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

Raymund N. Fantonalgo[1,2,3,4*] Maricel N. Falguisana[5]
1.Faculty of Natural Sciences, Senior High School Department, College of Education, University of the East-Manila Claro M. Recto Avenue, Sampaloc, 1008 Manila, Philippines
2.Environmental Science Department, School of Science and Engineering
Ateneo de Manila University, Katipunan Avenue, Loyola Heights,
1108 Quezon City, Philippines
3.Marine Science Institute, College of Science, University of the Philippines Diliman,
1101 Quezon City, Philippines
4.Faculty of Biological Sciences, Department of Sciences, College of Arts and Sciences, Western Institute of Technology, La Paz, Iloilo City, 5000 Philippines
5.Graduate School, College of Arts and Sciences, West Visayas State University,
La Paz, Iloilo City, 5000 Philippines

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*.

Table1. Heavy metal accumulation in different seaweeds at Kanyakumari, Tamil Nadu, India *(Source: Shanmugam et al., 2012)*

Heavy metals	Station (1)	*C. clavutum*	*S. wightii*	*C. sinuosa*	*S. hypnoides*	*V. pachynema*
Cd	Kanyakumari	0	0.023±0.015	0.006±0.001	0.300±0.050	0.034±0.040
Cu		4.16±0.080	3.17±0.23	0.300±0.10	6.55±0.195	4.51±0.121
Mn		2.42±0.158	1.58±0.072	2.86±0.119	3.03±0.018	0.62±0.11
Ni		0.463±0.63	0.803±0.57	0.16±0.034	0.452±0.38	0.226±0.24
Pb		0.26±0.026	0.2±0.026	0.3±0.019	0.34±0.04	0.25±0.013
Zn		1.04±0.039	0.71±0.018	0.85±0.026	1.22±0.021	0.83±0.083
Hg		0.01±0.009	0.00	0.01±0.001	0.01±0.002	0.01±0.001

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

Treatments	Gross photosynthetic rate[a]
Control	27.67 ± 7.62
50 μg Cu/L	23.68 ± 4.95
250 μg Cu/L	−0.99 ± 0.25
500 μg Cu/L	−0.845 ± 0.29

[a] Results shown as mg O_2/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, Zi and Hg) at varying concentrations (Table1). In the same study, *Sargassum wightii* and *Ulva reticulate* were found to absorb all the heavy metals analyzed except for Hg while *Centrocerous 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.

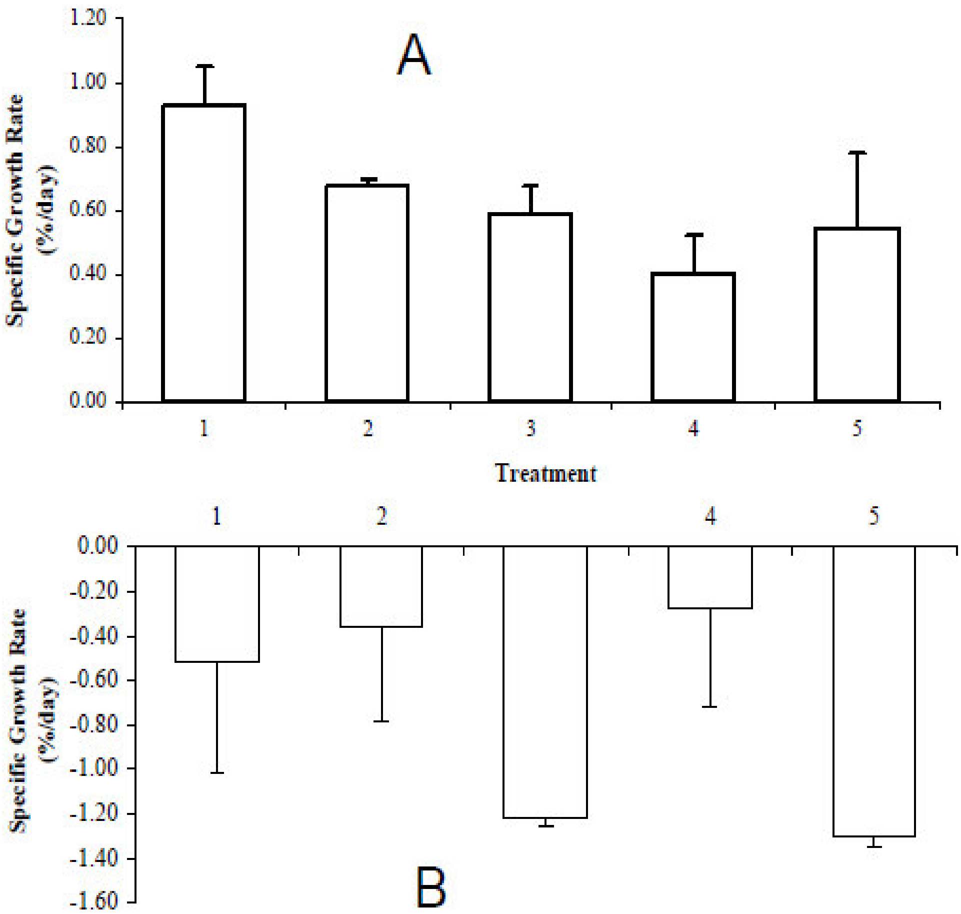

Figure1.Specific growth rate in biomass of (A) *Gracilaria coronopifolia* and (B) *Gracilaria eucheumoides(Error bars are standard errors with n =3)**(from Oloquin et al., 2009)*

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 dredgingand 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 -0.99O_2/mg/h and -0.845 O_2/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

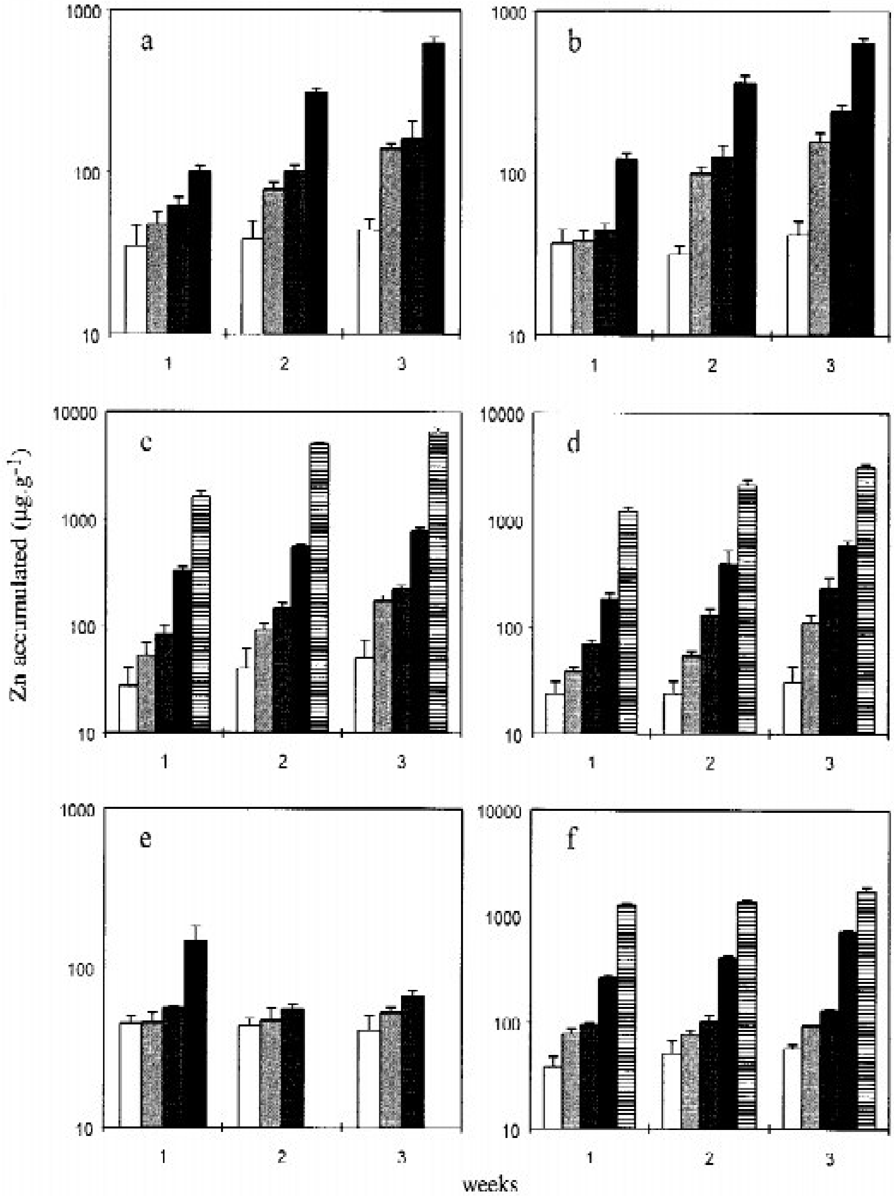

FIG. 2. Zinc accumulation ($\mu g \cdot g^{-1}$) by the six species at different zinc concentrations in sea water: control, □; 10 $\mu g \cdot liter^{-1}$, ▨; 20 $\mu g \cdot liter^{-1}$, ▩; 100 $\mu g \cdot liter^{-1}$, ■; and 1000 $\mu g \cdot liter^{-1}$, ▤, throughout the 3-week experimental time. (a) *Enteromorpha flexuosa;* (b) *Ulva lactuca;* (c) *Padina gymnospora;* (d) *Sargassum filipendula;* (e) *Hypnea musciformis;* (f) *Spyridia filamentosa.*

(adopted from Amado-Filho et al., 1997)

Table 3. Changes in photosynthetic pigments [µg/g – 1(FM)] on *G. domingensis* under cadmium treatment.

Treatment	Control	100 µM	200 µM	300 µM
Pmax	24.9 ± 0.001	21.6 ± 0.001	13.3 ± 0.97	8.4 ± 0.08
α	0.53 ± 0.003	0.03 ± 0.006	0.02 ± 0.002	0.02 ± 0.002

The values refer to mean ± SD, n = 4. Different lettersindicate significant differences according to Tukey'srange 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 ultra-structural 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 arrangementof thylakoid membranes in the chloroplast (Fig. 6).

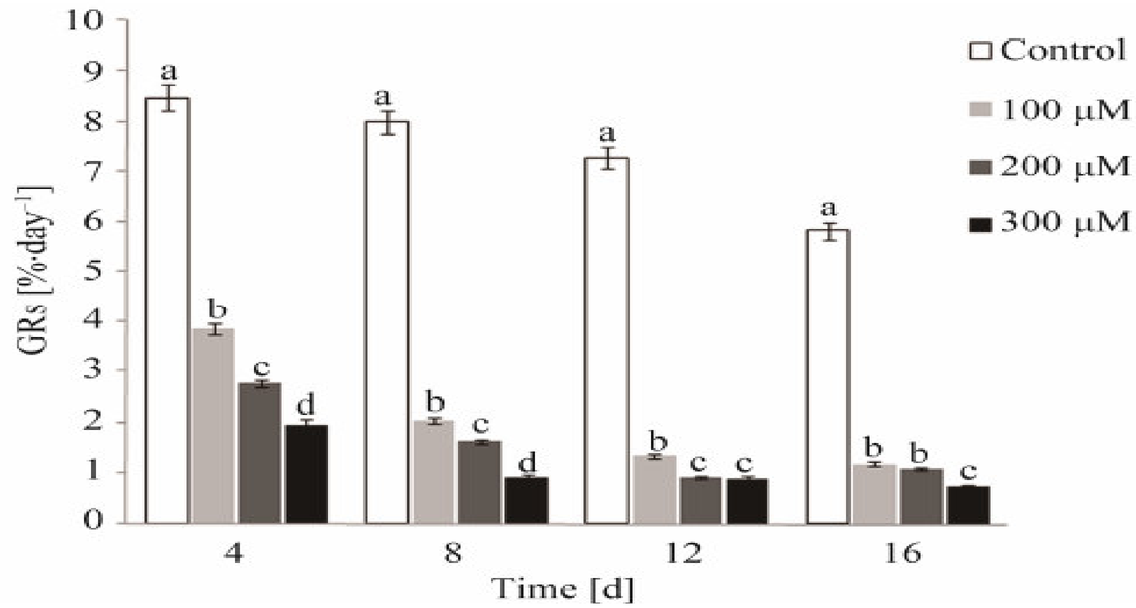

Figure3. Growth rates (GRs) of *G. domingensis* under cadmium treatment and control. Vertical bars represent ±SD for means (n=4). *Letters indicate significant differences according to Tukey's range test (p<0.05).* (*Source: Dos Santos et al., 2012*)

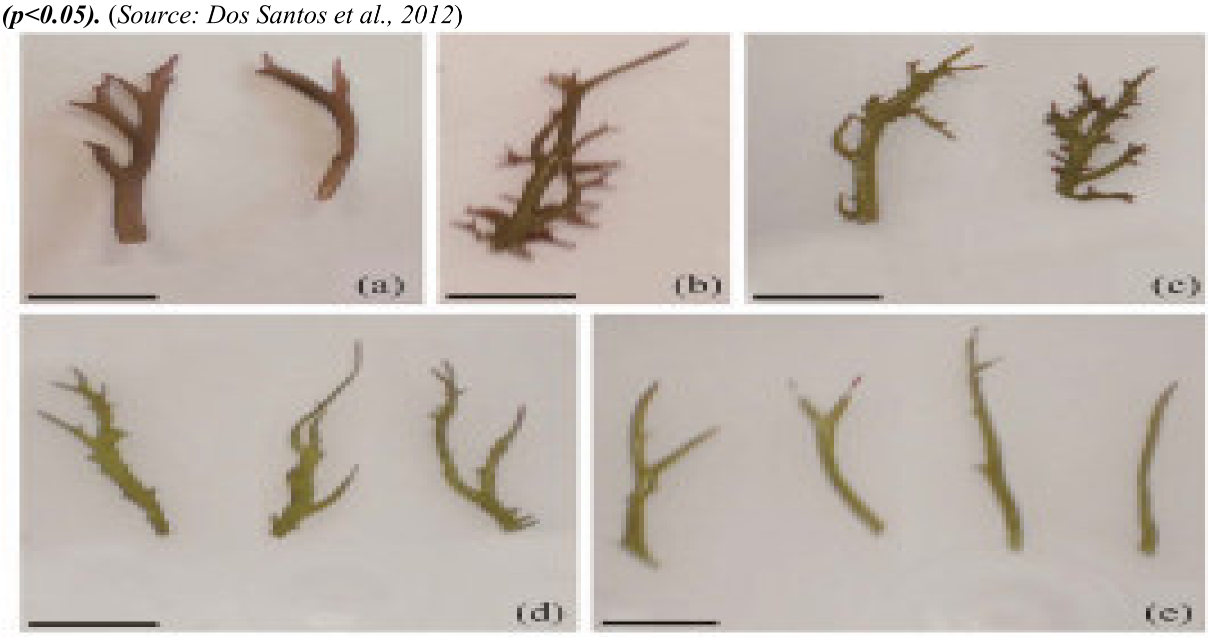

Figure4. Apical segments of *G. domingensis* according to the treatments. (a): Control initial; (b): Control after 16 days of culture; (c): Apical segments after 16 days of treatment with 100 μM of the cadmium; (d): Tallus after 16 days of treatment with 200 μM of the cadmium; (e): Apical segments after 16 days of treatment with 300 μM 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).

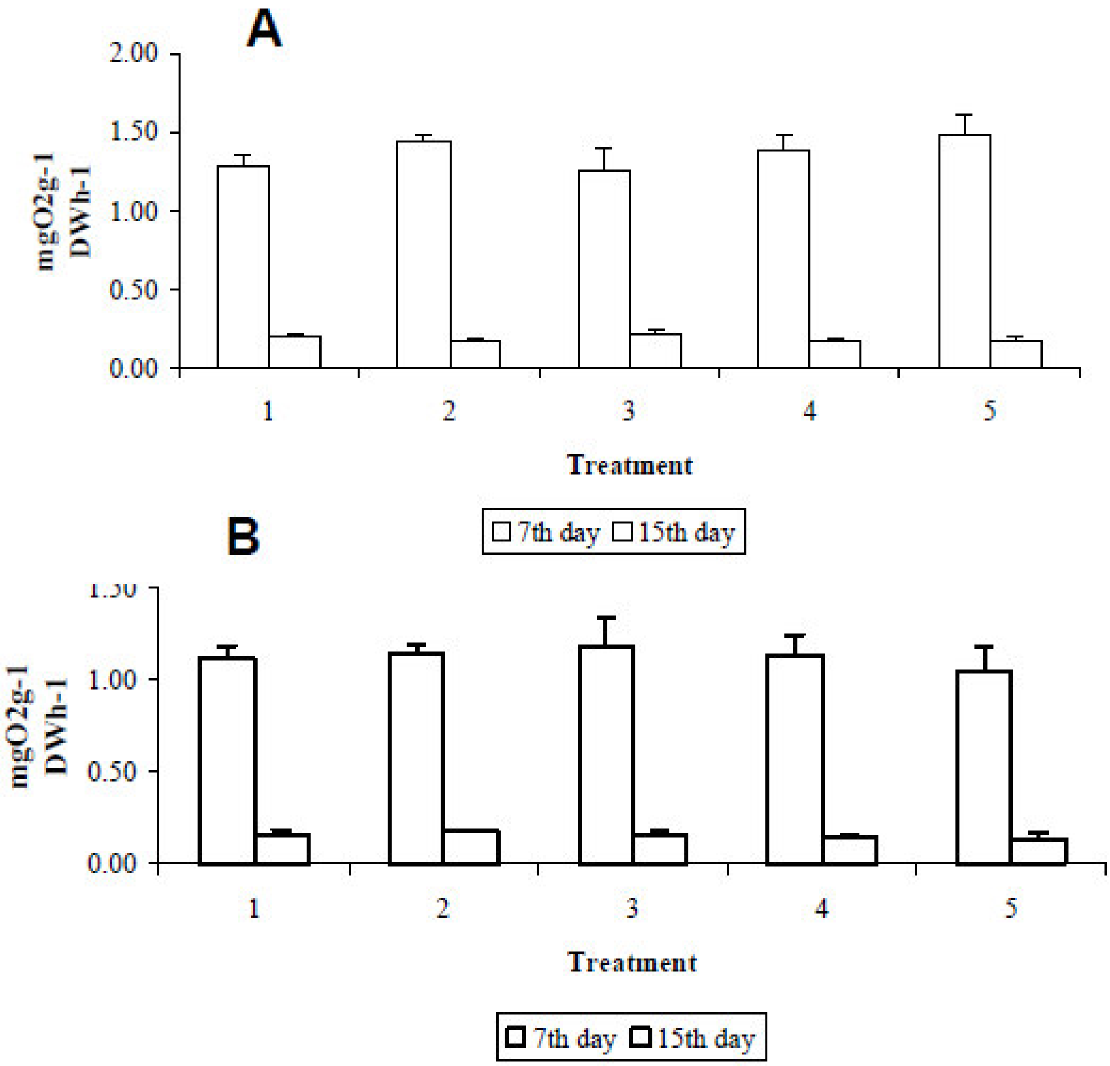

Figure5. Dissolved oxygen production of the two (A) *Gracilaria coronopifolia* and(B) *Gracilaria* eucheumoides on the 7th and 15th day of culture. (Error bars are standard errors where n=3) (adopted *from Ologuin et al., 2009*)

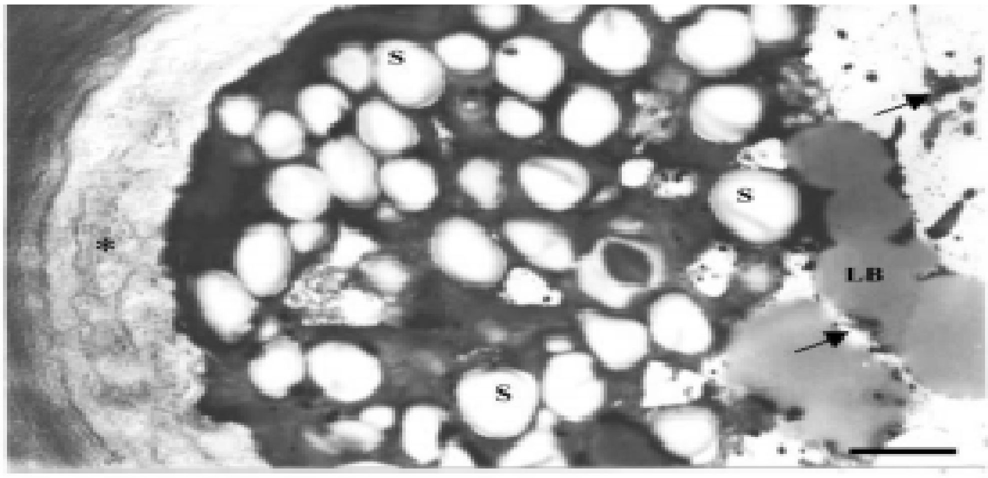

Figure6. Cell from the 250 mg Cu/L treatment showing the principalultra-structural changes, such as: increase in number of starch granules(S) and lipid bodies (LB), and electron-dense precipitates into the vacuoles (arrows). Swelling of the internal cell wall layers is also observable. Bar=0.5 mm. *(Source: Andrade et al., 2004)*

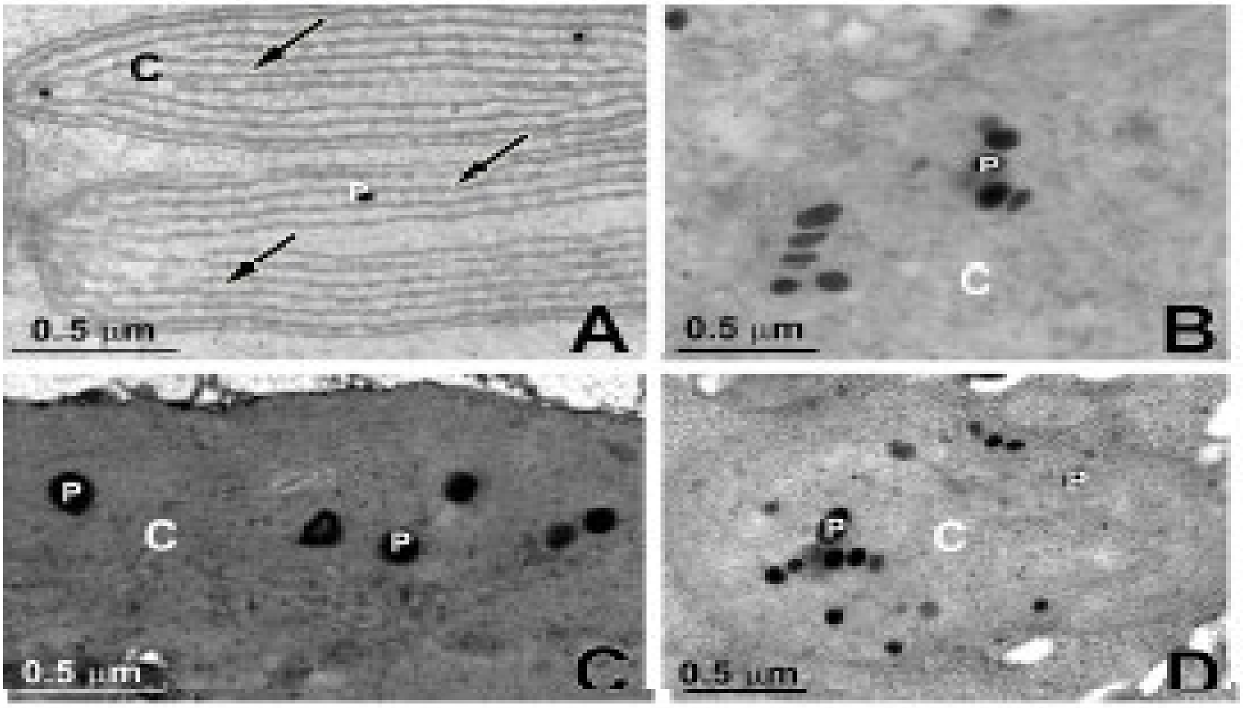

Figure7. Transmission electron microscopy of *G. domingensis chloroplasts* (C) under cadmium treatment. A: Control. Observe the thylakoids (arrows). Note the presence of plastoglobuli (P); B: Treatment with 100 uM of cadmium; C: Treatment with 200 uM of cadmium; D: Treatment with of 300 uM cadmium (*adopted from Dos Santos et al., 2012).*

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 concentration 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.

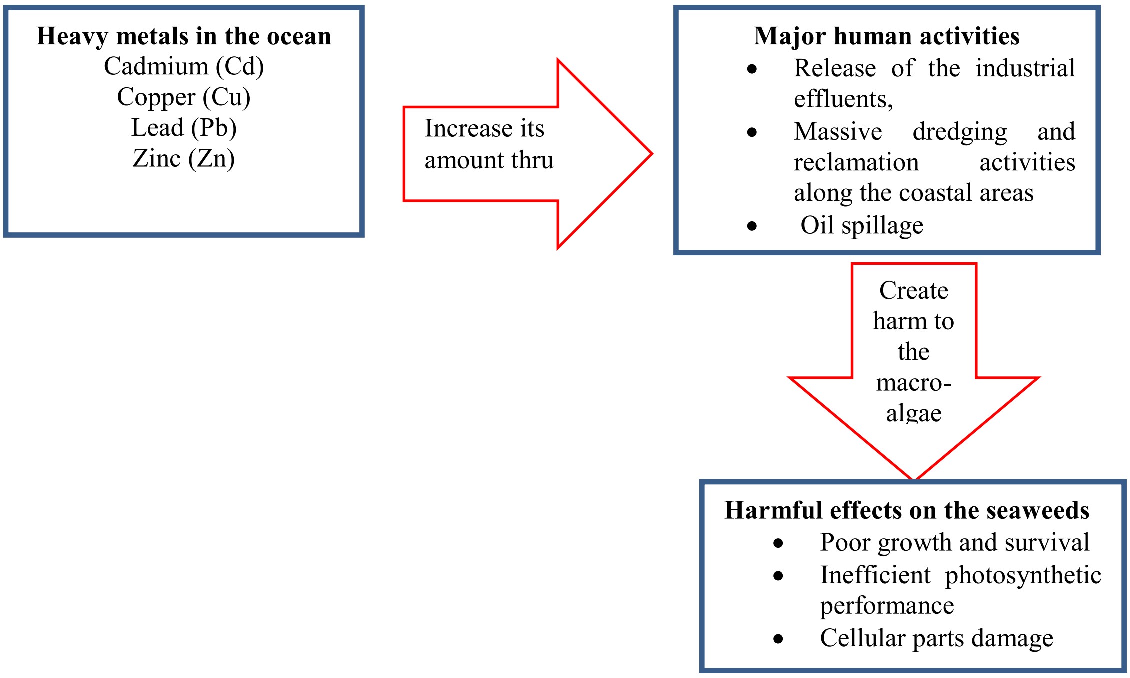

Figure 8. Concept map of the sources of heavy metals in the ocean and its harmful effects on the seaweeds

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.

Acknowledgement
The authors would like to thank the University of the East Manila, for financing the publication charge of this article; Prof. Dr. Ma. Lourdes S. McGlone of Marine Science Institute, University of the Philippines Diliman, for her valuable comments and suggestions for the improvement of this paper; Prof. Dr. Ian A. Navarrate, Environmental Science Department, Ateneo de Manila University for intense encouragement to finish this work; and Prof. Marianne Camoying of Senior High Department, University of the East-Manila for inspiring me to write this manuscript in spite of hectic schedule.

References

Ali, AHAM, Hamid, MA, and El-Azim, HA. (2011). Heavy metals distribution in the coral reef ecosystems of the Northern Red Sea.Helgoland Marine Research. 65(1), 67-80.

Al-Shwafi, NA and Rushdi, AI. (2008). Heavy metal concentrations in marine green, brown, and red seaweeds from coastal waters of Yemen, the Gulf of Aden. Environmental Geology. 55(3), 653-660.

Amado-Filho, GM, Karez, CS, Andrade, LR, Yoneshigue-Valentin,Y and Pfeiffer, WC. (1997). Effects on Growth and Accumulation of Zinc in Six Seaweed Species. Ecotoxicology and Environmental Safety. 37, 223-228.

Andrade, LR, Farina, M and Amado-Filho, G. (2004). Effects of copper on *Enteromorpha flexuosa*(Chlorophyta) in vitro. Ecotoxicology and Environmental Safety. 58, 117–125.

Cuong, DT, Karuppiah, S and Obbard, JP., 2008, Distribution of heavy metals in the dissolved and suspended phase of the sea-surface microlayer, seawater column and in sediments of Singapore's coastal environment. Environmental Monitoring and Assessment. 138 (1), 255-272.

Dictionary of Biology (2004). Retrieved March 20, 2017 from Encyclopedia.com: http://www.encyclopedia.com/science/dictionaries-thesauruses-pictures-and-press-releases/plastoglobulus.

Dos Santos, RW, Schmidt, EC,Martins, RDP, Latini, A, Maraschin, M, Horta, PA, and Bouzon, ZL. (2012).

Effects of Cadmium on Growth, Photosynthetic Pigments, Photosynthetic Performance, Biochemical Parameters and Structure of Chloroplasts in the Agarophyte *Gracilaria domingensis* (Rhodophyta, Gracilariales). American Journal of Plant Sciences. 3, 1077-1084.

Guerra, R, Pasteris, A, and Ponti, M. (2009). Impacts of maintenance channel dredging in a northern Adriatic coastal lagoon. I: Effects on sediment properties, contamination and toxicity. Estuar.Coast. Shelf Sci., 85, 134–142.

Hamza, W and Munawar, M. (2009). Protecting and managing the Arabian Gulf: past, present and future. Aquat. Ecosyst. Health Management, 12, 429–439.

Lenntech Water Treatment and Air Purification, 2004, Water Treatment, Published by Lenntech, Rotterdamseweg, Netherlands (www.excelwater.com/thp/filters/Water-Purification.htm)

Naser, HA. (2013). Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf: a review. Mar Pollut Bull. 72(1), 6-13.

Naser, H. (2011). Effects of reclamation on macrobenthic assemblages in the coastline of the Arabian Gulf: A microcosm experimental approach. Mar. Pollut. Bull., 62, 520–524.

Naser, H., Bythell, J., and Thomason, J. (2008). Ecological assessment: an initial evaluation of Ecological input in environmental impact assessment reports in Bahrain. Impact Assessment and Project Appraisal, 26, 201–208.

Ologuin, MM, Roa, EL, and Uy, WH. (2009). *In vitro* lead accumulation in *Gracilaria coronopifolia* and *Gracilaria eucheumoides.* Journal of Environment and Aquatic Resources. 1(1), 87-98.

Osuji, LC.and Onojake, CM. (2004). Trace Heavy Metals Associated with Crude Oil: A Case Study of Ebocha-8 Oil-Spill-Polluted Site in Niger Delta, Nigeria. Verlag Helvetica ChimicaActa, 1(11), 1708–1715.

Pratap, HB, Mamboya, FA, Mtolera, MSP, and Björk, M. (1999). The Effect of Copper on the Daily Growth Rate and Photosynthetic Efficiency of the Brown Macroalga *Padina boergensenii*. Proceedings of the Conference on Advances on Marine Sciences in Tanzania, Bilateral Marine Science Programme, pp. 185-192.

Shanmugam, A, Sudharsan, S, Seedevi, P, Ramasamy, P, Subhapradha, N, and Vairamani, S., (2012). Heavy metal accumulation in seaweeds and sea grasses along southeast coast of India Journal of Chemical and Pharmaceutical Research, 4(9), 4240-4244.

Sheng PX, Ting, Y, Chen, JP, and Hong, L. (2004). Sorption of Lead, Copper, Cadmium, Zinc and Nickel by Marine Algal Biomass: Characterization of Biosorptive Capacity and Investigation of Mechanisms. Journal of Colloid and Interface Science, 275(1), 131-141.

Singh, Vand Singh-Chandel, CP. (2006). Analytical study of heavy metals of industrial effluents at Jaipur, Rajasthan (India).J Environ Sci Eng. 48(2):103-8.

Wang, H., Cai, D., Yin, R., Dong, Y., Liu, X., Gao, H., Zhao, W., and Zhu, N. (2014). The Evaluation of Heavy Metals in Seawater of the Oil Spill Area in Bohai Bay (China) during the Summer. Advanced Materials Research, 1073(1076), 500-503.