seaweeds consumption.

**Acknowledgement:**
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**References:**
1. Agency for Toxic Substance and Disease (2012): Toxicological profile for cadmium, US Dept. of Health and Human Services, Public Health Service, Centres for Diseases Control, Atlanta, Georgia, USA.