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Presence of Heavy Metals in Feathers of Avian Species and in Soils of Barangay Ipil-Calancan Bay, Sta.Cruz, Marinduque Island, Philippines

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ABSTRACT

Heavy metals may contaminate food, water, and air and bring toxic effects to both wildlife and humans. This study sought to assess the concentrations of heavy metals in the feathers of avian species and in soils using X-ray fluorescence in Barangay Ipil-Calancan Bay, Sta. Cruz, Marinduque Island, Philippines. Iron, Cu, Zn, Mn, Cr, Sc, Pb, Sr, and Se were observed in all samples while Co and As were only found in sampled avian species. Among these heavy metals, the concentrations of As, Cr, Pb, Se, and Zn were beyond the critical levels which were reported in other studies. Highly significant concentrations of Cr, Cu, Fe, Sc, Sr, Zn, and Mn were observed in Philippine pied fantail, white browed crake, white-collared kingfisher and little heron. Arsenic accumulation was only observed in yellow-vented bulbul while Cu, Fe, Sr, Zn, and Cr were significantly lowest in pink-necked green pigeon and Tabon scrubfowl. The kingfisher, crake, scrubfowl, and fantail may be the important bioindicators of the area. This study found correlation between soil and feather heavy metal contaminations concerning Mo with Fe, Mn, Cr, V, Ti, and Sb, Mn with Rb and Sb, Se with Sc, and Zn with Sc. Heavy metals may cause security problems in the area such as with food,

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humans and ecosystems' health. The study also provides baseline data using a non-invasive technique for biomonitoring heavy metal contamination.

Keywords: Avian species, bioaccumulation, feathers, heavy metals, soils

INTRODUCTION

Heavy metals from mining activities are considered among the huge environmental problems as it may contaminate the soil, air, water, and food resources. Its bioaccumulation eventually harms wildlife and humans. Mining and ore processing ranked second among the top ten worst pollution industries in 2016 world's worst pollution problems reported by the Pure Earth and Green Cross Switzerland (2016). In humans, four of the top six toxic threats known were from heavy metals such as lead, mercury, chromium, and cadmium. These were estimated to put 66 million people at risk and accounted for 13,750,000 of Disability Life Years (DALYs) lost due to incapacitating, dreaded illnesses and mortality in developing nations (Pure Earth and Green Cross Switzerland, 2015). Accordingly, wildlife exposed to the heavy metal pollution were stunted, sensitive to parasites and pathogens, and of low survival and reproductive capacity. Considering these unwanted effects, it is important to study the present concentrations of heavy metals in areas affected by mining activities. This also helps monitor trends and evaluate ecological risks as well as provide information which is foremost in the decision making and provision of mitigating measures.

Bioaccumulation studies have been widely used along with other methods to determine the presence of heavy metals in the environment especially in the higher trophic levels. Bioaccumulation studies require a few samples and some tissues of organisms from the same area to provide precise information on the degree of habitat contamination (Hutton, 1981). Heavy metal pollution in birds can be assessed using different organs, tissues, feathers, pellets, feces, and eggs. Among these, feathers were widely used considering its feasibility than other methods involving tissue collection wherein the organism needs to be sacrificed or disturbed on its nest, while scouring of large forested area for pellets or fecal samples can be time and energy consuming. There are benefits of using feathers to quantify heavy metal contamination in avifauna (Movalli, 2000). Feathers are easy to collect, can be kept at room temperature, can be collected even from endangered species and harmless to the organism because feathers moult and eventually replaced with a new feather.

One of the ways by which heavy metal concentrations in the soil and feather can be determined is through X-ray fluorescence (XRF). XRF is a rapid and low-cost method used in the analysis of samples (Ulmanu et al., 2011). Hu et al. (2017) also stated that the XRF unlike the traditional laboratory methods of heavy metal analyses did not take much time and labor. Furthermore, the method is popular in different fields involving metals and its associated industries, study of earth and minerals, food industry and ecological management as well as reported by several authors in human health management (Al-Eshaikh & Kadachi, 2011)

According to Goede and de Bruin (1984), the heavy metal pollution studies using avian feathers began in 1966. Avian species may be contaminated through water, food, contact, respiration, and by deliberately taking in pebbles or soil particles and thus may reveal the ongoing pollution in the environment. Birds that are endemic or resident may provide clue on the level of heavy metal accumulation in the same area.

Heavy metal in avian species may come from the extraction of minerals and its associated activities like improper dumping of mine tailings and lack of technologies to regain chemicals used in its processing. Mine spill, open untreated tailings dam and dumping of contaminated mine gangue are among the causes of the heavy metal pollution in avian species, other wildlife, and in humans.

Study Area

Marinduque, an island province located 137 miles south of Manila is an ideal area to study heavy metals. The island located south of mainland Luzon only measures 172,700 hectares and is composed of six townships namely Boac, Gasan, Buenavista, Torrijos, Sta. Cruz, and Mogpog. In the municipality of Sta. Cruz, an eight-kilometer causeway was created from the mine tailings dumped in the vicinity of Barangay Ipil along Calancan Bay. The island province is also rich in biodiversity. In fact, seventy-five species of birds were observed in the island, of which, seventeen are endemic to the country and six are island endemic subspecies (Gonzalez & Dans, 2000). The possibility of detecting more species of birds in the said area is high as Sanchez (2015) captured some species that were not recorded in books such as by Kennedy et al. (2000).

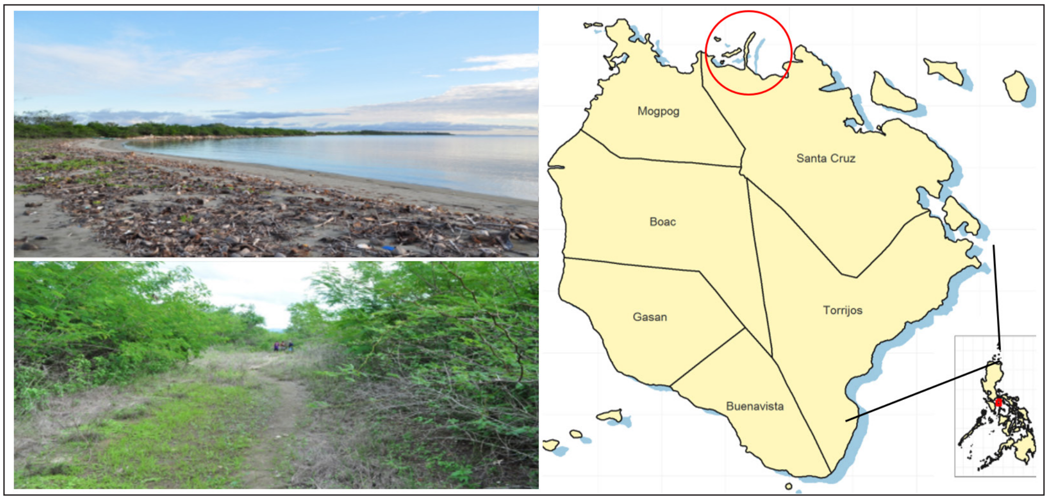

Figure 1. Map of Marinduque, its location (inset) and the study site (encircled red) (https://www.r-bloggers.com/creating-inset-map-with-ggplot2/)

This paper examined heavy metals in feathers of adult avian species captured from Barangay Ipil-Calancan Bay in the municipality of Sta. Cruz (Figure 1). This study sought to compare the present concentration of heavy metals in adult wild birds and pinpoint species that may be used as bioindicator or receptor species. Results of this study also provide baseline data on the level of heavy metal contamination in soil and birds and for comparison with future studies to monitor trends.

MATERIALS AND METHODS

All samples were collected with permission from the Department of Environment and Natural Resources. Birds were captured using mist nets and other indigenous traps. Collection of feathers from adult birds was done non-destructively. The feathers of the central tail, outermost primaries and secondaries of both wings, and some abdominal and scapular were pulled or cut using a sterile scissor. Newly grown or growing feathers were not removed to prevent bleeding and to ensure that only old plumages were utilized in this study. All feathers per individual bird were separately placed in a paper envelope coded with numbers corresponding with the list of those captured; the feathers contained in each envelope were then individually opened, cut into smaller pieces, packed in a polypropylene plastic, and sealed using a heat sealer. The soil samples, on the other hand, were collected from the 30cm and 60 cm depth in the site, air dried and kept in resealable plastic while in the field. After the fieldwork, the soil samples were air dried, packed and heat sealed. Each sealed polypropylene plastics containing the feathers and soils were then numbered accordingly. Lastly, the prepared samples were handed to the National Institute for Molecular Biology and Biotechnology of the University of the Philippines, Los Baños for XRF analysis to detect and quantify of the elements contained in the feathers and soils. Kruskal-Wallis and two tailed Pearson correlation were used to determine the differences and relationships of heavy metal concentrations between species and in soils.

RESULTS AND DISCUSSIONS

A total of 72 adult birds composed of 17 species and 11 families were captured. Of all the birds captured, only one was endemic, three endemic residents, and 10 were residents. Twelve of the species were common, three uncommon, and two fairly common. Only the range of the owl was not known as this owl had yet to be identified if it was a separate species but temporarily named for this study as Mantanani scops owl. Six species of wild doves or pigeons were netted, probably because the mangrove area and the trees that have grown in the causeway provided shelter and food. Of all the species of birds, the white collared kingfisher was relatively abundant (15.3%) and has the highest number of individuals captured. Based on relative abundance (RA, % of all species) the kingfisher was followed by zebra dove (11.1%), pied triller (9.7%), greater painted snipe (9.7%), yellow vented bulbul (8.3%), and island collared dove (6.9%) while the rest has four or less individuals captured (Table 1). Used nest mound of Tabon scrubfowls were also observed and three of this species were trapped.

Philippine duck (*Anas luzonica*), brahminy kite (*Haliastur indus intermedius*), purple heron (*Ardea purpurea*), osprey (*Pandion haliaetus melvillensis*), common moorhen (*Gallinula chloropus*), white breasted waterhen (*Amaurornis phoenicurus*), striated grassbird (*Megalurus palustris*), chestnut munia (*Lonchura malacca*), rails, Asian glossy starling (*Aplonis panayensis*), black-naped oriole (*Oriolus chinensis*), swiftlets, lowland white eye (*Zosterops meyeni),* and purple throated sunbird (*Nectarinia sperata*) were observed in the area.

Little is known on the accumulation of heavy metals and its present concentrations in birds from Marinduque Island especially in the tailings dumping site. Much of the studies on heavy metal pollution in the province were from sediments, fishes, corals, water, and other marine organisms. Twenty heavy metals out of the thirty-two elements identified by the XRF were used in this study. These heavy metals were As (Arsenic), Ba (Barium), Co (Cobalt), Cd (Cadmium), Cr (Chromium), Cu (Copper), Fe (Iron), Hg (Mercury), Mn (Manganese),

Table 1
List of wild avian species captured from the Barangay Ipil-Calancan Bay, Sta. Cruz, Marinduque Island, Philippines

Birds/Scientific name	**N=72**	**Range (Status)**	**RA**
Common emerald dove/*Chalcophaps indica*	4	Resident(Common)	5.5
Greater painted snipe/*Rostratula benghalensis*	7	Resident(Uncommon)	9.7
Island collared dove/*Streptopelia bitorquata*	5	Resident(Uncommon)*	6.9
Little heron/*Butorides striata carcinophilus*	2	Resident (Fairly common)	2.8
Mantanani scops owl/*Otus mantananensis*	3	? (Fairly common)*	4.2
Philippine bulbul/*Hypsipetes philippinus*	1	Endemic(Common)	1.4
Pied fantail/*Rhipidura nigritorquis*	3	Endemic(Common)[a]	4.2
Pied triller/*Lalage nigra*	7	Resident(Common)	9.7
Pink necked green pigeon/*Treron vernans*	3	Resident(Uncommon)	4.2
Spotted dove/*Streptopelia chinensis*	1	Resident(Common)	1.4
Tabon scrubfowl/*Megapodius cumingii pusillus*	3	Endemic Resident(Common)	4.2
White breasted woodswallow/*Artamus leucorhynchus*	3	Resident(Common)	4.2
White browed crake/*Porzana cinirea ocularis*	4	Endemic Resident(Common)	5.5
White collared kingfisher/*Halcyon chloris collaris*	11	Resident(Common)	15.3
White eared brown dove/*Phapitreron leucotis*	1	Endemic(Common)	1.4
Yellow vented bulbul/*Pycnonotus goiavier*	6	Endemic Resident(Common)	8.3
Zebra dove/*Geopelia striata*	8	Resident(Common)	11.1

Notes: All English and scientific names follow that of Kennedy et al. (2000), ***** = new record for the island province, [a] = lifted to species status (WBCP Checklist 2014), **?** = yet to be identified and classified

Mo (Molybdenum),Ni (Nickel), Pb (Lead), Sb (Antimony), Sn (Tin), Sc (Scandium), Se (Selenium), Sr (Strontium), Ti (Titanium), V (Vanadium), and Zn (Zinc).

The average of the three readings per individual of each species registered highest in Mantanani scops owl for Co, Pb, and Zn while Cr and Mn for Philippine bulbul. The yellow vented bulbul, Tabon scrubfowl, pied fantail, greater painted snipe, common emerald dove, and white collared kingfisher individually had the most elevated accumulation of Fe, Cu, Sc, Sr, and Se, respectively. Lowest average concentration of Fe and Cr was observed in pink necked green pigeon while Cu and Zn in white eared brown dove. Tabon scrubfowl, white collared kingfisher, little heron and spotted dove average for Mn, Sc, Se, and Sr were also respectively lowest (Figure 2).

The decelerating trend of heavy metals in wild avian feathers based on average concentration was Fe > Zn> Mn > Cu > Ti > Co > Cr > V> Mo > Sc > Pb > As > Se > Sr > Rb. On the other hand, Ba, Sb, Sn, Cd, Ni, and Hg were below the limit of detection. Sequentially, the highest to lowest concentration among the entire species of sampled birds was Tabon scrubfowl > Mantanani scops owl > Philippine bulbul > pied fantail > Mantanani Scops owl > Philippine bulbul > greater painted snipe > Mantanani scops owl > yellow vented bulbul > white collared kingfisher > common emerald dove. The Kruskal-Wallis test (Table 2) found highest concentrations among the sampled species especially with pied fantail for Cr and Cu and white browed crake for Fe and Sc. Strontium and Zn were also highly concentrated in significant amount with white collared kingfisher while Mn for little

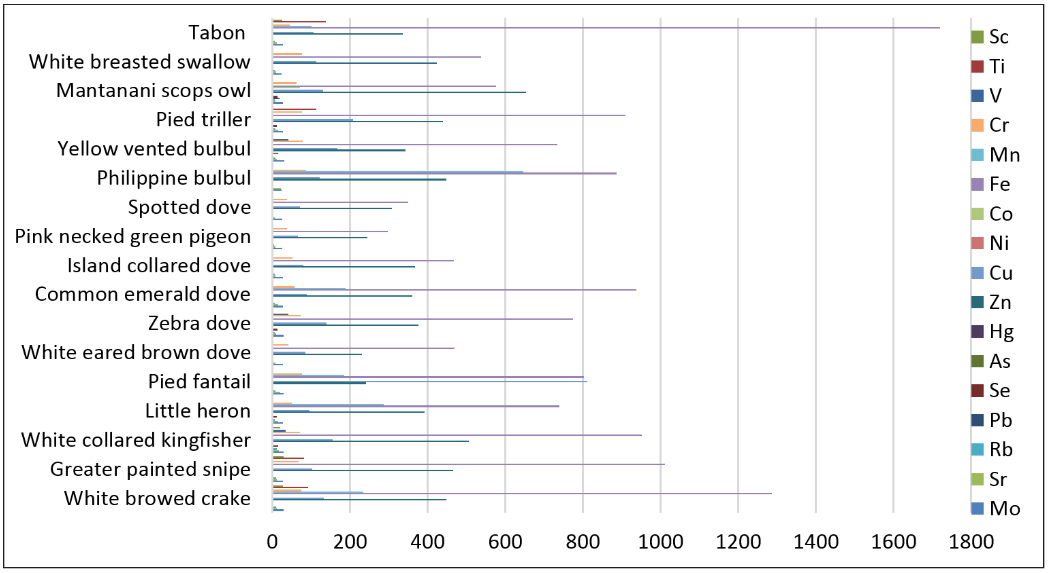

Figure 2. Heavy metal concentrations in wild avian species in Barangay Ipil-Calancan Bay, Sta. Cruz, Marinduque Island, Philippines

heron. Although Pb was high in all species and Se concentration in Mantanani scops owl was also elevated, both heavy metals were tested statistically trivial. The test also pointed out that most of the significant lowest accumulations were observed with Pink necked green pigeon (Cu, Fe, Sr, and Zn). Chromium was also observed to be concentrated at a significantly low amount in Tabon scrubfowl, including Sc and Mn with all birds except white browed crake and little heron.

The highest among the elements detected was Fe amounting to 1720.07mg/kg and found in Tabon scrubfowl. Iron also has the highest average concentrations in all sampled birds amounting to 791.17 mg/kg. This heavy metal can be elevated in most land-dwelling species as this essential element was also observed high by Sanchez (2015) with the red jungle fowl from the Marinduque Wildlife Sanctuary.

Cobalt, Pb and Zn were observed to be elevated in the Mantanani Scops owl. This owl prey upon small mammals, reptiles, large insects, and birds and most probably had acquired these metals from food. Elevated amount of Zn in raptorial birds was also observed in the study conducted by Nighat et al. (2013). According to Markowski et al. (2014), the presence of Cd can decrease the amount of Zn. On the other hand, increased Zn could prevent the harmful effect of Cd (Takekawa et al., 2002). The habit of deliberately taking in grit or small pebbles was thought to help in the digestion of food in owls may also add body burden of heavy metals. This habit was observed with the Philippine Scops owl *Otus megalotis megalotis*. The Philippine bulbul which can also be observed in the lowland and highland areas of the island province was detected to have much concentration of Cr and Mn. The yellow vented bulbul, a counterpart of the endemic bulbul was found to accumulate As. Both bulbul species may have accumulated the heavy metals from food and water in the area. Elevated concentrations of Cu were also observed with the pied fantail, an insectivorous and human refuse eater that occupies a wide range of habitat.

The statistical test regarding trophic level yielded highly significant concentrations of Cu (p = 0.000) with pied fantail together with pied triller and white breasted wood swallow. Significant concentrations of Sr, Mn, and Cr (p = 0.000, p = 0.002, and p = 0.005 respectively) were also observed with the insectivorous and frugivorous bulbuls that were sampled in this study. The concentrations of Fe in omnivores (greater painted snipe, Tabon scrubfowl, white browed crake and spotted dove) also tested highly significant (p = 0.001).Meanwhile, statistically significant (p = 0.040) amount of Se was observed with scops owl. Although the white collared kingfisher was observed to have the highest concentrations of Se among the sampled avian species, only Zn concentrations tested to be highly significant (p = 0.000).Increased concentrations of Se in the scops owl coincide with the findings of Ansara-Ross et al. (2015) where this element was found to be high in owls inhabiting near waterways. This suggests that birds living near waterways as well as those that largely get their food on tainted water are more prone to Se contamination. Sanchez (2015) also observed high Se concentrations in feathers of Indigo banded kingfisher from a different site.

Interestingly, the Pink-necked green pigeon inhabiting and foraging in the mangrove have four heavy metals (Cu, Fe, Sr, and Zn) of lowest amount among the group of birds from this site. The same elements were also observed low with the primary and secondary forest bird which is the tarictic hornbill (Sanchez, 2015). Both species rely on fruit bearing trees, palms, and berries. The pigeon might also forage in islets neighboring the tailings dumping site as well as in the nearby karst forest.

Of all the birds from this site having significant concentrations of heavy metals, the White collared kingfisher can be a good species to monitor bioaccumulation of Sr and Zn, the fantail for Cu and Cr, scops owl for Se and the crake for Fe and Sc (Table 2). The Yellow vented bulbul which was the only species detected to accumulate As on feathers can also be a receptor species for this element. The differences in the food item taken by each bird and the elimination processes may be the main factor in the accumulation of heavy metals on the feathers.

The descending order of the heavy metals detected on the soil samples was Fe > Ti > Cu > Mn > Sr > Ba > V > Zn > Cr > Sc > Sb > Pb > Sn> Rb > Mo > Cd and As. Selenium, Hg, Ni, and Co were below the limits of detection. The concentration of Pb, Zn, and Cr were higher than the Maximum Allowable Concentration (MAC) of substances in soil according to the USSR State Committee for Science and Technology while Mo, Ba, and Sn, Cd, and Cu, respectively, did not pass the category A, B, and C of the Dutch Soil Clean up Act (Beyer, 1990). The As concentration was

Table 2
Differences between heavy metal bioaccumulation (mg/kg) in various species of birds from Barangay Ipil-Calancan Bay, Sta. Cruz, Marinduque Island, Philippines

Heavy metals	**High species**	**Mean rank**	**Low species**	**Level of significance (p = < 0.05)**
Cr	Pied fantail	66.00±5.00	Tabon scrubfowl	0.000
Cu	Pied fantail	60.68±6.88	Pink necked green pigeon	0.000
Fe	White browed crake	60.25±2.67	Pink necked green pigeon	0.000
Mn	Little heron	50.50±33.0	All except Tabon scrubfowl Common emerald dove	0.000
Pb	All	34.5	All	1.000
Sc	White browed crake	50.50±33.5	All	0.002
Se	Mantanani scops owl	45.00±33.5	All except Pied triller	0.333
Sr	White-collared kingfisher	52.64±7.33	Pink necked green pigeon	0.001
Zn	White-collared kingfisher	16.67±3.33	Pink necked green pigeon	0.000

higher than the limits set by United States Environment Protection Agency (US EPA, 2002) and the New York State Department of Environmental Conservation (NYS DEC, 2006). Copper, Cr and Cd were also beyond the standards by the NYS DEC.

Using the two-tailed Pearson correlation, Mo from soil was found to be significantly correlated (0.01**, 0.05* level) with Fe**, Mn*, Cr*, V**, Ti* and Sb** while Zn with Sc**, Se with Sc** and Mn with Rb* and Sb* from collected feather samples. Studies of Van Der Merwe et al. (2011), Frantz et al. (2012), Torres et al. (2010), Markowski et al. (2014), Adout et al. (2007), and Levedeba (1997) found elevated heavy metal concentration such as Mn, Pb, Zn in bird's tissue were observed in contaminated sites, urban, farmland, and parkland than built up and rural areas. Contamination may imply correlation between feathers and soil in this present study as the sampling site was the tailing dumping area. Probably, the heavy metals in the feathers were from the environment and the contaminated food or water ingested in the area as all avian species subjected in this study were adult residents.

According to Theuerkauf et al. (2015) heavy metals are deleterious to diverse life forms. Essential heavy metals such as Se, Cr, Mn, Fe, Co, and Ni, may also be toxic in great amounts while Hg, Cd, and Pb are the non-essential and highly noxious. Detection of significant levels of As in feathers is hard because studies are limited (Burger et al., 2015). Arsenic was observed in a single species of bird burdened with 14.91 mg/kg. The As concentrations in the study by Burger et al. (2015) from shorebirds gathered were lower compared with this study. Iron and Zn detected in this study were lower with the concentrations in the Barn owl reported by Denneman and Douben (1993).

Generally, for the avian species, the trend in heavy metal concentration in this study was different with Abbasi et al. (2015) aside from Fe and Cu as consecutively being the highest. Cadmium and Ni concentrations were not detected in this study but detected with the research mentioned. Iron was the highest but followed by Cr instead of Cu and Ni was also present in studies by Theuerkauf et al. (2015). It was said that the low concentrations or below detection levels of Cd can be due to its non-accumulating capacity in feathers (Cochrane & Trust, 1996). Bond and Lavers (2010) cited that only 30% of Cd concentrations could be found on feathers. Meanwhile, the highest concentration of Fe in this study was higher than reported by Theuerkauf et al. (2015) but lower than that of Lervik (2012). Interspecies and intra-species variation in the concentrations of Fe in avian species was also observed by Goede and de Bruin (1984). These differences in concentrations of Fe between species and within the same species may also be detected with other heavy metals. According to Keith et al. (1989), differences in feather heavy metal concentrations are affected by the relative presence of the elements in the home range of each individual bird. Furthermore, factors such as gender, food preference, behavior, physiology, general health condition, and age among others, may play in this variation.

Heavy metal contamination may be through ingestion or contact with tainted matter. It was mentioned that proper cleaning of the feathers prior to analysis is vital when monitoring level of contamination via food (Denneman & Douben, 1993). But despite of rigid cleaning, some researchers like Denneman and Douben (1993) and Dmowski (1999) declared that most of the contamination could not be removed and washing could modify the quantity of the heavy metals endogenously present. On the other hand, washing hundreds of feathers and drying them was unsafe and may expose it to impurities other than those present at the study site. Keith et al. (1989) also noted that the plumage type, washing and evaluation procedures might influence variations in the element profiles. In this study, the feathers were not washed to determine the presence of contamination and samples were also subjected to XRF. Detection of heavy metals in feathers means contaminants are present in the environment and since all the sampled avian species were resident and endemic only proved that the contaminants were acquired from food and water in the habitat.

CONCLUSION

Quantification and understanding of heavy metals being a health and security threat to ecosystems, its components as well as to humans, is important in the decision making. The presence of heavy metals in feathers denotes that the contamination has reached higher trophic levels. Avian species either wild or domesticated provide nutrients to humans. Consumption of heavy metal laden food, water, and inhalation and direct contact with contaminated matters may imperil humans- its food and health security. This may also create a domino effect leading to disruption in the normal functioning of the ecosystem, biodiversity loss, and decreased ecosystem services.

The results of this study dictate that heavy metals abound in the area and affecting avian species. This may bring health and reproductive problems with avian species that may lead to imbalance in nature. Consequently, the problems that heavy metals may bring may greatly affect humans, their health, and livelihood. Some people especially those that hunt and or eat avian flesh may accumulate more of the noxious heavy metals.

To assess the effect of the heavy metals to humans in the area and to alleviate further health and economic problems it may bring, it is recommended for future studies to investigate the concentration and presence of the heavy metals in the edible parts and eggs of the free-range poultry and other food available for humans. The presence of heavy metals in the locals must also be investigated while planting of flora with high remediation capacity must be done. These can be done by the students of local educational institutions in partnership with the Department of Environment and Natural Resources and the Local Government Units. Replication of other past studies conducted in the area must also be done to monitor trends. The local people in this study site were participative however; sacrificing their poultry would require payment to compensate for their livelihood and other economic needs. On the other hand, for the results to reflect the true environmental condition, the poultry that would be studied must be free range, hatched, and raised in the same area.

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