Detrimental Effects of the Selected Heavy Metals to Seaweeds: A Review

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Abstract
Heavy metal pollution becomes one of the alarming environmental problems of the ocean ecosystem. The major human activities which have contributed to the elevated level of these metals in the ocean include the release of the industrial effluents, massive dredging and reclamation activities along the coastal areas, and oil spillage. The heavy metals that have reached the ocean are being absorbed by the marine organisms such as seaweeds and they are accumulated in their thalli. Among macro-algae, excessive accumulation of these heavy metals could cause poor growth and survival, inefficient photosynthetic performance, and cellular parts damage. Zinc, Lead, and Cadmium were the most common heavy metals which inhibited the growth of the seaweeds or even caused its death. Exposure of the algae to higher concentrations of Copper, Lead, and Cadmium could lead to inefficient photosynthetic performance. Copper and Cadmium have been known to cause cellular parts damage among the seaweeds.

Keywords: Heavy metals, growth rate, organelles, photosynthesis, seaweeds

Introduction

Human civilization has considered ocean as an infinite source of food items, a boundless sink for the pollutants and a tireless sustainer of the coastal habitats. This great misconception has aggravated the marine pollution in some extent. In modern society, the unregulated anthropogenic activities cause the increase in the amount of the pollutants that directly and indirectly enter the marine environment (Pratap et al., 1999; Sheng et al., 2004). The influx of these harmful substances goes beyond the capacity of the ocean to de-pollute and cleanse itself; hence, this condition poses a tremendous threat to the ocean biodiversity. Among the pollutants that greatly affect the marine biodiversity are the heavy metals. These metals are stable and cannot be broken down, which make it easy for them to accumulate in the environment (Lenntech Water Treatment and Air Purification, 2004). Its rapid buildup in the marine water makes the organisms highly vulnerable to accumulate in their body parts which consequently affect its physiological and biochemical functions.

In view of the purpose of heightening the pollution awareness of the humankind, this paper generally aims to discuss the detrimental effects of the selected heavy metals to the different species of the seaweeds. Specifically, this tackles the distribution of the selected heavy metals in the ocean, heavy metals accumulated in the seaweed thalli, causes of the heavy metal pollution in the ocean and harmful effects of these substances to the seaweeds.

Distribution of the Selected Heavy Metals in the Ocean

Heavy metals are ubiquitous in the nature. They are found everywhere in varying concentrations due to the natural processes and man-made activities. In the ocean, these substances are relatively well distributed. Cuong et al (2008) reported that the lowest concentrations of heavy metals in the dissolved phase and suspended particulate matter were most frequently found in the subsurface water while the highest concentrations were mostly observed in the sea-surface micro-layer and bottom water. In the study of Ali et al (2010), they revealed that the levels of heavy metals were considerably elevated in seawater, sediments and corals collected from the reef sites exposed to the increased environmental contamination. They also observed that soft corals of genera Lithophyton, Sarcophyton, and Sinularia showed higher concentrations of Zn, Pb, Cd and Ni than hard coral genera Acropora and Stylophora.
Table 1. Heavy metal accumulation in different seaweeds at Kanyakumari, Tamil Nadu, India (Source: Shanmugam et al., 2012)

<table>
<thead>
<tr>
<th>Heavy Metals</th>
<th>Station (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C. clavatum</td>
</tr>
<tr>
<td>Cd</td>
<td>4.16±0.080</td>
</tr>
<tr>
<td>Cu</td>
<td>2.43±0.158</td>
</tr>
<tr>
<td>Mn</td>
<td>0.463±0.63</td>
</tr>
<tr>
<td>Ni</td>
<td>0.12±0.026</td>
</tr>
<tr>
<td>Pb</td>
<td>4.92±0.39</td>
</tr>
<tr>
<td>Zn</td>
<td>0.00±0.00</td>
</tr>
<tr>
<td>Hg</td>
<td>0.00±0.00</td>
</tr>
</tbody>
</table>

Table 2. Gross photosynthetic rate (GPR) of Enteromorpha flexuosa exposed to different Cu concentrations (adopted from Andrade et al., 2004)

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Gross photosynthetic rate*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>27.67±7.62</td>
</tr>
<tr>
<td>50 µg Cu/L</td>
<td>23.68±4.95</td>
</tr>
<tr>
<td>100 µg Cu/L</td>
<td>-0.99±0.25</td>
</tr>
<tr>
<td>150 µg Cu/L</td>
<td>-0.84±0.29</td>
</tr>
</tbody>
</table>

* Results shown as mg O₂/mg/h (mean±SD).

Heavy Metals Accumulated in the Seaweeds

Seaweeds have inherent capacity to absorb heavy metals from marine water. This intrinsic ability allows these organisms to accumulate much amount of heavy metals over time. Previous investigations had observed the accumulation of the selected heavy metals in the different species of seaweeds. The study of Shanmugam et al. (2011) showed that the five species of seaweeds have accumulated seven heavy metals (Cd, Cu, Mn, Ni, Pb, Zn and Hg) at varying concentrations (Table 1). In the same study, Sargassum wightii and Ulva reticulate were found to absorb all the heavy metals analyzed except for Hg while Centrocerus clavutum was able to accumulate the said metals except for Cd (Table 1). Investigation of Topcuologu et al. (2010) also observed the presence of the heavy metals in selected algal species. They have found out that Co, Cr, Cu, Fe, Mn, Ni and Zn have been accumulated in Antithamnion curicuatum, Cd in Chaetomorpha gracilis and Pb in Pterocladia capillacea. In Yemen, Al-Shwafi and Rushdi (2008), investigated the concentration levels of heavy metals in different species of the main three marine algal divisions (green, brown and red) from the Gulf of Aden coastal waters. Results of the study indicated that the concentrations of heavy metals in all algal species were in the order of Fe>Cu>Mn>Cr>Zn>Ni>Pb>Cd>V>Co.
Causes of Heavy Metal Pollution in the Ocean

Heavy metals in the ocean come in two major sources: natural and anthropogenic sources. Concerning natural sources, these metals enter the sea usually through riverine influx (after weathering and erosion of rocks) and atmospheric deposition (dust particles from the volcano materials). In moderate quantity, the effects of these natural sources are highly manageable by the ocean itself. However, the problems on the heavy metal pollution in the ocean become alarming due to the intense anthropogenic activities. Human-related activities that have elevated the level of the heavy metals in the ocean include coastal reclamation and dredging, industrial discharge and oil spills.

Coastal and marine environments are the prime target for most of the major housing, recreational, and economic developments (Naser et al., 2008). In Arabian Gulf, for example, Hamza and Munawar (2009) estimated that more than 40% of the coasts have been developed from these activities. The coasts which are undergoing rapid construction activities are often associated with intensive dredging and reclamation (Naser, 2011). Dredging and reclamation processes are typically associated with short and long term chemical impacts. It has been observed by Guerra et al. (2009) that elevated levels of heavy metals are mobilized during dredging and reclamation activities.

Some of the pollutants that originated from the industry’s discharge commenced its route through the river. Singh and Singh-Chandel (2009) revealed that wastewater released to the river contains high concentration of Cu, Fe, Mn, Ni and Zn. During the duration of the flow, some of these accumulated, interacted and settled with the living organisms and the sediments while others finally reached the coastal and marine environment. Industrial discharge significantly contributed to the increased level of heavy metals in the ocean the moment they reached the marine environment.

The heavy metals Ni, V, Cu, Cd, and Pb are normal constituents of crude oil (Osuji and Onojake, 2004) and they contaminated the ocean water, sediments and marine organisms during the oil spill incident. When seawater samples from the ocean of the oil spill area in Bohai Bay were collected by Wang et al (2014) during summer 2013, they found out that the order of content from high to low of the heavy metals was Zn, Cu, Cr, As, Pb, Cd,
Hg, Zn, Cu in surface seawater while Zn, Cu, As, Cd, Pb, Hg in the bottom.

**Damaging Effects of Some Heavy Metal Exposure to the Seaweeds**

Accretion of the heavy metals in the ocean makes the seaweeds highly susceptible to accumulate these metals in its thalli. Although some of these metals like Zinc and Iron are essential to their growth and metabolic processes, however; excessive concentration can cause toxicity which will consequently create harmful effects to the physiological and biochemical processes of these organisms. These harmful effects include inhibition of the growth, reduction of the photosynthetic activity and destruction of the cellular parts.

**Growth Inhibition**

One of the detrimental effects of heavy metal accumulation on the seaweeds is growth inhibition. Several experiments have suggested that exposure of the seaweeds to high concentration of the heavy metals—both essential and non-essential has a negative impact to its growth. For instance, Ologuin et al (2009) reported that exposure of *Gracilaria coronopifolia* to 0.02, 0.10, 1.0 and 5.0 ppm of Lead for 15 days brought a very minimal specific growth in biomass ranging from 0.04 to 0.92% only (Fig. 1). Amado Filho et al. (1997), on the other hand, observed that six species of seaweeds died after three days of exposure to 5000 µg Zn/L (Fig. 2). *E. flexuosa, U. lactuca,* and *H. musciformis* died during the first 7 days and *H. musciformis* died after 15 days when they were exposed to 1000µg Zn/L. Like Zinc and Lead, Cadmium had potentially inhibited the growth of the seaweeds. In the study of dos Santos (2012), minimal growth rate of *Gracilaria domingensis* was observed after 16 days in culture and exposure to cadmium in various concentrations (Fig. 3). Poor growth rate of this alga was mainly attributed by bleaching of the apical segments which ultimately led to weight loss and tissue damage (Fig. 4).

**Reduction of the Photosynthetic Activity**

Heavy metals have the ability to alter some of the metabolic processes of the seaweeds. One of these activities being affected by the heavy metal accumulation is its food making process called as photosynthesis. Copper, Cadmium, and Lead are some of the known heavy metals that have shown negative effects on the said biological process. It was demonstrated that exposure of the green alga *Enteromorpha flexuosa* to Copper for five days at concentrations of 250 ug/L and 500 ug /L reduced its photosynthetic rate to -0.99O₂/mg/h and -0.845 O₂/mg/h; respectively (Table 2). Like Copper, Cadmium also altered the photosynthetic activity of the seaweeds. The maximum photosynthetic rate (Pmax) and photosynthetic efficiency (α) values of *Gracilaria domingensis* decreased after culture with Cadmium for 16 days (Table 3) (dos Santos et al., 2012). Ologuin et al (2009) observed a significant decline in the oxygen production among *Gracilaria coronopifolia* and *Gracilaria eucheumoides* from day 7 to day 15 of culture when they were exposed to 0.02, 0.10, 1.0 and 5.0 ppm lead (Fig. 4). The reduction of the photosynthetic activity of the different species of seaweeds may potentially be associated to the abrupt decrease in its pigment content due to the damaging effects of the heavy metals.
Table 3. Changes in photosynthetic pigments [µg/g – 1(FM)] on *G. domingensis* under cadmium treatment.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Control</th>
<th>100 µM</th>
<th>200 µM</th>
<th>300 µM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pmax</td>
<td>24.9 ± 0.001</td>
<td>21.6 ± 0.001</td>
<td>13.3 ± 0.97</td>
<td>8.4 ± 0.08</td>
</tr>
<tr>
<td>α</td>
<td>0.53 ± 0.003</td>
<td>0.03 ± 0.006</td>
<td>0.02 ± 0.002</td>
<td>0.02 ± 0.002</td>
</tr>
</tbody>
</table>

The values refer to mean ± SD, n = 4. Different letters indicate significant differences according to Tukey’s range test (p < 0.05)

(Source: Dos Santos et al., 2012)
Cellular Parts Damage
Aside from inhibition of the growth and reduction of the photosynthetic activity, heavy metals could also cause damage of the cellular parts of the seaweeds. The targets of the heavy metals are the major organelles of the cells of the algae. Andrade et al (2010) reported that the cells of Enteromorpha flexuosa showed several ultrastructural changes when exposed to 250 mg Cu/L. There were structural alterations that were noted during the duration of the exposure. These ultra-structural modifications observed include thickened and smoothened cell wall internal layers, an increase in the number of starch granules, presence of numerous electron-dense precipitates into vacuoles, and increase of dimension and number of cytoplasmic lipid droplets and disrupted, swollen, and dilated arrangement of thylakoid membranes in the chloroplast (Fig. 6).

Figure 3. Growth rates (GRs) of G. domingensis under cadmium treatment and control. Vertical bars represent $\pm$SD for means (n=4). Letters indicate significant differences according to Tukey’s range test (p<0.05). (Source: Dos Santos et al., 2012)

Figure 4. Apical segments of G. domingensis according to the treatments. (a): Control initial; (b): Control after 16 days of culture; (c): Apical segments after 16 days of treatment with 100 $\mu$M of the cadmium; (d): Tallus after 16 days of treatment with 200 $\mu$M of the cadmium; (e): Apical segments after 16 days of treatment with 300 $\mu$M of the cadmium. Scale bars = 1 cm (adopted from Dos Santos et al., 2012)

Organelle that is greatly prone to disruption once exposed to the high concentration of Cadmium is chloroplast. Cadmium could create structural modification in the algal chloroplast the same way copper has exhibited in the structure itself. It was indicated by dos Santos et al. (2012) that after 16 days of culture with 100
µM, 200 µM, and 300 µM of cadmium, *G. domingensis* chloroplasts showed visible changes in ultra-structural organization with irregular morphology. Observations revealed that its thylakoids were disrupted and the number of plastoglobuli increased in the chloroplasts (Fig. 7). Plastoglobuli are described as densely staining droplets existing in large numbers; most often found in plastids of the plant cells (Dictionary of Biology, 2004). These structures are present in the chloroplast; however, they have been masked by the green chlorophyll. In terms of composition, these are mainly composed of lipid pigments (Dictionary of Biology, 2004).

Figure 5. Dissolved oxygen production of the two (A) *Gracilaria coronopifolia* and (B) *Gracilaria eucheumoides* on the 7th and 15th day of culture. (Error bars are standard errors where n=3) (adopted from Ologuin et al., 2009)
Conclusion and Future Directions

Heavy metal pollution becomes one of the alarming environmental problems of the ocean ecosystem. The major human activities which have contributed to the elevated level of these metals in the ocean include the release of the industrial effluents, massive dredging and reclamation activities along the coastal areas, and oil spillage. The heavy metals that have reached the ocean are being absorbed by the marine organisms such as seaweeds and they are accumulated in their thalli. Among macro-algae, excessive accumulation of these heavy metals can cause poor growth and survival, inefficient photosynthetic performance, and cellular parts damage. Zinc, Lead, and Cadmium were the most common heavy metals which inhibited the growth of the seaweeds or caused its death. Exposure of the algae to higher concentrations of Copper, Lead, and Cadmium could lead to inefficient photosynthetic performance. Copper and Cadmium have been known to cause cellular parts damage among the
seaweeds.

**Figure 8. Concept map of the sources of heavy metals in the ocean and its harmful effects on the seaweeds**

Human-related activities elevated the heavy metals in the ocean, hence; heavy metal pollution becomes more intense over time. Intense pollution has brought great impacts to the marine organisms especially the seaweeds. Higher concentration of these metals inhibited the growth of the seaweeds, reduced its photosynthetic performance and destroyed its cellular structure. With these harmful effects, programs and projects in order to protect the seaweeds should be initiated and implemented. Awareness of the people on heavy metal pollution should be heightened so that they may restrict their activities that can possibly escalate the level of the heavy metals in the ocean. Potential research on improving the resistance of the seaweeds against heavy metal pollution should be explored in the future endeavor. Other harmful activities of these metals on the macro-algae should be considered for future investigation.

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