ISSN 1908-9058
Volume 8
January - December
2015

PUP JOURNAL of science and technology

scitech

Official Journal of Science and Technology
Polytechnic University of the Philippines
Sta. Mesa, Manila, Philippines

Polytechnic University of the Philippines
Office of the Vice President for Research, Extension, and Development

Produced by:
Institute for Science and Technology Research

Cover Design & Layout by:
Jesusana S. Dejito

Technical Assistance by:
Publications Office

PUP Journal of Science and Technology

Volume 8, January to December 2015
ISSN 1908-9058

Journal Description

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C O N T E N T S

OCCURRENCE OF LEAD, CADMIUM AND MERCURY IN SEAWEEDS FROM CALATAGAN, BATANGAS, PHILIPPINES

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Abstract: Eating seaweeds have many nutritional benefits to the body. Seaweeds also have many industrial uses such as bioremediation of polluted water. Batangas, Philippines is an industrial province located near the coast where seaweeds are abundant. This study is on the occurrence of heavy metals in seaweeds taken from Calatagan, Batangas, Philippines, and shows that all of the seaweeds tested are within the international food standard limitation except for one *Caulerpa lentillifera* sample. Moreover, estimated daily intake and health hazard calculation do not indicate potential health risks.

Keywords: *seaweeds, macroalgae, heavy metals, AAS, Hg, Cd, Pb*

1. INTRODUCTION

Calatagan, Batangas (13° 50´ latitude and 120° 38´ longitude) lies in the southwestern most of the province of Batangas in a peninsula approximately one hundred and ten (110) kilometers south of the City of Manila in the Philippines. The western shoreline of Calatagan is reef-bounded and has shallow waters with low fish corrals and abundant seaweeds. Seaweed products constitute one of the important export industries in the Philippines.

Seaweeds or macroalgae are species of marine plants and algae that grow in ocean, rivers and lakes. They are classified as green, brown and red algae. A variety of seaweeds are edible and eaten by many people around the world for nutritional and health reasons. The chemical composition of seaweeds is comprised of proteins, amino acids and minerals such as iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), and iodine (I) (Misurcova, 2011). It also contains vitamins, lipids and fibers. The high nutrient content of seaweeds makes it a good source of nutritional requirements. In fact, seaweeds are one of the most important sources of calcium (El-Said & Sikaily, 2013).

Many years ago, the Philippines was one of the world's biggest exporters of seaweeds. About 800 species of seaweeds can be found in the Philippines. However, recently, other countries like Indonesia overtook the country's production of seaweeds. To date, the Bureau of Fisheries and Aquatic Resources is finding a way to address the challenge of producing quality seaweeds for both export and local consumption.

Among the non-food uses of seaweeds is for bioremediation of polluted water. It is in this light that the researchers became interested on the ability of the macroalgae to uptake heavy metals. Some researchers have reported chemical composition including heavy metal concentration in seaweeds from their countries (Brandon *et al.*, 2014; Hwang *et al.*, 2010; Ito & Hori, 2010; Polat & Ozogul, 2008; Smith *et al.*, 2010). This study aims to show the level of concentration of heavy metals in seaweeds taken from Calatagan, Batangas in the Philippines. The health hazard of eating contaminated seaweeds is also discussed.

2. METHODOLOGY

Eucheuma cottoni, Eucheuma alvarezii, Eucheuma denticulatum and Caulerpa lentillifera seaweed samples were taken by hand from Barangay 1, Poblacion, Calatagan, Batangas. The samples were washed and sun dried for about 15 days.

About 7.5 g of dried samples were wet digested using diluted nitric acid (HNO_3), concentrated perchloric acid ($HClO_4$), and hydrochloric acid (HCl). It was then filtered and transferred to a clean container. The digested samples were analysed using a Shimadzu atomic absorption spectrophotometer (AAS) AA-6800 for lead (Pb) and cadmium (Cd) with the parameter set to standard operating system. Around 2.5 g of dried seaweeds were processed using automatic mercury (Hg) analyser via hydride vapor generator AAS.

For calibration, blank, 0.1 mg/kg, 0.2 mg/kg, and 0.4 mg/kg Pb and Cd standards were prepared. These standards were analysed using AAS to check linearity of the instrument.

3. RESULTS AND DISCUSSION

The dried seaweeds had hard and rubbery characteristics. Salt accumulation can also be observed at the surface of the samples after drying. It is assumed that the salt does not interfere with the Hg, Cd and Pb measurements.

3.1 Analytical technique and reliability of data

The results of the calibration curves for AAS are shown in Figures 1 and 2. The R^2 is near 1 and the values are linear, indicating that the results of the analysis are reliable.

Linearity of the calibration curve is very important in determining whether your analytical results are giving true value. The calculation of your prepared standard should be very close to the calculated value. In this analysis, a linear graph assures the values reported by the instrument are true values.

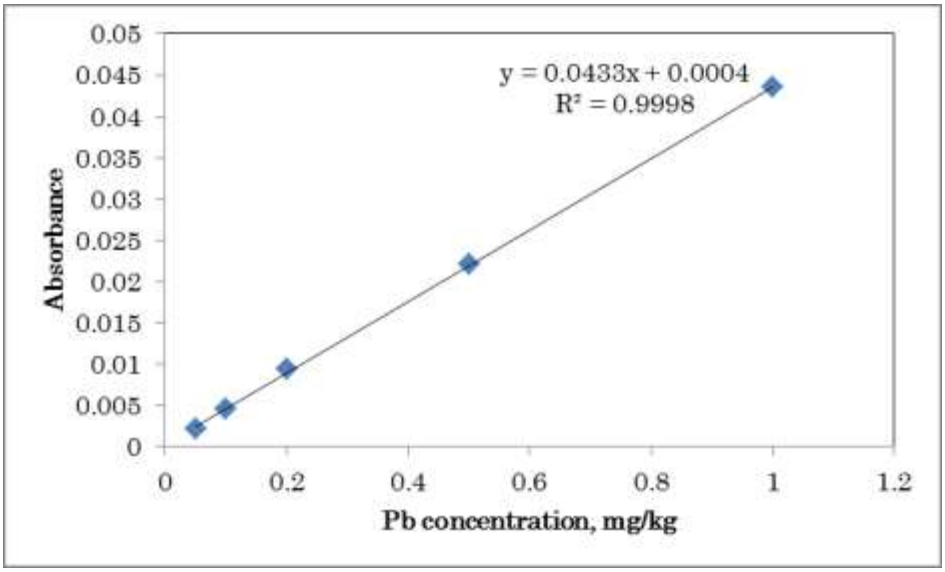

Figure 1. Calibration curve of lead (Pb) in flame atomic absorption spectrophotometer (AAS). A near 1 value for R^2 indicates reliability of the results.

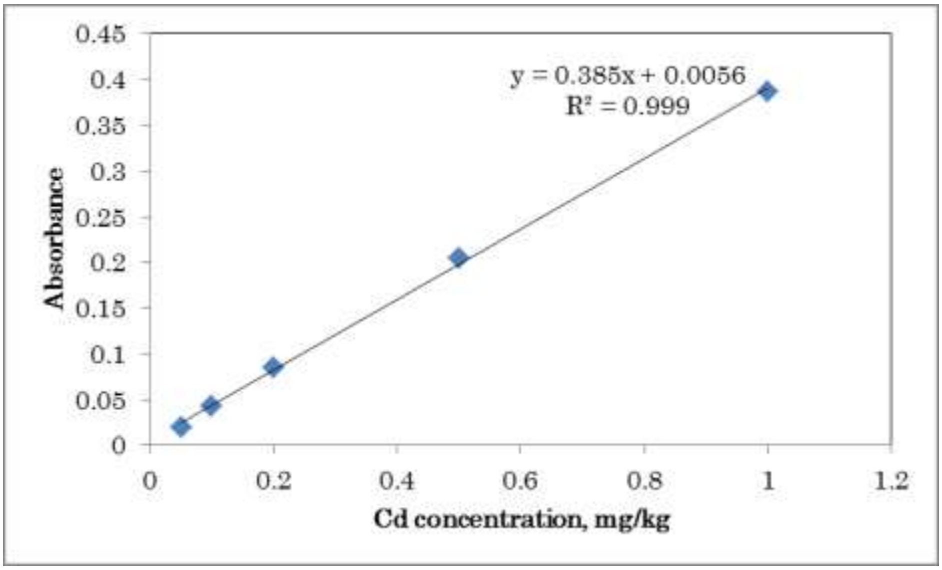

Figure 2. Calibration curve of cadmium (Cd) in flame atomic absorption spectrophotometer (AAS). A near 1 value for R^2 indicates reliability of the results.

3.2 Concentration of lead, cadmium and mercury in seaweeds taken from Calatagan, Batangas

The concentrations of lead (Pb), cadmium (Cd) and mercury (Hg) in seaweeds from Calatagan, Batangas were relatively constant all throughout the four month period (September to December 2005).

Figure 3 shows the total Pb content in seaweeds collected from Calatagan, Batangas. There was a general decreasing trend from the first sampling to the last except for *Caulerpa lentillifera*. The level of Pb content in all samples were below the standard limits for Pb of the European Commission (5 mg/kg) and Codex Alimentarius (2 mg/kg) in seaweeds.

Figure 4 shows the concentration of Cd in seaweeds. The Cd content of the samples was relatively uniform except for higher level in *Eucheuma alvarezii* between September to October sampling. The allowable limit of Cd is less than 1 mg/kg which indicates that the Cd content in all seaweed samples were acceptable.

The levels of Hg sampled in September to December were almost constant. However, Figure 5 shows that *Caulerpa lentillifera* sampled in December have more than double the standard limits for Hg. All other samples have concentrations lower than 1 mg/kg. Comparing the Hg, Cd and Pb concentrations shown in Figure 6 indicates that all were generally low. Hwang *et al.* (2010) reported that total Hg, Pb, and Cd contents determined from 426 samples of average dry weight concentrations of seaweed sold in Korea in 2007 to 2008 were: Hg= 0.01 mg/kg (from 0.001 to 0.050), Pb= 0.7 mg/kg (less than the limit of detection (LOD) to 2.7), and Cd= 0.50 mg/kg (less than the LOD to 2.9).

3.3 Sources of Pb, Cd, and Hg in Calatagan, Batangas

The Provincial Government of Batangas, Philippines (2008) has reported industrial waste pollution, air pollution, and mining and quarrying activities in the province, including Calatagan. Magoling (2015) mentioned that occasional oil spillage occur in Calatagan. These activities might be the main sources of Cd, Pb and Hg taken up by the algae. Furthermore, Imani *et al.* (2011) proved that seaweeds can be an important tool for bioremediation of heavy metals in water.

There are studies that show the amount of heavy metals in seaweeds in other countries. Lee and Park (2012) have reported a pH dependent biosorption of metal ions including Pb^{2+} and Cd^{2+} in brown algae collected from the southern coast of South Korea. This means that if the ocean, river, or lake maintains its natural pH, biosorption of heavy metals in macroalgae is weak. However, once the water is polluted, changing its pH to 2-4 from its normal 6-8, higher uptake of heavy metal by the macroalgae is expected.

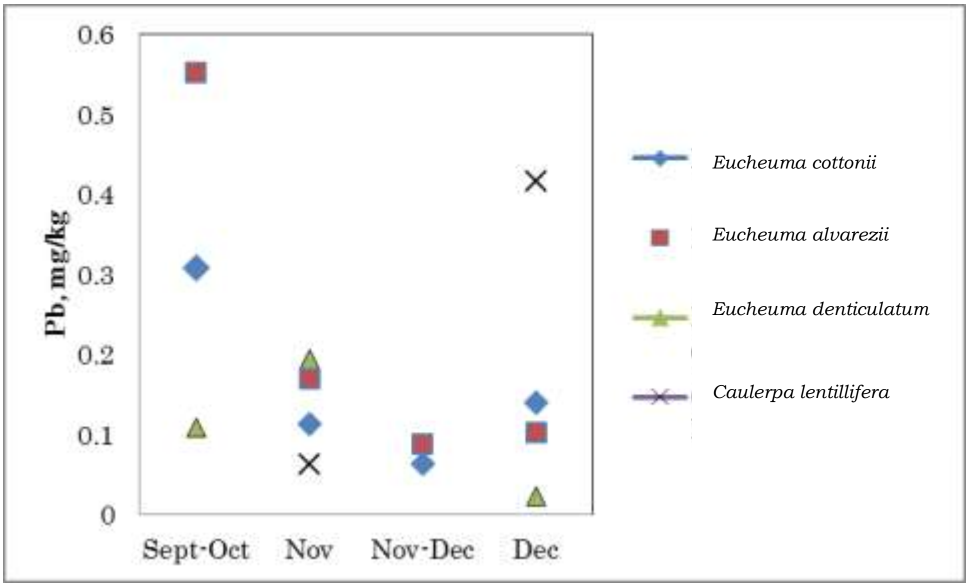

Figure 3. Lead (Pb) content in various seaweed samples taken from Calatagan, Batangas (September to December 2005).

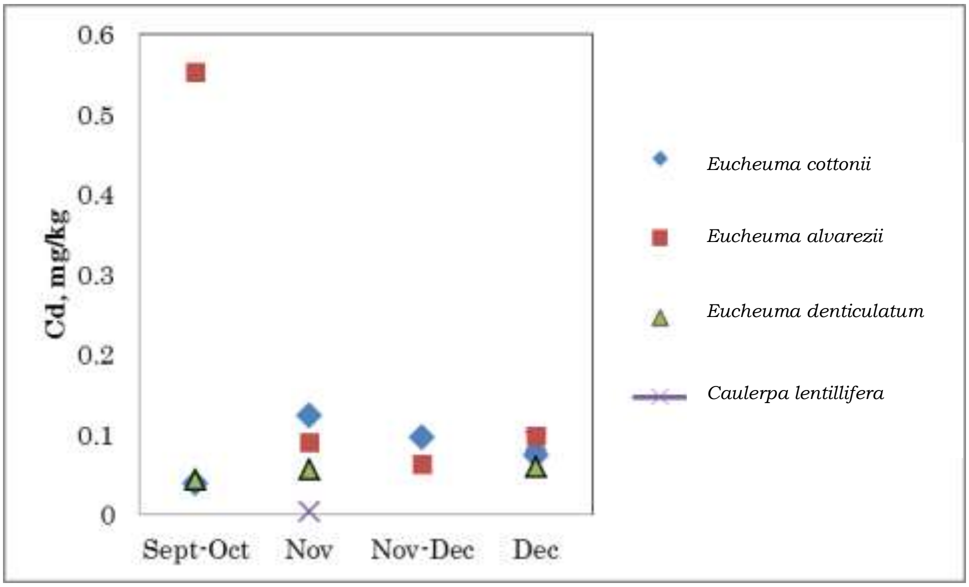

Figure 4. Cadmium (Cd) content from seaweed samples taken from Calatagan, Batangas (September to December 2005).

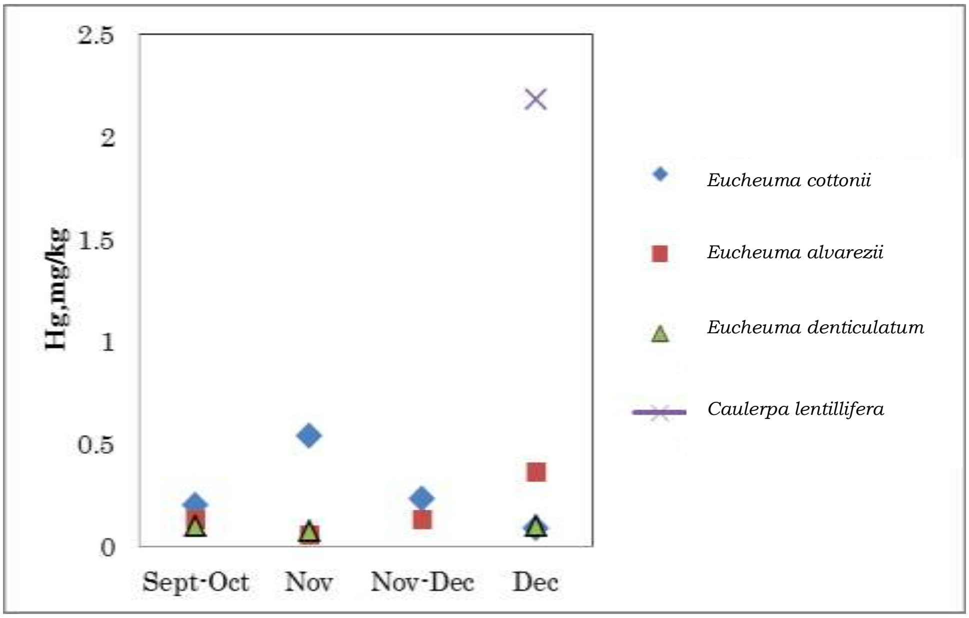

Figure 5. Mercury (Hg) content from Calatagan, Batangas (September to December 2005).

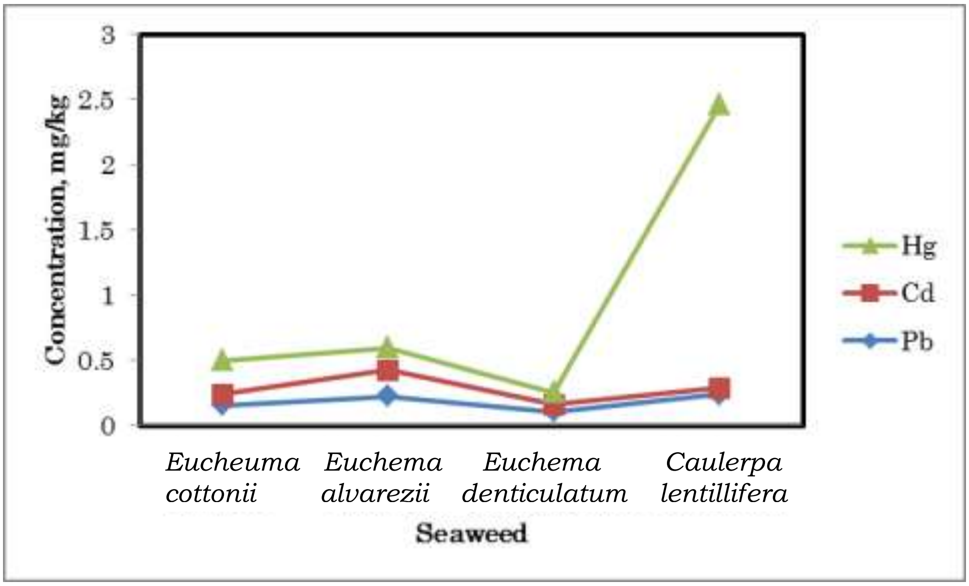

Figure 6. Comparison of heavy metal concentration in the seaweed samples (September to December 2005).

3.4 Health hazards of Pb, Cd, and Hg in seaweeds

To determine whether the results demonstrate that the studied edible algae is fit for human consumption, the estimated daily intake and health hazard were determined.

For example, for an 18-year-old person weighing 50 kg who has been eating seaweeds every day since he or she was 1 year old, the estimated daily intake (EDI) can be calculated as:

$$\text{EDI (mg/kg/day) adult} = \frac{(C \times IR \times EF \times ED)}{(BW \times AT)}$$

$$= \frac{2.18 \text{ mg/kg x } 0.227 \text{ kg/day x } 365 \text{ days/year x } 18 \text{ years}}{50 \text{ kg x } 17 \text{ years x } 365 \text{ days/year}}$$

where:

C = average concentration (in milligrams per kilogram) of the contaminant

IR = the ingestion rate for adult 0.227 kg/day (8-oz meal)

EF = exposure frequency, or number of exposure events per year of exposure (365 days/year)

ED = exposure duration, or the duration over which exposure occurs (lifetime exposure)

BW= body weight

AT = averaging time, or the period over which cumulative exposures are averaged (noncancer/lifetime = ED × 365 days/year)

Hwang *et al.* (2010) reported that the intakes of total Hg, Pb, and Cd from seaweed for a Korean were estimated to be 0.11, 0.65, and 0.45 µg/kg body weight per week, respectively. The concentrations arrived at in this study are very low in comparison (Table 1).

The potential for adverse effects can be calculated using the hazard quotient (HQ) for noncarcinogens.

$$HQ = \frac{\text{EDI mg/kg/day}}{\text{reference dose mg/kg/day}}$$

where:

EDI = estimated daily intake

As shown in Table 2, all of the hazard quotients of the seaweeds taken from Calatagan, Batangas are lower than 1.0. A value lower than or equal to 1.0 indicates that the degree of exposure is relatively safe. The Hwang *et al.* (2010) results, with a calculated consumption of 8.5 g/day of the samples analysed, represent 0.2 to 6.7% of the respective weekly intake (World Health Organization). The consumption of commercially available seaweeds in Korea also has low probability of health risks from these metals.

Table 1. Estimated daily intake (EDI) of seaweeds for an 18-year-old person.

Seaweeds	**mg/kg/day**		
	Pb	**Cd**	**Hg**
Eucheuma cottonii	0.01526	0.00808	0.02571
Eucheuma alvarezii	0.02228	0.01954	0.01643
Eucheuma denticulatum	0.01064	0.00519	0.00894
Caulerpa lentillifera	0.02341	0.00469	0.21250

Table 2. Hazard quotient (HQ) of seaweeds in an 18-year-old person.

Seaweeds	**HQ**		
	Pb	**Cd**	**Hg**
Eucheuma cottonii	0.053574	0.02835	0.09023
Eucheuma alvarezii	0.078184	0.06859	0.057645
Eucheuma denticulatum	0.037346	0.018200	0.03136
Caulerpa lentillifera	0.082148	0.01646	0.745789

4. CONCLUSIONS

As the Philippines is doing its best to produce quality seaweeds for local and worldwide consumption, it is important to know their possibility of heavy metal contamination. The concentrations of Pb, Cd and Hg in selected Philippine seaweeds are presented. The results show that the general averages are acceptable based on World Health Organization (WHO) standards and do not have significant hazardous health effects.

5. RECOMMENDATIONS

It is recommended that stricter industrial policy should be implemented to avoid the accumulation of hazardous concentrations of heavy metals in seaweeds.

6. ACKNOWLEDGMENTS

Authors Concepcion and Borja want to thank the Mines and Geosciences Bureau and Bureau of Fisheries and Aquatic Resources for the use of their instruments, and for their guidance in the sampling of seaweeds.

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Volume 8 January to December 2015