Assessment of Concentration Levels of Heavy Metals in Selected Fish Species from the Macajalar Bay Area in Misamis Oriental

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Abstract

Concentration levels of zinc, lead, copper, chromium and cadmium in the edible and inedible parts of different fish species from three sampling sites in Macajalar Bay Area and one in Camiguin Island were determined using anodic stripping voltammetry to assess the extent of metal contamination on fish in the area. The concentration levels of metal analytes in edible parts were compared to those in inedible parts of fish. The metal concentrations in fish and water samples were also compared to the maximum permissible levels set by authorities.

Concentration levels in microgram per gram $(\mu g/g)$ or parts per million (ppm) were generally higher in the inedible compared to the edible parts of fish. Average concentration ranges for zinc metal were from below detection limit to 21.08 and 31.34 $\mu g/g$ wet basis (26.89 and 47.84 $\mu g/g$ dry basis) in edible and inedible parts, respectively. Lead was not detected in the edible part while the average concentration range in the inedible parts is from below detection limit to 0.770 $\mu g/g$ wet basis (1.18 $\mu g/g$ dry basis). Average copper ranges from below detection limit to 26.826 and 33.901 $\mu g/g$ wet basis (34.22 and 51.76 $\mu g/g$ dry basis) in the edible and inedible parts, respectively. Cadmium and chromium concentrations were below detection limit in both parts during the two sampling periods. Concentrations of metal analytes in fish in wet basis were used in the subsequent calculation of bioaccumulation factors (BAF).

DOROTHY CAMINOS – PERUELO is an Instructor of the Chemistry Department, Xavier University, Cagayan de Oro City; MARIO B. CAPANGPANGAN, Ph.D., is a Professor of Chemistry Department, College of Science and Mathematics, MSU-IIT, Iligan City Copper metal in the edible parts of fish exceeded the maximum permitted concentration set by Australia / New Zealand Food Authority (ANZFA) and the maximum permissible levels in water supporting aquatic life set by the U.S. Environmental Protection Agency (U.S. EPA). Zinc in edible parts of fish exceeded the maximum permissible levels of trace metals for water suitable for fish/shellfish growth set by the Department of Environment and Natural Resources (1990).

Metal levels in water were also determined to assess the bioaccumulation factors (BAF) of analyte metals in fish. Mean concentrations were 0.075 μ g/mL, 0.010 μ g/mL and 0.333 μ g/mL for zinc, lead and copper, respectively. The mean zinc and lead concentrations in water were below the maximum permissible levels set by the U.S. EPA and by the DENR while the mean copper concentration exceeded the permissible level in water supporting aquatic life set by the U.S. EPA. Other metals such as cadmium and chromium were below the maximum permissible limit set by the agencies.

Bream ("Bodbod"), and parrot fish ("Molmol") were found to exhibit positive bioaccumulation for metal analytes. Bream has the potential to bioaccumulate zinc (BAF=120.09) and copper (BAF=130.67). On the other hand, parrot fish has the potential to bioaccumulate copper only (BAF = 159.0).

Keywords: heavy metals, fish, Macajalar Bay Area, bioaccumulation factor, anodic stripping voltammetry

Introduction

Metals occur naturally in the environment and are present in rocks, soil, plants, and animals. Metals occur in different forms: as ions dissolved in water, as vapors, or as salts or minerals in rock, sand, and soil. They can also be bound in organic or inorganic molecules, or attached to particles in the air. Both natural and anthropogenic processes and sources emit metals into air and water. Heavy metals in surface water systems can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs. Excess metal levels in surface water may pose a health risk to human beings and to environment.

Plants and animals depend on some metals as micronutrients. Zinc, chromium and copper are needed by plants and animals in minute amounts.

However, certain metals can also be toxic like cadmium and lead, even in relatively small amount, and therefore pose a risk to the health of animals and people.

If an organism's uptake of a metal is greater than its ability to get rid of it, the metal will accumulate (Spacie and Hamelink, 1985). Heavy metals tend to accumulate in storage compartments. For example, cadmium accumulates preferentially in the kidneys, mercury in the liver, and lead in the skeleton. The accumulation can continue throughout the organism's life and is the major cause of chronic toxicity. In contrast to organic pollutants, metals accumulate in protein tissues and bone rather than fat. Bioaccumulation is the amount of substance taken up by an organism directly from water (bioconcentration) and through diet (dietary accumulation) (Chapman et al., 1996). Fish is used in bioaccumulation tests because it is higher tropic level organism and is usually eaten by man (Olaifa et al., 2004).

Macajalar Bay is susceptible to heavy metal pollution because industrial plants are also located near this area. This bay is the mouth of many sewage and river systems including Biga-an and Iponan Rivers in the city and in other parts of Misamis Oriental. It is a fact that coastal and estuarine areas around Macajalar Bay are heavily industrialized and populated. Hence, anthropogenic and industrial sources of heavy metals can have severe and obvious impact on the local environment (DENR, 1991).

It was reported in 1996 (Ratilla, 1999) that Biga-an river in Cagayan de Oro was allegedly contaminated with heavy metals and cyanide from waste disposal of small scale mining activities operating upstream of the river disposal of small scale mining activities operating upstream of the river specifically in Gango Libona, Bukidnon. Continuing mining operations not only in this area but also upstream of Iponan River present a problem because waste effluents find their way downstream into the bay since both rivers are emptying

along Macajalar Bay Area. Macajalar Bay is the source of fish for the residents in this part of Misamis Oriental. Hence this study was conducted, to evaluate the quality of Misamis Oriental. Hence this study was conducted, to evaluate the quality of fish, which is the important protein source for the local population. Three fish, which is the important protein and and one in Camiguin sampling stations were chosen in Macajalar Bay Area and one in Camiguin

Island.

Objectives of the Study

This research study has the following primary objectives:

1) Determine the concentrations of heavy metals specifically lead, copper, cadmium, chromium, and zinc in edible and inedible parts of selected fish species obtained from three sampling stations, namely El Salvador, Tagoloan, and Jasaan (all in Macajalar Bay Area in Misamis Oriental) and from a reference area in Camiguin Island.

- 2) Compare the concentrations of these metals in edible and inedible parts of fish.
- 3) Compare and determine if the concentration levels of analyte metals in fish and water samples exceed the maximum permissible levels for heavy metals set by recognized organizations such as the U.S. Environmental Protection Agency (U.S. EPA), World Health Organization (WHO), Australia/New Zealand Food Authority (ANZFA), and the Department of Environment and Natural Resources (DENR), Philippines.
- 4) Determine the concentrations of analyte metals in water to be used in the subsequent calculation of bioaccumulation factors of the analyte metals in fish.

Experimental

Sampling. The fish samples were obtained from local fishermen or from fishermen who regularly fish in Macajalar Bay. The edible parts (which consists of fleshy meat and skin of the body) were separated from the inedible parts (which consists of head, bone, fin, scales, tail, liver and entrails). Tissues were cut into small pieces and homogenized in a blender. Samples were frozen until analysis. To obtain a representative sample from the bulk sample, cone and quartering method was employed from a 250-gram bulk sample in wet basis.

Water samples were collected by grab sampling using one-liter acidwashed plastic containers. To preserve the samples, pH was adjusted to <2 and then refrigerated until analysis. Temperature and pH were determined in situ using a portable instrument for pH and temperature.

Two sampling periods were conducted in this study. The first was done on the first week of April 2003 and the second was conducted on the first week of June 2003.

Digestion of fish samples. Digestion of fish samples was done using the Open-Beaker Method (Ratilla, 1999). 0.2-0.5 g of fish sample was accurately weighed in a 150-mL beaker, the sample was added with 5 mL conc. nitric acid then covered with a watch glass. The mixture was boiled gently for 30 minutes on a hot plate. After 30 minutes, the mixture was cooled and added with 2 mL 60% perchloric acid and 10 mL of conc. nitric acid. The mixture was heated again to near dryness. The cover and wall of the beaker were washed with 5 mL of deionized water, and the solution was heated to the evolution of dense white fumes. The beaker was cooled and then added with 10 mL of 5% nitric acid to dissolve the salts. The resulting solution was quantitatively transferred to a 25.0 mL volumetric flask and diluted with water washings from the digestion beaker. The sample was ready for determination using anodic stripping voltammetry.

Analysis of fish samples using Anodic Stripping Voltammetry. Digest of fish and water samples were analyzed by Anodic Stripping Voltammetry (ASV), using Metrohm Voltammetric Analyzer (Switzerland), Model 693 (VA Processor) and Model 694 (VA Stand), by mixing 100 μ L of digest with 19 mL of de-ionized water and 2 mL of ammonium nitrate solution as supporting electrolyte. The mixture was analyzed by ASV and peak current was determined. The concentration of the analyte was calculated using the equation of the regression line obtained from the standard calibration curve prepared previously for each metal standard. The current reading is directly proportional to the concentration of metals in the samples.

Results and Discussion

Metals in Fish Samples. Comparison of metal concentrations was done using fish species Bream or "Bodbod" caught from four sampling areas in two periods.

Figures 1 and 2 show relative levels of metals in edible and inedible parts of fish ("Bodbod") from four sampling areas and during two sampling periods. The concentrations of analyte metals in this study were generally higher in the inedible parts compared to the edible parts of fish. The observed higher concentration of metals in the inedible parts such as fish head, tail, gills, liver, kidney, entrails, fin, scales, and bones is generally observed in many studies. As reported by Sorensen (1991) as cited in Jagoe et al., (1997), fish excrete lead rapidly, and levels in fish muscle tends to be fairly low compared to kidney, liver, gill and bone. Unlike other metals such as mercury, lead does not bioaccumulate in muscles, and lead content does not typically increase with increased fish size (Wiener and Giesy 1979). As shown in Table 3, uptake of lead via intestines is 5-10 % while uptake via lungs is 30-50%. On the other hand, efficiency half-life of lead is 40 days in soft tissues and 20 years in bones. Lead concentrations in this study are below detection limit in the edible parts which is lower than what was reported by Schmitt et al. (1984) (up to 1.3 µg/g dry weight) in edible tissues of suckers downstream from lead mine in Chernobyl.

As shown in Table 1, zinc concentration in the edible parts of fish ranged from below detection limit to as high as 21.08 µg/g (wet basis) for El Salvador fish samples. This concentration suggests point source contamination because El Salvador is near Iponan River, the area where mining operations are taking place Salvador is near Iponan River. The researcher cannot explain the unusually high upstream of the river. The researcher cannot explain the unusually high concentration (88.99 µg/g wet basis) of zinc in the inedible parts of Camiguin fish sample. Table 2 shows the average lead concentration in edible, inedible and whole fish during the first and second sampling. Results show that lead (Pb) concentrations are below detection limit for all fish species during the first sampling in both parts of fish but was detected (0.770 μ g/g wet basis) in the inedible part of fish from Tagoloan during the second sampling.

Table 3 shows the average copper (Cu) concentration in edible, inedible and whole fish during the first and second sampling. As shown in the table, copper concentrations were below detection limit in the edible parts of fish while the sample from El Salvador showed detectable level of 2.107 μ g/g (wet basis) in the inedible parts during the first sampling. During the second sampling, copper concentration ranged from below detection limit to as high as 18.235 μ g/g (wet basis) for edible and from below detection limit to 26.826 μ g/g for the inedible parts.

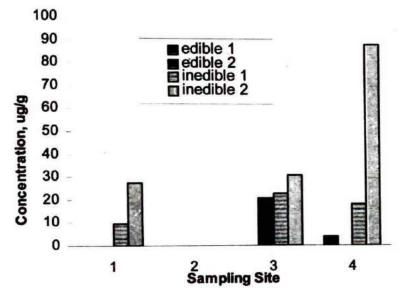


Figure 1. Comparison of average zinc concentrations in fish

and whole fich during

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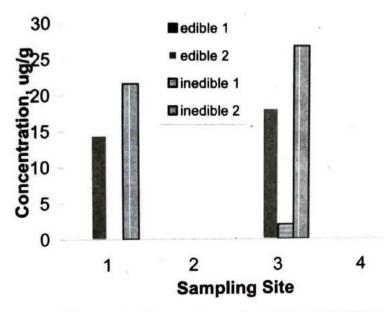


Figure 2. Comparison of average copper concentrations in fish

| Table 1. | Average zinc concentration in edible, inedible and whole fish during |
|----------|--|
| | the first and second sampling |

| | | Zinc | | tion, µg/g (w SD), N=3 | et basis) | |
|--------------------------|--|---|---|---|-----------------------|-------------------|
| | | First Samp | | | econd Samp | ling |
| Sample ID "Bodbod" -J | E <dl< th=""><th>I 9.473 (24.2)</th><th>W <dl< th=""><th>E <dl< th=""><th>I 33.114 (22.3)</th><th>W 16.930</th></dl<></th></dl<></th></dl<> | I 9.473 (24.2) | W <dl< th=""><th>E <dl< th=""><th>I 33.114 (22.3)</th><th>W 16.930</th></dl<></th></dl<> | E <dl< th=""><th>I 33.114 (22.3)</th><th>W 16.930</th></dl<> | I 33.114 (22.3) | W 16.930 |
| "Bodbod"-T | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.119 (3.2)</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td>0.119 (3.2)</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td>0.119 (3.2)</td><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td>0.119 (3.2)</td><td><dl< td=""></dl<></td></dl<> | 0.119 (3.2) | <dl< td=""></dl<> |
| "Bodbod"-E | <dl< td=""><td>22.920 (3.5)</td><td>6.918</td><td>21.081 (12.1)</td><td>31.341 (4.2)</td><td>24.247</td></dl<> | 22.920 (3.5) | 6.918 | 21.081 (12.1) | 31.341 (4.2) | 24.247 |
| "Bodbod"-C | 3.866 (14.0) | 18.129 (12.0) | 11.48 | <dl< td=""><td>88.993 (13.5)</td><td>23.191</td></dl<> | 88.993 (13.5) | 23.191 |

J=Jasaan, T= Tagoloan, E=El Salvador, C= Camiguin, ID= Identification, <DL =below detection limit, minimum detection limit = 5ppb, E = edible, I = inedible, W = whole fish

| | |] | | entration, µg | g/g | |
|-------------|---|---|---|---|---|-------------------|
| ~ | Fir | st Samplir | ng | | ond Samplin | ng |
| Sample ID | E | Ι | W | Е | I | W |
| "Bodbod" -J | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| "Bodbod"-T | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.770 (3.2)</td><td>0.375</td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td>0.770 (3.2)</td><td>0.375</td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td>0.770 (3.2)</td><td>0.375</td></dl<></td></dl<> | <dl< td=""><td>0.770 (3.2)</td><td>0.375</td></dl<> | 0.770 (3.2) | 0.375 |
| "Bodbod"-E | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| "Bodbod"-C | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |

Table 2. Average lead concentration in edible, inedible and whole fish during the first and second sampling

J=Jasaan, T= Tagoloan, E=El Salvador, C= Camiguin, available, ID= Identification, <DL =below detection limit, minimum detection limit = 5ppb, E = edible, I = inedible, W = whole fish

 Table 3. Average copper concentration in edible, inedible and whole fish during the first and second sampling

| | | С | | centration, µ SD). N=3 | g/g | |
|--------------------------|--|--|--|---|---|-------------------|
| | Fi | rst Samplir | | | ond Samplin | ng |
| Sample ID "Bodbod" -J | E <dl< th=""><th>I <dl< th=""><th>W <dl< th=""><th>E 21.581 (0.55)</th><th>I 23.009 (9.0)</th><th>W 22.480</th></dl<></th></dl<></th></dl<> | I <dl< th=""><th>W <dl< th=""><th>E 21.581 (0.55)</th><th>I 23.009 (9.0)</th><th>W 22.480</th></dl<></th></dl<> | W <dl< th=""><th>E 21.581 (0.55)</th><th>I 23.009 (9.0)</th><th>W 22.480</th></dl<> | E 21.581 (0.55) | I 23.009 (9.0) | W 22.480 |
| "Bodbod"-T | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| "Bodbod"-E | <dl< td=""><td>2.107 (68.2)</td><td><dl< td=""><td>26.826 (3.7)</td><td>33.901 (3.2)</td><td>30.527</td></dl<></td></dl<> | 2.107 (68.2) | <dl< td=""><td>26.826 (3.7)</td><td>33.901 (3.2)</td><td>30.527</td></dl<> | 26.826 (3.7) | 33.901 (3.2) | 30.527 |
| "Bodbod"- C | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |

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J=Jasaan, T= Tagoloan, E=El Salvador, C= Camiguin, available, ID= Identification, <DL =below detection limit, minimum detection limit = 5 ppb, E = edible, I = inedible, W = whole fish

Influence of Rain Events on Metal Concentrations in Fish. The observed higher concentration of the analyte metals in fish samples during the second sampling compared to the first sampling may be due to the rain event that occurred a few days before, and during the night before, the second sampling was conducted. Studies conducted by Meylan et al. (2003) showed that large increases of dissolved copper concentration (from 40 nM to 118 nM) and dissolved zinc concentration (from 45 nM to 147 nM) occur during heavy rain events in the Furtbach stream in Zurich, Switzerland. The steep increases of metal concentrations were due to the release of metals from contaminated sediments induced by the heavy rain events. Increases in free copper and free zinc ions in the water were also observed during the onset of heavy rain events. Similarly, when the rain stopped, the dissolved metal concentration in the stream dropped rapidly (Meylan et al, (2003). Another reason is that the rain events have increased the metal loading because domestic and industrial wastewater effluents and runoffs from rivers upstream of the Macajalar Bay area have come their way to the bay.

Effects of Point and Non-Point Sources on the Concentration of Metals in Fish Samples. As shown in Figures 1 and 2 and Table 2, copper and zinc were detected in "Bodbod" from Jasaan and El Salvador, lead in Tagoloan while zinc in Camiguin. Higher concentrations of zinc and copper were observed in fish from El Salvador compared to the other sites. These observations suggest point source and anthropogenic sources. Natural sources such as chemical and physical weathering of igneous rocks and metamorphic rocks and soil also contribute to metal loading. Anthropogenic sources such as runoffs from mining operation upstream of the MBA, and point sources such as domestic wastewater effluents, industrial effluents and waste sludges from industrial plants may have contributed to metal loading. El Salvador is moderately populated and industrial plants are also located in the estuarine areas of Macajalar Bay. The higher concentration of metals in El Salvador suggests point source contamination from mining operations near this area specifically upstream of Iponan River, which still continue up to the present.

Otherr factors that may have influenced the increased in metal loading are atmospheric sources as well as air and water quality in this part of Macajalar Bay Area. Air quality between Tagoloan and Jasaan is considered polluted as assessed by the DENR-Region X. These metals may be released to the atmosphere by smelting and coal combustion, as well as from automobiles fueled with leaded gasoline. Industrial plants also may have contributed to the atmospheric pollution in the area. Van Hassel et al. (1980) reported whole-body lead contents up to 42.4 µg/g (dry weight) in darters from streams near heavily traveled highways. Macajalar Bay Area, specifically, El Salvador, Tagoloan and Jasaan are near a heavily traveled highway. Furthermore, industrial plants and residential areas near estuarine are also located near the area. These probably explain the elevated levels of the metals in this study. Another possible reason for the elevated levels of metals in Tagoloan and Jasaan is point-source contamination due to mining activities upstream of Biga-an River, which is emptying into MBA. Surface runoffs from mining operations upstream of Biga-an River may have come their way to Tagoloan and Jasaan because these places are near the area. As reported by Ratilla (1999), elevated levels of mercury and lead in sediments and water samples are caused by point-source contamination upstream of the river.

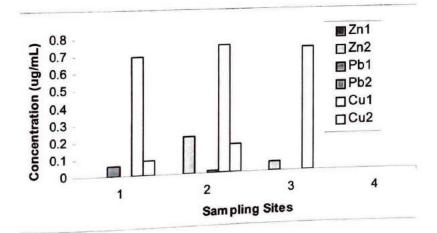
Metal Concentration in Fish Versus Fish Size. The range of zinc concentration in this study (<DL to $24.247 \mu g/g$ wet basis (as shown in Table 3) in whole fish is much higher than the studies reported by Cronin et al. (1998) (2.2 – 6.7 mg/Kg dry basis) in deep sea fish from North Atlantic. It was also noted in their study that zinc concentration in Mediterranean grenadier decreased with increasing length/age of fish. This probably explains the high concentrations of metals in fish obtained in this study because fish that were used in this study were small fishes. It only shows that smaller fish tend to have higher concentration levels of metals than bigger fish. It may be that smaller fish select different food items than larger ones, and that the preferred foods of the smaller fish have higher levels of metals. It could also be due to fish size. Metal levels in smaller fish size become more concentrated than in bigger fish size because the metals are less distributed and less regulated in smaller body size than in bigger body size.

Detected Metal Analytes in Water. Lead was detected in Tagoloan water while copper in three sites for the first sampling as shown in Table 4 and in Figure 3. Zinc, lead and copper were detected in Jasaan water samples while zinc and copper in El Salvador and Tagoloan water samples respectively during the second sampling. Table 4 shows that zinc, lead and copper concentrations ranged from <DL to 0.217 µg/mL, <DL to 0.06 µg/mL, <DL to 0.757 µg/mL, respectively, during the two sampling periods. Copper and lead concentrations were relatively higher during the first sampling while zinc concentration was relatively higher during the second sampling for all sampling sites as shown in Figure 3. Cadmium and chromium metals were not detected in water samples during the first and second sampling periods.

| | Average Metal Concentrations (µg/mL)* | | | | | | | |
|------------------|--|---|-----------------|---|---|-------------------|--|--|
| Sampling Site | | irst Samplin (%RSD), N= | | Second Sampling (%RSD), N=2 | | | | |
| | Zn | Pb | Cu | Zn | Pb | Cu | | |
| Tagoloan | <dl< td=""><td>0.060 (12.3)</td><td>0.693 (15.3)</td><td><dl< td=""><td><dl< td=""><td>0.088 (20.2)</td></dl<></td></dl<></td></dl<> | 0.060 (12.3) | 0.693 (15.3) | <dl< td=""><td><dl< td=""><td>0.088 (20.2)</td></dl<></td></dl<> | <dl< td=""><td>0.088 (20.2)</td></dl<> | 0.088 (20.2) | | |
| Jasaan | <dl< td=""><td><dl< td=""><td>0.757 (18.4)</td><td>0.217 (14.5)</td><td>0.012 (39.3)</td><td>0.164 (18.6)</td></dl<></td></dl<> | <dl< td=""><td>0.757 (18.4)</td><td>0.217 (14.5)</td><td>0.012 (39.3)</td><td>0.164 (18.6)</td></dl<> | 0.757 (18.4) | 0.217 (14.5) | 0.012 (39.3) | 0.164 (18.6) | | |
| El Salvador | <dl< td=""><td><dl< td=""><td>0.734 (12.0)</td><td>0.056 (39.6)</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td>0.734 (12.0)</td><td>0.056 (39.6)</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | 0.734 (12.0) | 0.056 (39.6) | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> | | |
| Camiguin | NS | NS | NS | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> | | |

Table 4. Average metal concentrations in water

NS= no sample, minimum detection limit = 5ppb, *cadmium and chromium concentrations are not presented because they were not detected



2 = Jasaan, 1 = Tagoloan, 3 = El Salvador, 4 = Camiguin

Figure 3. Comparison of average metal concentrations in water

Comparison of Metal Concentrations in Fish in this Study to Allowable Levels Set by Different Authorities. The World Health Organizations (WHO) suggests that fish for human consumption should contain less than 0.3 lead µg/g dry wt (World Health Organization, 1972). As shown in Table 5, the lead concentrations in fish (edible part) in this study were found to be all below detection limit and thus, are within the permissible level set by WHO.

Table 5 also shows a comparison of heavy metal concentrations in fish in this study to the maximum permitted concentration set by authorities. Note that copper metal in edible part of fish exceeded the maximum permitted concentration set by Australia / New Zealand Food Authority (ANZFA) and the maximum permissible levels in water supporting aquatic life set by the US Environmental Protection Agency (US EPA). Zinc in edible part of fish exceeded the maximum permissible levels of trace metals for water suitable for fish/shellfish growth as set by the DENR (1990). Other metals such as cadmium and chromium were below the maximum permissible limit set by authorities.

| Table 5. | Comparison of heavy metal concentrations in fish in this study to the |
|----------|---|
| | maximum permitted concentration set by authorities |

| Heavy Metal | • | T Concentr E (I | MPC, ANZFA , ppm (mg/Kg) body weight | MPL for V Support Aquatic Lif | ing | | |
|----------------|--|---|---|---|--------------|-----------|--------------|
| | JAS | TAG | El S | CAM | | U.SEPA | DEN R |
| Zn | <dl th="" ·<=""><th>· <dl< th=""><th><dl-26.9< th=""><th><dl-4.9< th=""><th>150</th><th>Not avail</th><th>2</th></dl-4.9<></th></dl-26.9<></th></dl<></th></dl> | · <dl< th=""><th><dl-26.9< th=""><th><dl-4.9< th=""><th>150</th><th>Not avail</th><th>2</th></dl-4.9<></th></dl-26.9<></th></dl<> | <dl-26.9< th=""><th><dl-4.9< th=""><th>150</th><th>Not avail</th><th>2</th></dl-4.9<></th></dl-26.9<> | <dl-4.9< th=""><th>150</th><th>Not avail</th><th>2</th></dl-4.9<> | 150 | Not avail | 2 |
| Pb | . <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>1.5</td><td>0.10</td><td>0.02</td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td>1.5</td><td>0.10</td><td>0.02</td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td>1.5</td><td>0.10</td><td>0.02</td></dl<></td></dl<> | <dl< td=""><td>1.5</td><td>0.10</td><td>0.02</td></dl<> | 1.5 | 0.10 | 0.02 |
| Cu | _ <dl-27.5< td=""><td><dl< td=""><td><dl-34.2< td=""><td><dl< td=""><td>10</td><td>0.020</td><td>Not avail</td></dl<></td></dl-34.2<></td></dl<></td></dl-27.5<> | <dl< td=""><td><dl-34.2< td=""><td><dl< td=""><td>10</td><td>0.020</td><td>Not avail</td></dl<></td></dl-34.2<></td></dl<> | <dl-34.2< td=""><td><dl< td=""><td>10</td><td>0.020</td><td>Not avail</td></dl<></td></dl-34.2<> | <dl< td=""><td>10</td><td>0.020</td><td>Not avail</td></dl<> | 10 | 0.020 | Not avail |
| Cd | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.20</td><td>0.012</td><td>0.01</td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td>0.20</td><td>0.012</td><td>0.01</td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td>0.20</td><td>0.012</td><td>0.01</td></dl<></td></dl<> | <dl< td=""><td>0.20</td><td>0.012</td><td>0.01</td></dl<> | 0.20 | 0.012 | 0.01 |
| Cr | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl ·</dl </td><td>Not avail</td><td>0.10</td><td>0.05</td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl ·</dl </td><td>Not avail</td><td>0.10</td><td>0.05</td></dl<></td></dl<> | <dl< td=""><td><dl ·</dl </td><td>Not avail</td><td>0.10</td><td>0.05</td></dl<> | <dl ·</dl | Not avail | 0.10 | 0.05 |

Zn = zinc, Pb = lead, Cu=copper Cd=cadmium, Cr=chromium, MPC=maximumpermissible concentration, MPL = maximum permitted levels, <DL = belowdetection limit, minimum detection limit = 5 ppb, JAS = Jasaan water, TAG = Tagoloan water, ELS = El Salvador water, CAM = Camiguin water, ANZFA = Australia / New Zealand Food Authority, U.S.EPA = United States Environmental Protection Agency, DENR = Department of Environment and Natural Resources, Philippines On the other hand, Table 6 shows a comparison of heavy metal concentrations in water in this study to water quality criteria for human consumption set by authorities. Note in the table that copper metal in water samples exceeded the maximum permissible levels in water supporting aquatic life set by the US Environmental Protection Agency (US EPA).

Bioaccumulation Factors. Shown in Table 7 are the calculated bioaccumulation factors (BAF) for zinc, lead, and copper in different fish species. Results showed that zinc, lead, and copper metals are positive to bioaccumulation process. Bream ("Bodbod"), long-nosed trevally ("Talakito") and Parrot fish ("molmol") were found to have positive bioaccumulation for metal analytes, with the following bioaccumulation factors: bream for zinc (BAF=120.09); bream for copper (BAF=130.67), and parrot fish for copper (BAF=159.02). According to the European Commission policy as reported by Ratilla (1999), these fish species which exhibit bioaccumulation factors of greater than 100 are considered to have the potential to bioaccumulate metals and can be considered as "dangerous to the environment" because they could impair the health of an organism or predators feeding on that organism.

| Conc | This | Study n Range (| ppm) | WHO, 1993 | EU STD, | Supp | n Water orting |
|--|---|--|---|--|--|---|--|
| JAS | TAG | ELS | CAM | (ppm) | (ppm) | US- | DENR |
| <dl-< td=""><td><dl< td=""><td><dl- 0.202</dl- </td><td><dl< td=""><td>*0.</td><td>300</td><td>Not avail</td><td>2</td></dl<></td></dl<></td></dl-<> | <dl< td=""><td><dl- 0.202</dl- </td><td><dl< td=""><td>*0.</td><td>300</td><td>Not avail</td><td>2</td></dl<></td></dl<> | <dl- 0.202</dl- | <dl< td=""><td>*0.</td><td>300</td><td>Not avail</td><td>2</td></dl<> | *0. | 300 | Not avail | 2 |
| <dl-< td=""><td><dl-< td=""><td><dl< td=""><td><dl< td=""><td>0.01</td><td>0.01</td><td>0.10</td><td>0.02</td></dl<></td></dl<></td></dl-<></td></dl-<> | <dl-< td=""><td><dl< td=""><td><dl< td=""><td>0.01</td><td>0.01</td><td>0.10</td><td>0.02</td></dl<></td></dl<></td></dl-<> | <dl< td=""><td><dl< td=""><td>0.01</td><td>0.01</td><td>0.10</td><td>0.02</td></dl<></td></dl<> | <dl< td=""><td>0.01</td><td>0.01</td><td>0.10</td><td>0.02</td></dl<> | 0.01 | 0.01 | 0.10 | 0.02 |
| 0.131- | <dl-< td=""><td><dl- 0.734</dl- </td><td><dl< td=""><td>2</td><td>2</td><td>0.02</td><td>Not avail</td></dl<></td></dl-<> | <dl- 0.734</dl- | <dl< td=""><td>2</td><td>2</td><td>0.02</td><td>Not avail</td></dl<> | 2 | 2 | 0.02 | Not avail |
| | | | <dl< td=""><td>0.003</td><td>0.005</td><td>0.012</td><td>0.01</td></dl<> | 0.003 | 0.005 | 0.012 | 0.01 |
| <dl< td=""><td></td><td></td><td></td><td>0.05</td><td>0.05</td><td>0.10</td><td>0.05</td></dl<> | | | | 0.05 | 0.05 | 0.10 | 0.05 |
| | JAS <dl- 0.324 <dl- 0.012</dl- </dl- | Concentration JAS TAG <dl-< td=""> <dl< td=""> 0.324 - <dl-< td=""> <dl-< td=""> 0.012 0.066 0.131- <dl-< td=""> 0.757 0.693 <dl< td=""> <dl< td=""></dl<></dl<></dl-<></dl-<></dl-<></dl<></dl-<> | JAS TAG ELS <dl-< td=""> <dl< td=""> <dl-< td=""> 0.324 0.202 <dl-< td=""> <dl-< td=""> 0.012 0.06 0.131- <dl-< td=""> 0.757 0.693 <dl< td=""> <dl-< td=""> <dl< td=""> <dl-< td=""></dl-<></dl<></dl-<></dl<></dl-<></dl-<></dl-<></dl-<></dl<></dl-<> | Concentration Range (ppm) JAS TAG ELS CAM <dl-< td=""> <dl< td=""> <dl< td=""> <dl< td=""> 0.324 0.202 <dl-< td=""> <dl-< td=""> <dl< td=""> 0.012 0.06 0.131- <dl-< td=""> <dl-< td=""> 0.757 0.693 0.734 <dl< td=""> <dl< td=""> <dl< td=""> <dl< td=""> <dl< td=""> <dl< td=""></dl<></dl<></dl<></dl<></dl<></dl<></dl-<></dl-<></dl<></dl-<></dl-<></dl<></dl<></dl<></dl-<> | THIS Study Concentration Range (ppm) 1993 (ppm) JAS TAG ELS CAM (ppm) CAM (ppm) | This Study N103, Concentration Range (ppm) 1993 STD, JAS TAG ELS CAM (ppm) 1998 JAS TAG ELS CAM (ppm) 1998 OL- CDL- CAM (ppm) 1998 OL- CAM (ppm) 1998 OL- CDL (ppm) (ppm) O.202 *0.300 O.202 *0.01 0.01 OL- <t< td=""><td>$\begin{array}{c c c c c c c c c c c c c c c c c c c$</td></t<> | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |

| Table 6 | Comparison of heavy metal concentrations in water in this study to |
|----------|--|
| Table 0. | water quality criteria for human consumption set by authorities |
| | water quality criteria for human consumption set by dutientities |

Cr < DL < DL < Cu=copper Cd=cadmium, Cr=chromium, MPL = maximum Zn = zinc, Pb = lead, Cu=copper Cd=cadmium, Cr=chromium, MPL = maximum permitted levels, <DL = below detection limit, minimum detection limit = 5 ppb, * Hungary Standard Category V for heavily polluted water, JAS = Jasaan water, Hungary Standard Category V for heavily polluted water, CAM = Camiguin water EU= TAG = Tagoloan water, ELS = El Salvador water, CAM = Camiguin water EU= European Commission (1998), WHO = World Health Organizations (1993), and water supporting aquatic life set by the US Environmental Protection Agency, and DENR = Department of Environment and Natural Resources, Philippines

| Table 7 | Metal bioaccumulation | factors in selected fish species |
|---------|-----------------------|----------------------------------|
|---------|-----------------------|----------------------------------|

| Sample ID | Bioaccu | mulation (BAF) | Factor | Significance |
|---------------------------|---------|-------------------|--------|--|
| | Zn | Рь | Cu | *BAF > 100: Substance is considered to have the potential to bioaccumulate and can be considered as "dangerous to the environment |
| | | | | **BAF > 500: Substance is considered hazardous |
| "Bodbod" (Bream) | 120.09 | | 130.67 | |
| "Molmol" (Parrot fish) | 30.69 | - | 159.02 | |

BAF=Bioaccumulation Factor or BCF = Bioconcentration Factor, BAF or BCF is the ratio of metal concentration in fish sample (wet basis) to metal concentration in water or matrix, i.e.,

> BAF = Metal conc. in sample (wet basis) Metal conc. in water sample

* Under the European Commission Policy ** Under the Canadian Toxic Substances Management Policy

Conclusions

In line with the objectives of this study, selected fish species and water samples collected from three sampling sites in Macajalar Bay area and one from reference site in Camiguin Island were analyzed for the presence of zinc, lead, copper, cadmium and chromium by anodic stripping voltammetry. Concentration levels of metal analytes were compared in the edible and inedible parts of fish. Metal analyte concentrations in fish were generally higher in the inedible parts compared to the edible parts of fish. Average zinc concentration ranged from below detection limit to 21.08 and 31.34 μ g/g wet basis (26.89 and 47.84 μ g/g dry basis) in the edible and inedible parts, respectively. Average lead concentration in the edible parts were below detection limit while in the inedible parts was from below detection limit to 0.770 μ g/g wet basis (1.18 μ g/g dry basis). Average copper concentration ranged from below detection limit to 26.826 and 33.901 $\mu g/g$ wet basis (34.22 and 51.76 μ g/g dry basis) for the edible and inedible parts, respectively. Metal concentrations in fish were higher during the second sampling compared to the first sampling due to the rain event that occurred during the second sampling.

Copper metal concentration in the edible part of fish were found to exceed the maximum permitted concentration set by Australia/New Zealand Food Authority (ANZFA) of 10 ppm and maximum permissible levels in water supporting aquatic life set by the US Environmental Protection Agency (US EPA) of 0.02 ppm. Zinc concentrations in edible part of fish were also found to exceed the maximum permissible levels of trace metals for water suitable for fish/shellfish growth set by the DENR (1990) of 2 ppm. Other metals such as lead, cadmium and chromium were below the maximum permissible limit set by authorities

Bream ("Bodbod") and Parrot fish ("molmol") were found to exhibit positive bioaccumulation for metal analytes with the following bioaccumulation factors: bream for zinc (BAF=120.09); bream for copper (BAF=130.67), and parrot fish for copper (BAF=159.02).

With all these results, this study could hopefully provide a scientific baseline data for future use that could help researchers, concerned individuals, organizations and policy makers in the formulation of policies and regulation towards the minimization of heavy metal contamination in water and consequently in fish in the area.

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