RESEARCH ARTICLE

Profiling of Heavy Metals in Mackerel Tuna (*Euthynnus affinis*) and Seawater and Bottom Sediments in Sarangani Coastline, Southern Philippines

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Abstract

Heavy metals have the ability to accumulate in the human body and disrupt functions of some body organs. These metals can find their way into humans by consumption of metal-contaminated fish. In this study, the presence of heavy metals was assessed in muscle tissues of mackerel tuna (*Euthynnus affinis*), locally known as "kawakawa," collected from General Santos City Fish Port (GSCFP) and Kiamba fish landing sites. Heavy metal presence was also evaluated in seawater and bottom sediments samples collected along the Sarangani coastline. Cadmium (Cd) and lead (Pb) were analyzed using atomic absorption spectrophotometry (AAS); while mercury (Hg), through cold vapor atomic absorption spectrophotometry (CVAAS). Results revealed that the three samples from GSCFP had Hg concentrations ranging from 0.045 to 0.108 mg·kg^{-1}, below the limit set by the United States Food and Drug Administration (US FDA). In the case of Cd, 0.095 mg·kg^{-1} Cd was detected from only one out of six samples taken from Kiamba, which exceeded the limit of 0.05 mg·kg^{-1} prescribed by the US FDA, US Environmental Protection Agency (US EPA), and the European Commission (EC). The data generally indicates that the tuna samples do not pose a serious threat to the health of the consumers. Sediments obtained from Sarangani coastline showed presence of Pb at 62.27 mg·kg^{-1}, which is also below the 128 mg·kg^{-1} limit. Assessment of pollution status of the study area revealed that the bottom sediments can be classified as unpolluted to moderately polluted based on the levels of Cd, Pb, and Hg, implying minimal heavy metal exposure of this tuna species from the two sampling areas. To ensure no incremental contamination of seawater and bottom sediments occurs, developmental and anthropogenic activities, such as the indiscriminate disposal of industrial and domestic wastes that may be possible sources of heavy metals, should be regulated and more stringent effluent standards adopted.

Keywords: *Euthynnus affinis*; bottom sediments; cadmium; lead; mercury; seawater

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Profiling of Heavy Metals in Mackerel Tuna (*Euthynus affinis*) and Seawater and Bottom Sediments in Sarangani Coastline, Southern Philippines

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Introduction

Mercury (Hg), lead (Pb), and cadmium (Cd) are the most hazardous heavy metals in aquatic system due to their capacity to bioaccumulate in the food chain (Besada et al. 2006). In aquatic systems, fish are known as the primary route of heavy metal exposure (Nsikak et al. 2007) and are capable of accumulating heavy metals in their flesh with concentration greater than that at bottom sediments and water (Wong et al. 2001). It is imperative to study and monitor the levels of heavy metals in fish to guarantee that excessive levels are not transferred to humans through fish consumption (Adeniyi and Yusuf 2007).

Tuna is recognized as a predator able to concentrate large amounts of heavy metals since they mostly feed on small aquatic organisms like fish, crustaceans, and cephalods (Ashraf 2006; Carpenter and Neim 2001). Tuna is a fish from the mackerel family (Scombridae) which is warm-blooded and swims at good speed continuously in exchange for oxygen (Yamaguchi and Harrisson 2005). According to Zaragoza et al. (2004), there are 21 tuna species that dominate the Philippine waters. Among these 21 species, four species formed the bulk of catches, namely, yellowfin tuna (*Thunnus albacores*), skipjack tuna (*Katsuwonus pelamis*), eastern little tuna locally known as "kawakawa" (*Euthynnus affinis*), and frigate tuna (*Auxis thazard thazard*). Mackerel tuna or "kawakawa" is a medium-sized fish that has two dorsal fins separated by a narrow interspace and anal fin succeeded by 6 to 8 anal finlets (Collette 2001). The color of its back is dark blue and its belly and lower portion of the body is white. It has black spots on its chest between pectoral and pelvic fins (van der Elst 1993).

The Philippines is currently ranked as the seventh largest canned and processed tuna manufacturer in Asia, next only to Thailand (Greenpeace 2016). The leading producer of sashimi grade tuna is General Santos City (Figure 1), dubbed as the "tuna capital of the Philippines" and is home to seven tuna processing plants (Goldenstate College 2010). The proximity of General Santos City to tuna-rich fishing grounds, including the Moro Gulf, Sulu Sea, Mindanao Sea, and adjacent Celebes Sea, is a great advantage (SEAFDEC 2008). The Celebes part of the Philippines is the country's biggest tuna fishing ground, the coastline of which includes that of Sarangani Province in Mindanao. Sarangani is at the southernmost tip of Mindanao Island and comprise seven municipalities, namely, Alabel, Glan, Kiamba, Maasim, Maitum, Malapatan, and Malungon. These municipalities, except Malungon, are situated along the coast (DOH-CHD SOCCSKSARGEN 2014). The province borders South Cotabato and Davao del Sur to the north, and Davao Occidental to the east with a 230-km (140 miles) coastline along the Sarangani Bay and Celebes Sea. The 215,950-ha Sarangani Bay is identified as a rich spawning ground for tuna and tuna-like species, including sardines (*lupoy* or *tamban*), that serve as food for tuna. The bay is also known for its rich biodiversity, being home to at least three large marine turtles, seacows, several species of sharks (including whale sharks), whales, and dolphins.

In recent years, however, Sarangani and General Santos City have been subjected to progressive and rapid development that led to environmental issues like sedimentation from mining activities and industrial pollution in Sarangani Bay (de Jesus et al. 2001). Various metallic and nonmetallic deposits are found in

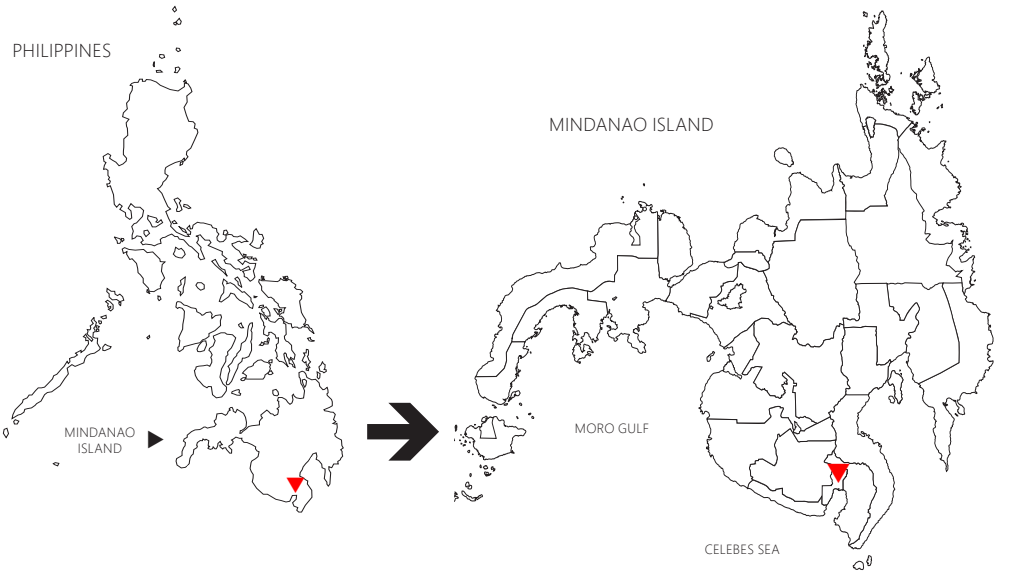

FIGURE 1 Location of General Santos City and Sarangani Province, Mindanao Island, Southern Philippines

Sarangani and General Santos City (de Jesus et al. 2001). Metallic deposits in the municipalities of Alabel, Kiamba, Maasim, and Maitum in Sarangani Province include copper (Cu), gold (Au), iron (Fe), and silica (Si); and in General Santos, Cu, Fe, Au, and silver (Ag) are being mined (de Jesus et al. 2001).

In gold mining, metallic Hg is used to form gold amalgam. This practice causes contamination on the area and aquatic system, which leads to exposure of the population to metallic Hg (Harari et al. 2012). Moreover, mining companies use zinc (Zn) dust with Cd impurities (Tetteh et al. 2010) and Pb for gold extraction (Calain 2012).

According to de Jesus et al. (2001), a study conducted by Industrial Environmental Management Project (IEMP) in 1997 showed elevated concentrations of the heavy metals Cd, Pb, and Hg in the waters of Sarangani Bay. From fifteen sampling points, average heavy metal content of 0.049 mg·L^{-1} for Cd, 0.614 mg·L^{-1} for Pb, and 0.001 mg·L^{-1} for Hg were detected.

This study assessed the extent of heavy metals contamination of the fishing waters and bottom sediments along the coast of Sarangani Bay. The physical properties, such as pH and temperature of seawater, were also determined as it affects the metal uptake by aquatic organisms. The determination of heavy metals content in the muscle tissues of tuna samples that spawn along the bay, specifically the mackerel tuna or "kawakawa" (*E. affinis*), was also done.

Materials and Methods

Tuna Samples Collection and Preparation

Mackerel tuna samples were obtained from General Santos City Fish Port (GSCFP) and Kiamba fish landing site from 24 to 26 October 2013. All samples were randomly selected for purchase from the market stalls, labeled and placed in freezer before further preparation for heavy metal analysis. The samples from GSCFP, which weighed between 330 to 3240 g with length ranging from 27.5 to 56.0 cm, were caught in Tawi-Tawi and Sentro (Celebes Sea). Samples from Kiamba fish landing site, which were caught in the fishing waters adjacent to Kiamba, weighed from 60 to 90 g with lengths varying from 15 to 24.5 cm.

Laboratory materials used for sample preparation were cleaned with liquid soap and washed with distilled water twice before use. Six tuna samples per sampling point were prepared for analysis. The length of tuna samples

(in cm) were first measured using a flexible tape measure. Total length is the length from the tip of the longest jaw or the end of the snout to the longest caudal lobe pushed together (Khan et al. 2004). Muscle tissues to be used for analysis were separated from the bones, fins, skin, and guts since according to Tanee et al. (2013), muscle is the major tissue of interest for heavy metal contamination as it is widely consumed by people. Three hundred grams of muscle tissues were placed in a double polyethylene plastic and labeled and coded. Materials used for sample preparation were washed with distilled water twice every after collection from each sample.

Acid Digestion of Tuna for Heavy Metals Analysis

Tuna samples were homogenized using a blender equipped with stainless steel blade and placed in a labeled plastic container. An aliquot of 3-g sample was selected at random and placed in a 200-mL beaker. Triplicates were prepared for each type of sample, and the beakers with sample were placed in a laminar flow clean air cabinet. To prepare samples for Hg analysis, 10 mL of (1+1) mixture of HNO_3-$HClO_4$ was added to each beaker followed by addition of 5 mL of H_2SO_4. If samples are not fully digested, (1+1) mixture of HNO_3-$HClO_4$ was further added to maximum volume of 20 mL. Heavy metal analysis for Hg was done using cold vapor atomic absorption spectrophotometry (CVAAS) (Tüzen 2003).

To prepare samples for Pb and Cd analyses, addition of 10 mL HNO_3 to each beaker was done followed by addition of 1 mL H_2O_2. The beakers were then covered and shaken lightly, then heated at 200–250 °C using hot plate for 30 min. The digested samples were then removed from hot plate and allowed to cool. Distilled water was added to a volume of 50 mL while mixing thoroughly. Heavy metal analyses for Cd and Pb were done using atomic absorption spectrophotometry (AAS) (Tüzen 2003).

Seawater and Bottom Sediment Samples Collection and Preparation

Polyethylene bottles with screw caps for seawater sample collection were first washed using detergent, then with 10% v/v HNO_3. The acid-washed bottles and containers were rinsed with de-ionized water and dried in laminar flow hood for 2 h. Selection of sampling stations for seawater and bottom sediments were done according to the location of principal sources of tuna catch based on the survey conducted earlier in the study. A total of three sampling stations were selected as representative regions of Sarangani coastline, namely, Barangay Poblacion (05°59'08" N; 124°37'01" E) and Kling (05°56'05" N; 124°43'26" E), both in the municipality of Kiamba, as stations 1 and 2, respectively; and Barangay Kablacan (05°51'31" N; 124°56'48" E) in the municipality of Maasim as station 3. Shallow coastal water areas were selected since it was assumed that sea adjacent to sampling stations has normal current circulation. According to Rajamohan et al. (2010), normal current circulation of the sea is inclined to concentrate heavy metals and other pollutants along the coastline since the currents prohibit mixing of pollutants (heavy metals) in the shallow part to the deeper part of the sea. Each sampling station was stratified into three divisions based on depth. Triplicates per stratum were obtained. Using an improvised water sampler, seawater was collected at depth of 0.25, 1.00, and 2.00 m below the water surface corresponding to the first, second, and third layers, respectively. The water sampler was rinsed with distilled water every after collection from a layer. Two liters of water sample was collected per replicate in each stratum. The collected seawater sample was stored in two decontaminated 1-L polyethylene bottles. The pH of the water sample was determined onsite using pH meter (pH 600 Milwaukee) while salinity and temperature were measured using DURAC® Hydrometer and DeltaTRAK Model #12207 thermometer, respectively. Water samples were then preserved by adding concentrated HNO_3 at pH 2–4 and chilled for heavy metal determination (Radojevic and Bashkin 1999).

Bottom sediment samples were obtained in the same location as seawater samples. The 3 kg of bottom sediment collected were first screened to remove unwanted particles such as roots, worms, and other solid particles. The sediment sample was then placed in polyethylene plastics and placed in ziplock plastic container.

Acid Digestion of Seawater for Heavy Metal Analysis

For analysis of Cd and Pb, 100 mL of seawater sample was placed in 125-mL conical flasks and digested with concentrated HNO_3 until a clear solution was obtained. The solution was filtered and the filtrate transferred into 50-mL volumetric flask diluted to the mark with distilled water and was mixed thoroughly (Sabo et al. 2013).

To prepare seawater samples for Hg analysis, the sample was first filtered using 0.45-µm membrane filter. After filtration, 2 L of water sample was transferred to a 2-L separatory funnel. Ten milliliters of 20 N H_2SO_4 and 5 mL of 0.5% $KMnO_4$ solution were added, mixed, and allowed to stand for 5 min. Then, 20 mL of 10 N NaOH was added to neutralize the mixture after which 5 mL of 10% $NH_2OH{\cdot}HCl$ was added. The mixture was shaken and allowed to stand for 20 min, after which 5 mL of 10% ethylenediaminetetraacetic adic (EDTA) solution was added to the mixture and shaken. Ten milliliters of purified 0.01% dithizone-toluene was then added and shaken vigorously for 1 min to extract Hg in the sample. The mixture was again allowed to stand for 1 h. The resulting mixture in toluene phase was transferred to a 10-mL conical centrifuge tube with glass stopper and centrifuged at 1200 rpm for 3 min. Seven milliliter of toluene phase mixture was transferred to digestion flask and evaporated to dryness on water bath at 60 °C. One milliliter of distilled water was added followed by addition of 2 mL of (1+1) mixture of HNO_3-$HClO_4$ and 5 mL of H_2SO_4. The resulting mixture was heated on a hot plate at 200 to 230 °C for 30 min and allowed to cool. Then, distilled water was added until 50 mL of the mixture was obtained. The 50-mL mixture was mixed well and used as sample test solution (Suzuki 2004).

Acid Digestion of Bottom Sediments for Heavy Metal Analysis

The sediment samples were allowed to dry at room temperature before acid digestion. Sediment samples for Cd and Pb analyses were placed in porcelain crucibles and oven dried at 80 °C for 24 h. The dried samples were then ground using porcelain mortar and pestle, then sieved using 200 µg sieve screen. Triplicates from each sampling station were obtained for heavy metal analysis. One-half gram of the sieved sample was placed in a 100-mL beaker with 5 mL distilled water. The sample was then digested using 5 mL of Aqua-regia (nitro-hydrochloric acid), then cooled and filtered through Whatman 541 filter paper into a 100-mL volumetric flask. Distilled water was added to the mark. The mixture was mixed thoroughly to obtain a homogenized solution, then transferred to a labeled sample bottle (Sabo et al. 2013).

For Hg analysis, 0.5 g wet weight sample was placed in a digestion flask. One milliliter of distilled water was added, followed by addition of 2 mL of (1+1) mixture of HNO_3-$HClO_4$ and 5 mL of H_2SO_4. The resulting mixture was heated at 200 to 230 °C for 30 min and allowed to cool. Distilled water was then added until a volume of 50 mL mixture was obtained. The 50-mL mixture was thoroughly mixed and used as sample test solution (Suzuki 2004).

Heavy Metal Analysis

Determination of mercury. For mercury analysis, the fixed volumes (generally 10 mL of each blank test solution), standard test solution and sample test solution were placed in reaction vessel of the mercury analyzer. One milliliter of $SnCl_2$ solution was added for reduction reaction after reaction vessel was stoppered firmly. Air was circulated through four-way stopcock to allow the mercury vapor to come to equilibrium. The acidic gases generated by the reaction were swept into NaOH solution. After 30 s, the four-way stopcock was rotated through 90° and the mercury vapor was swept into the absorption cell. Response was recorded on the strip chart recorder as a very sharp peak. Peak heights were used for

computations (Voegborlo and Akagi 2005). The detection limits of the mercury analyzer used for mercury in tuna, seawater, and bottom sediment samples are 0.0417 mg·kg^{-1}, 2.5 × 10^{-4} mg·L^{-1}, and 0.0417 mg·kg^{-1}, respectively (Suzuki 2004). Mercury analysis was performed using Shimadzu AA-6300 equipped with mercury analyzer.

Determination of Cd and Pb. For analysis of both Cd and Pb, 10 mL sample test solution was introduced in AAS (Shimadzu AA-6300). The detection limits of AAS for Cd in tuna, seawater, and bottom sediment samples are 0.083 mg·kg^{-1}, 0.005 mg·L^{-1}, and 0.083 mg·kg^{-1}, respectively.

While for Pb, the detection limits in tuna, seawater, and bottom sediment samples are 2.5 mg·kg^{-1}, 0.01 mg·L^{-1}, and 2.5 mg·kg^{-1}, respectively.

Assessment of Sediment Pollution

To assess the sediment pollution, only geoaccumulation index was used as described by Diatta et al. (2008). Geoaccumulation index allows the assessment of contamination by heavy metal by comparing current and preindustrial metal contents in the sediment and can be computed using the equation described by Chaudhuri et al. (2007). The concentration of heavy metal in the Earth's crust is used as geochemical background. The following geochemical backgrounds were used: 0.20 mg·kg^{-1} for Cd, 12.5 mg·kg^{-1} for Pb, and 0.08 mg·kg^{-1} for Hg (Carvalho et al. 1997). Calculated Geoaccumulation Index (I_{geo}) values were used to assess the sediment quality in the study area.

Statistical and Data Analyses

Coefficient of variation was used to compare the physical properties of seawater samples at different depths of the three sampling stations. The coefficient of variation is defined as a measure of variability of data computed by dividing standard deviation by the mean (Reid 2014).

Analysis of Safety Levels

In the analysis of the safety levels of heavy metal content of tuna samples, standard safety limits of the US Environmental Protection Agency (US EPA), US Food and Drug Administration (US FDA), and European Commission (EC) were used.

Results and Discussion

Heavy Metals in Tuna

Results of heavy metals analysis of the *E. affinis* samples show three out of six samples were found to contain Hg in the range of 0.045 to 0.108 mg·kg^{-1}. The values, however, did not exceed the 1 mg·kg^{-1} limit prescribed by US EPA, FDA, and EC. Both Cd and Pb were not detected in all *E. affinis* samples from GSCFP (Table 1).

Hg and Pb were not detected in all *E. affinis* samples from Kiamba fish landing site (Table 1). In the case of Cd, 0.095 mg·kg^{-1} was detected, which exceeded the limit of 0.05 mg·kg^{-1} prescribed by the US EPA, FDA, and EC. According to Muntau and Baudo (1992), the possible sources of Cd that enter aquatic environment and affect fish are deposition from atmosphere by fuel combustion, use of agricultural fertilizer, mining residues, and wastewater discharge. The presence of Cd in sample 6 is probably due to mining activities near the fishing waters and the slow excretion of Cd by the fish. The presence of a mining company, the Kiamba Mining Corporation (KMC), near the study area as reported by Duerme (2013) may have aggravated Cd contamination due to emissions of zinc (Zn) dust with Cd impurities (Tetteh et al. 2010). Once Cd is absorbed by the fish, it is concentrated in the liver due to soluble metallothioneins (Gašpić et al. 2002; George and Olsson 1994; Phillips and Rainbow 1992). Metallothionein is a low-molecular-weight protein whose apoprotein, thionein, is induced by exposure to heavy metals and provides a protective role against the toxic effects of these metals by sequestering and thus reducing the amount of the free metal ions (Davis et al. 2012). Kumar et al. (2007) also found that Cd has an

TABLE 1 Mean heavy metal concentration of *E. affinis* samples from General Santos City Fish Port (GSCFP) and the Kiamba fish landing site in Sarangani, Southern Philippines

Samples	Length (cm)	Weight (g)	Mercury ($mg \cdot kg^{-1}$)	Cadmium ($mg \cdot kg^{-1}$)	Lead ($mg \cdot kg^{-1}$)
General Santos City Fish Port					
1	55.7	3240	0.045	ND	ND
2	54.6	2120	ND	ND	ND
3	56.0	2700	0.108	ND	ND
4	54.5	2400	ND	ND	ND
5	54.0	2600	0.067	ND	ND
6*	27.5–32.5	330–490	ND	ND	ND
Kiamba fish landing site					
1*	22.5–24.5	180–210	ND	ND	ND
2*	15.0–17.5	40–60	ND	ND	ND
3*	16.0–17.5	50–80	ND	ND	ND
4*	16.5–19.0	50–90	ND	ND	ND
5*	18.0–20.0	50–80	ND	ND	ND
6*	17.3–19.8	50–80	ND	0.095	ND
US Environmental Protection Agency and Food and Drug Administration limits			1	0.05	0.5
European Commission limit			1	0.05	0.2

*Composite sample. The values for length and weight shown are the minimum and maximum range of the values recorded from individual fish sample
ND = Not detected: Hg < 0.0417 $mg \cdot kg^{-1}$; Cd < 0.083 $mg \cdot kg^{-1}$; Pb < 2.5 $mg \cdot kg^{-1}$.

inactive site of detoxification in the liver, thus the metal is not easily transported from the liver to other tissues like muscles.

Lead, on the other hand, is distributed directly to kidneys, bones, and muscle tissues since the cytosol in the liver does not contain proteins with high affinity for Pb (Gašpić et al. 2002). Even if Pb is directly distributed in tissues, low concentrations were observed in the samples.

According to Kojadinovic et al. (2006), Hg in muscle tissues had a direct relationship with the length of the fish. As shown in the results, Hg was detected in half of the samples from GSCFP while none was detected in samples from Kiamba fish landing site. This could be due to shorter lengths of samples from Kiamba fish landing site as compared to the length of tuna from General Santos fish port, which is consistent with the findings of Kojadinovic et al. (2006).

E. affinis is commonly found in coastal waters (Collette 2001). Small-sized *E. affinis* with lengths of 20 to 40 cm are commonly found in 0 to 50 m water depth while those with length greater than 40 cm are found in 50 to 200 m water depth (Yesaki 1994). From the results, it can be deduced that majority of the samples from GSCFP were fished at 50 to 200 m depth, while the samples from Kiamba were fished at 0 to 50 m water depth. A study conducted by Kojadinovic et al. (2006) showed that bioaccumulation of Hg is linked with feeding behavior in relation to depth of the water. According to Monteiro et al. (1996), bioaccumulation of mercury increases with depth due to poor oxygenation in deep waters, which leads to increased methylation of Hg. In this study, Hg content was detected in samples from GSCFP, most of which were fished from deep waters, while no Hg was detected from the smaller-sized samples from Kiamba fish landing site, which were fished from shallow waters. This could be explained by the findings of Monteiro et al. (1996).

Physical Properties of Seawater

There seems to be consistency in the values of the parameters in all layers of sampling sites (Table 2). The average seawater temperature ranged from 32.4 °C at the surface to 31.66 °C at 2 m below the surface, which is higher than the maximum temperature observed in the tropics. According to MarineBio (2015), the temperature of the sea surface is within the range of 27 to 30 °C near the equator, where the maximum value occurs a few degrees of latitude north of the equator. Further increase in water temperature may lead to increase metabolic rate of aquatic organisms that may result in higher metal uptake rate (Degnon et al. 2012).

The average pH of the seawater samples was found to be 8.24 at the surface to 8.5 at 2 m below the surface, which is neutral and within the range of pH in saline waters (Table 3). According to US Environmental Protection Agency (2006), estuarine pH levels generally average between 8.0 and 8.6 in the more saline areas. Zeitoun and Mehana (2014) cited that water acidification may affect accumulation of fish by altering solubility of metal or damage of epithelia, promoting permeability of metals.

TABLE 2 Physical properties of seawater from three sampling stations along Sarangani coastline, Southern Philippines

Station	Location	Depth (m)	Temp (°C)	pH
1	Poblacion, Kiamba	0.25	29.5–38.3	8.2–8.3
		1.00	29.4–37.8	8.1–8.2
		2.00	29.4–39.4	8.1–8.2
2	Kling, Kiamba	0.25	29.8–33.7	8.1–8.2
		1.00	29.4–33.2	8.2–8.3
		2.00	29.6–32.5	8.2–8.3
3	Kablacan, Maasim	0.25	29.5–35.1	8.3–8.4
		1.00	28.7–33.1	8.3
		2.00	28.4–31.6	8.3

Heavy Metals in Seawater

In all seawater samples, Cd, Pb, and Hg were not detected (Table 4). This implies that the concentration of heavy metals, if at all present, is below 2.5×10^{-4} mg·L^{-1} for Hg, 0.005 mg·L^{-1} for Cd, and 0.01 mg·L^{-1} for Pb. The trace amount of heavy metals in the seawater samples can be attributed to the absence of industrial and commercial activity along the coastline.

Heavy Metals in Sediments

Results showed that Cd, Pb, and Hg were not detected in station 1 (Kiamba) and station 3 (Kablacan) (Table 5). In station 2 (Kling), Pb was detected at a mean concentration of 62.27 mg·kg^{-1}. The concentration of Pb, however, did not exceed the 128 mg·kg^{-1} limit prescribed by National Oceanic and Atmospheric Administration (NOAA).

The presence of Pb in sediments at Kling is probably due to gold mining activities in the area (de Jesus et al. 2001). The presence of a mining company in Kiamba, specifically Kiamba Mining Corporation (KMC) (Duerme 2013), may have aggravated Pb contamination. Lead is used for gold extraction (Calain 2012), and Howard and Olulu (2012) noted that it is possible for Pb to persist longer in sediments and affects aquatic food chain since it has low solubilty, resistant to microbial degradation, and has longer residence time as compared to other heavy metals.

Sediment Quality

The Cd, Hg, and Pb of bottom sediments in station 1 (Poblacion in Kiamba) and station 3 (Kablacan in Maasim) are below the detection limits (Hg < 0.0417 mg·kg^{-1}; Cd < 0.83 mg·kg^{-1}; Pb < 2.5 mg·kg^{-1}) (Table 6) and therefore within the range of two index values, $I_{geo} < 0$ or $0 < I_{geo} < 1$ (Table 7). Hence, the sediments in these two sampling sites can be classified as either "practically unpolluted" or "unpolluted to moderately polluted" by all metals depending on the actual concentration of the metals in the area. For station 2 at Kling, Kiamba, the area can be classified as either "practically unpolluted" or "unpolluted to moderately polluted" only for Cd

TABLE 3 Statistical data of the physical properties of seawater from three sampling sites in Sarangani, Southern Philippines

Properties	Depth (m)	Range of values	Coefficient of variation	Statistical mean
Temperature (°C)	0.25	29.5–33.2	4.68	32.40 ± 1.54
	1.00	28.7–32.6	4.57	31.93 ± 1.46
	2.00	28.4–31.0	6.52	31.66 ± 2.06
pH	0.25	8.1–8.4	0.98	8.24 ± 0.08
	1.00	8.1–8.3	1.10	8.23 ± 0.09
	2.00	8.1–8.3	0.83	8.25 ± 0.07

TABLE 4 Mean heavy metal concentration of seawater in three sampling stations in Sarangani, Southern Philippines

Station	Location	Depth (m)	Cadmium ($mg \cdot L^{-1}$)	Lead ($mg \cdot L^{-1}$)	Mercury ($mg \cdot L^{-1}$)
1	Poblacion, Kiamba	0.25	ND	ND	ND
		1.00	ND	ND	ND
		2.00	ND	ND	ND
2	Kling, Kiamba	0.25	ND	ND	ND
		1.00	ND	ND	ND
		2.00	ND	ND	ND
3	Kablacan, Maasim	0.25	ND	ND	ND
		1.00	ND	ND	ND
		2.00	ND	ND	ND
US Environmental Protection Agency limit			0.0088	0.0081	0.0001
Department of Environment and Natural Resources–Environmental Management Bureau limit			0.01	0.05	0.002

ND = Not detected: Hg < 2.5×10^{-4} $mg \cdot L^{-1}$; Cd < 0.005 $mg \cdot L^{-1}$; Pb < 0.01 $mg \cdot L^{-1}$.

TABLE 5 Mean heavy metal concentration of bottom sediments in three sampling stations in Sarangani, Southern Philippines

Station	Location	Cadmium ($mg \cdot L^{-1}$)	Lead ($mg \cdot L^{-1}$)	Mercury ($mg \cdot L^{-1}$)
1	Poblacion, Kiamba	ND	ND	ND
2	Kling, Kiamba	ND	62.27	ND
3	Kablacan, Maasim	ND	ND	ND
National Oceanic and Atmospheric Administration limit		4.9	128	0.696

ND = Not detected: Hg < 0.0417 $mg \cdot kg^{-1}$; Cd < 0.83 $mg \cdot kg^{-1}$; Pb < 2.5 $mg \cdot kg^{-1}$.

TABLE 6 Calculated geoaccumulation indices of heavy metal in three sampling stations in Sarangani, Southern Philippines

Station	Location	Cadmium ($mg \cdot L^{-1}$)	Lead ($mg \cdot L^{-1}$)	Mercury ($mg \cdot L^{-1}$)	Sediment quality
1	Poblacion, Kiamba	-	-	-	Unpolluted to moderately polluted
2	Kling, Kiamba	-	0.52	-	Unpolluted to moderately polluted
3	Kablacan, Maasim	-	-	-	Unpolluted to moderately polluted

TABLE 7 Classes of geoaccumulation index*

Class	Index value	Sediment quality
0	$I_{geo} < 0$	Practically unpolluted sediment
1	$0 < I_{geo} < 1$	Unpolluted to moderately polluted
2	$1 < I_{geo} < 2$	Moderately polluted
3	$2 < I_{geo} < 3$	Moderately to strongly polluted
4	$3 < I_{geo} < 4$	Strongly polluted
5	$4 < I_{geo} < 5$	Strongly polluted to extremely polluted
6	$5 < I_{geo}$	Extremely polluted

*Adapted from Rabajczyk et al. (2011)

and Hg since Pb was detected in the area. The geoaccumulation index of Pb in station 2 (Kling) was computed to be 0.52, which is within the range of $0 < I_{geo} < 1$. The sediment can therefore be classified as "unpolluted to moderately polluted" by Pb. The status of pollution of sediments in the area can be explained by the absence of industrial and commercial activity in the vicinity of the sampling stations. According to Rabajczyk et al. (2011), moderately to highly polluted sediments are observed in areas with factories and high human and commercial activities.

Summary and Conclusion

The amount of Hg in mackerel tuna (*E. affinis*) may be dependent on the size of the fish and the depth of the fishing waters where increased methylation of Hg occurs in deep waters due to poor oxygenation. The three *E. affinis* samples from GSCFP with lengths ranging from 27.5 to 56.0 cm, which were fished from deep waters, were found to contain Hg at concentrations ranging from 0.045 to 0.108 mg·kg^{-1}. The concentration, however, did not exceed the limits set by US EPA, US FDA, and EC, which is 1 mg·kg^{-1}. The concentration of Cd and Pb were below the detectable concentration of 0.83 mg·kg^{-1} and 2.5 mg·kg^{-1}, respectively. One out of six *E. affinis* samples from the Kiamba fish landing site, with lengths ranging from only 20 to 40 cm and which were fished in shallow waters, were found to contain only Cd at concentration of 0.095 mg·kg^{-1}. The Pb and Hg in all *E. affinis* samples in Kiamba fish landing site were below detectable level. It can be concluded that the *E. affinis* samples from all sampling sites seem to pose no threat to the consumers. However, in future studies, instruments that can detect low concentration of heavy metals such as Pb should be used. In the case of Pb, although the metal was not detected, there could be a high concentration of metal in the fish samples as the limit of detection of the instrument used, which is 2.5 mg·kg^{-1}, is high compared to the standard limit of 0.5 and 0.2 mg·kg^{-1} set by the regulating bodies.

Heavy metal analysis in seawater from all sampling stations in Kiamba and Maasim showed that there were no Cd, Pb, and Hg detected in the seawater samples. Sediments obtained from Kling showed presence of Pb at 62.27 mg·kg^{-1}, which did not exceed the 128 mg·kg^{-1} limit set by NOAA. The presence of Pb is probably due to gold mining activities in the area where the presence of a mining company in Kiamba may have aggravated Pb contamination. An assessment of bottom sediment pollution in three sampling stations using the geoaccumulation index showed that the sediments at all sampling stations can be classified as "unpolluted to moderately polluted" by Cd, Pb, and Hg, which can be explained by the absence of industrial and commercial activity in the vicinity.

Finally, in order to protect public health, it is essential to keep heavy metal contaminants from various sources at levels that do not cause health concerns. Maximum levels of heavy metals such as Cd, Pb, and Hg must be safe and as low as reasonably achievable based upon good manufacturing and agricultural/fishery practices.

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References

Adeniyi AA, Yusuf KA. 2007. Determination of heavy metals in fish tissues, water and bottom sediments from Epe and Badagry Lagoons, Lagos, Nigeria. Environ Monitor Assess. 37:451–458.

Ashraf W. 2006. Levels of selected heavy metals in tuna fish. Arab J Sci Eng. 31(1A):89–92.

Besada V, González JJ, Schultze F. 2006. Concentraciones de mercurio, cadmio, plomo, arsènico, cobre y zinc en atùn blanco, rabil y patudo procedentes del ocèano atlàntico. Cienc Mar. 32(2B):439–445.

Calain P. 2012. What is the relationship of medical humanitarian organisations with mining and other extractive industries?. PLoS Med 9(8):e1001302.

Carpenter KE, Neim VH, editors. 2001. The living marine resources of the Western Central Pacific. Volume 6, Bony fishes, part 4 (Labridae to Latimeridae), estuarine crocodiles, sea turtles, sea snakes and marine mammals. FAO species identification guide for fishery purposes. Food and Agriculture Organization of the United Nations, Rome (p. 3381–4281).

Carvalho ML, Ferreira JG, Amorim P, Marques MIM, Ramos MT. 1997. Study of heavy metals and other elements in macrophyte algae using energy-dispersive x-ray fluorescence. Environ Toxicol Chem. 16(4):807–812.

[DOH-CHD SOCCKSARGEN] Center for Health and Development, Department of Health, SOCCSKSARGEN. 2014. Sarangani province. 3 March 2014. http://chd12.doh.gov.ph/index.php/profile/sarangani.

Chaudhuri A, Mitra M, Havrilla C, Waguespack Y, Schwarz J. 2007. Heavy metal biomonitoring by seaweeds on the Delmarva Peninsula, east coast of the USA. Bot Mar. 50:151–158.

Collette BB. 2001. Scombridae. In: Carpenter KE, Neim VH, editors. The living marine resources of the Western Central Pacific. Volume 6, bony fishes, part 4 (Labridae to Latimeridae), estuarine crocodiles, sea turtles, sea snakes and marine mammals. FAO species identification guide for fishery purposes. Food and Agriculture Organization of the United Nations. Food and Agriculture Organization of the United Nations, Rome, p. 3721–3735.

Davis R, Goncalves R, Ziolli R, de Campos R. 2012. A novel report of metallothioneins in fish bile: SDS-PAGE analysis, spectrophotometry quantification and metal speciation characterization by liquid chromatography coupled to ICP-MS. Aquat Toxicol. 116-117: 54–60.

de Jesus EA, Diamante-Fabunan DAD, Nañola Jr. CL, White AT, Cabangon HJ. 2001. Coastal environmental profile of the Sarangani Bay area, Mindanao, Philippines. Coastal Resource Management Project, Cebu City, Philippines.

Degnon RG, Dahouenon-Ahoussi E, Adjou ES, Soumanou MM, Dolganova NV, Sohounhloue DCK. 2012. Heavy metal contamination of the Nokoué Lake (Southern Benin) and the dynamic of their distribution in organs of some fish's species (*Mugil cephalus* L. and *Tilapia guineensis*). J Anim Sci Adv. 2(7):589–595.

Diatta JB, Chudzinska E, Wirth S. 2008. Assessment of heavy metal contamination of soils impacted by a zinc smelter activity. J Elementol. 13(1):5–16.

Duerme SJ. 2013. Mining group strengthens support to national government's greening program. 23 March 2014. http://r12.pia.gov.ph/index.php?article=2301377229078.

Gašpić ZK, Zvonarić T, Vrgoč N, Odžac N, Barić A. 2002. Cadmium and lead in selected tissues of two commercially important fish species from the Adriatic Sea. Water Res. 36(20):5023–5028.

George SG, Olsson PE. 1994. Metallothioneins as indicators of trace metal pollution. In: Kramer KJM, editor. Biomonitoring of coastal waters and estuaries. CRC Press, Boca Raton, FL, p. 151–178.

Goldenstate College. 2010. Profile of General Santos City. 3 March 2014. http://www.goldenstate.edu.ph/news/97-profile-of-general-santos-city.html.

Greenpeace. 2016. From sea to can: 2016 Southeast Asia canned tuna ranking. http://www.greenpeace.org/seasia/PageFiles/742678/Greenpeace-Canned%20Tuna%20Report%202016%20online.pdf

Harari R, Harari F, Gerhardsson L, Lundh T, Skerfving S, Strömberg U, Broberg K. 2012. Exposure and toxic effects of elemental mercury in gold-mining activities in Ecuador. Toxicol Lett. 213(1):75–82. doi:10.1016/j.toxlet.2011.09.006.

Howard IC, Olulu BA. 2012. Metal pollution indices of surface sediment and water from the upper reaches of Sombriero River, Niger Delta, Nigeria. Our Nature. 10:206–216.

Khan RG, Pearson DE, Dick EJ. 2004. Comparison of standard length, fork length, and total length for measuring west coast marine fishes. Mar Fish Rev. 66(1):31–33.

Kojadinovic J, Potier M, Le Corre M, Cosson RP, Bustamante P. 2006. Mercury content in commercial pelagic fish and its risk assessment in the Western Indian Ocean. Sci Total Environ. 366(2–3):688–700.

Kumar P, Prasad Y, Patra AK, Swarup D. 2007. Levels of cadmium and lead in tissues of freshwater fish (*Clarias batrachus* L.) and chicken in Western UP (India). Bull Environ Contam Toxicol. 79(4):396–400.

[MarineBio] MarineBio Conservation Society. 2015. The ocean and temperature. 30 August 2015. http://marinebio.org/oceans/temperature/

Monteiro LR, Costa V, Furness RW, Santos RS. 1996. Mercury concentrations in prey fish indicate enhanced bioaccumulation in mesopelagic environments. Mar Ecol Prog Ser. 141:21–25.

Muntau H, Baudo R. 1992. Sources of cadmium, its distribution and turnover in the freshwater environment. ARC Sci Publ. 118:133–148.

Nsikak UB, Joseph PE, Akan BW, David EB. 2007. Mercury accumulation in fishes from tropical aquatic ecosystems in the Niger Delta, Nigeria. Curr Sci. 92:781–785.

Phillips DJH, Rainbow PS. 1992. Biomonitoring of trace aquatic contaminants. Elsevier, Oxford, UK.

Rabajczyk A, Jozwiak MA, Jozwiak M, Kozlowski R. 2011. Heavy metals (Cd, Pb, Cu, Zn and Cr) in bottom sediments and the recultivation of Kielce Lake. Polish J Environ Study. 20(4):1013–1019.

Radojevic M, Bashkin VN. 1999. Practical environmental analysis. Royal Society of Chemistry, Cambridge, UK.

Rajamohan R, Rao TS, Anupkumar B, Sahayam AC, Balarama Krishna MV, Venugopalan VP, Narasimhan SV. 2010. Distribution of heavy metals in the vicinity of a nuclear power plant, east coast of India: with emphasis on copper concentration and primary productivity. Indian J Mar Sci. 39(2):182–191.

Reid HM. 2014. Introduction to statistics: fundamental concepts and procedures for data analysis. SAGE Publications, Los Angeles, CA.

Sabo A, Gani AM, Ibrahim AQ. 2013. Pollution status of heavy metals in water and bottom sediment of river delimit in Jos, Nigeria. Am J Environ Protection. 1(3):47–53.

[SEAFDEC] Southeast Asian Fisheries Development Center. 2008. Report on the on-site training for the handling of tuna on board handline bancas. 2 October 2013. http://map.seafdec.org/downloads/pdf/report_training_fishhandling_Philippine.pdf.

Suzuki T. 2004. Mercury analysis manual. Ministry of the Environment, Tokyo, Japan.

Tanee T, Chaveerach A, Narong C, Pimjai M, Punsombut P, Sudmoon R. 2013. Bioaccumulation of heavy metals in fish from the Chi River, Maha Sarakham Province, Thailand. Intl J Biosci. 3(8):159–167.

Tetteh S, Golom AA, Essumang DK, Zugle R. 2010. Levels of mercury, cadmium, and zinc in the topsoil of some selected towns in the Wassa West district of the Western region of Ghana. Soil Sediment Contam. 19(6):635–643.

Tüzen M. 2003. Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. Food Chem. 80(1):119–123.

[US EPA] United States Environmental Protection Agency. 2006. Voluntary estuary monitoring manual. 30 August 2015. http://water.epa.gov/type/oceb/nep/upload/2009_03_13_estuaries_monitor_chap11.pdf

van der Elst R. 1993. A guide to the common sea fishes of Southern Africa. Struik, Cape Town, South Africa.

Voegborlo RB, Akagi H. 2005. Determination of mercury in fish by cold vapour atomic absorption spectrophotometry using automatic mercury analyzer. Food Chem. 100:853–858.

Wong CK, Wong PP, Chu LM. 2001. Heavy metals concentrations in marine fishes collected from fish culture sites in Hong Kong. J Arch Environ Contam Toxicol. 40(1):60–69.

Yamaguchi R, Harrisson J. 2005. Roy's fish and seafood: recipes from the Pacific rim. Ten Speed Press, Berkeley, CA.

Yesaki M. 1994. A review of the biology and fisheries for (*Euthynnus affinis*) in the Indo-Pacific region. In: Shomura RS, Majkowski J, and Langi S, editors. Interactions of Pacific tuna fisheries. FAO Fisheries Technical Paper 2:388–409.

Zaragoza EC, Pagdilao CR, Moreno EP. 2004. Fisheries for tuna and other pelagic fishes. In: Silvestre G, Green SJ, White AT, Armada N, Luna C, Cruz-Trinidad A, and Carreon III MF, editors. Turbulent seas: the status of Philippine marine fisheries. Department of Agriculture–Bureau of Fisheries and Aquatic Resources, Manila, Philippines, p. 38–41.

Zeitoun MM, Mehana ESE. 2014. Impact of water pollution with heavy metals on fish health: overview and updates. Glob Vet. 12(2):219–231.