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Determination of mercury accumulation of *Pistia stratiotes* lam in lower Agusan River, Butuan City, Philippines

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Abstract

The result of the study was a big help as an additional data or information regarding the alarming contamination of toxic waste in lower Agusan River and in Butuan Bay. It focuses on the determination of the level of mercury absorption of *P. stratiotes* and in the soil in the three sites along the lower portion of the Agusan River. Samples of soils and *P. stratiotes* plant commonly known as "water cabbage" were collected in different sites in Lower Agusan River, Mindanao Philippines for mercury determination. They were analyzed using Atomic Absorption Spectrophotometer (AAS). Results revealed an average mercury concentration in plant samples (0.23 mg/kg) in Site 1, followed by Site 3 (0.18mg/kg) while site 2 had the lowest mercury contamination with (0.08mg/kg) while soil samples obtained a higher concentration in all sites. These results revealed that all sites were contaminated with mercury that surpasses the standard values recommended by World Health Organization. The impact of mercury pollution in Agusan River had affected already not only from the sources of contamination but extends all the way down to Butuan Bay where the river drains.

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Introduction

Alarming report of waste contamination in Agusan River ignited and convened many social scientists, environmentalist and even the stakeholder to do research to answer the vital question whether Agusan River is really contaminated with heavy metals. Several studies shows that aquatic effluents from industrial, agricultural, household run-offs, transport animal and human excretions and domestic waste contribute to the heavy metal concentration in the Agusan River. In the study of (Roa *et al.*, 2010) stated that metal concentrations in soil sediment in Agusan River ranged from 2.85 to 341.06 mg/kg for Hg, 0.05 to 44.46 mg/kg for Cd and 2.20 to 1256.16 mg/kg for Pb.

In 2006 study, by the Department of Health Region XI, found fish samples from Agusan Marsh, had mercury content higher than the allowable limit of 0.3 microgram per gram. Furthermore, (Fundador *et al.* 1984) detected mercury in sediments from seven stations that stretched from the mouth of Agusan River to approximately 10 kilometres away. In the recent study conducted by (Cabuga *et al.* 2016) both found high concentration of mercury in the muscles of both fishes they studied in lower Agusan River and exceeded the standard allowable limits for fish muscles and sediments established by World Health Organization.

These reports pose a warning and a potential threat of bioaccumulation of mercury for humans and aquatic organisms that utilize the river. Further, continuous discharge of mercury through the process of methylation from small scale mining activities in the headwater of the river may pose potential risks in the years to come without appropriate intervention.

Recent concerns regarding the environmental contamination have initiated the development of appropriate technologies to assess the presence and mobility of metals in soil, (Honggang *et al.*, 2011) water, and wastewater. Absorption of metals from soil water to soil particles is the most important chemical determinant that limits mobility in soils (Reeves, 2000). Heavy metals from soil enter plants primarily through the root system.

In general, plant roots are the most important site for uptake chemicals from soil (Sarma,2011).

Bioaccumulation takes the advantage of the unique and selective uptake capabilities of plant root systems, together with the translocation.

In the study of (Rai *et al.*, 2011) reported that Water hyacinth (*Eichornia crassipes*) and water cabbage (*P. stratiotes*) both are aquatic plants, appeared to be the most effective absorbent of mercury in the water contaminated with heavy metal concentration. *P. stratiotes* is one of the most abundant aquatic plants found in Agusan River together with other species (*Eichornia crassipes*, *Azolla pinnata, Ipomoea aquatica, Hydrilla verticilata, Nympaea lotus* and *Hanguana malayana*).

Agusan River passes through Butuan City in the northeast part of Mindanao where it empties into Butuan Bay.

It provided livelihood to 200,000 people in the region. Little did they know that harm is already piling up from many anthropogenic activities that drain in Butuan bay. This study aims to determine the levels of mercury in *P. stratiotes* plant and sediments in the three sites along the lower portion of Agusan River. Thus, this study was a big help as an additional data or information regarding the alarming contamination of toxic waste in lower Agusan River and in Butuan Bay.

Materials and methods

Sampling Design

Three sampling sites were selected (S1- Mouth of Agusan River; S2- near Butuan City , S3- 2 kilometres away from site 2 upper portion). Geographic Positioning System (GPS) was used to locate specific areas and were marked for future use (Fig. 1).

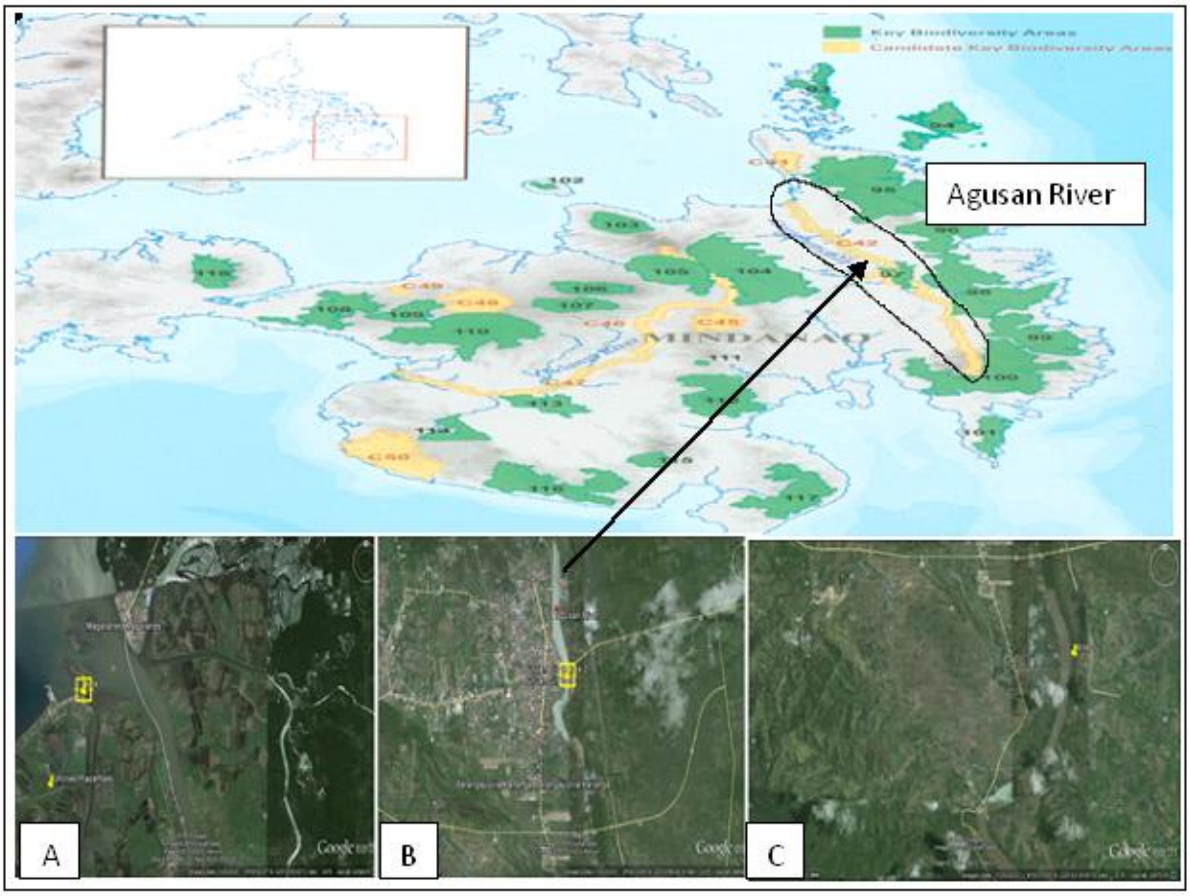

Fig. 1. Map of Philippines (Inset) and Mindanao showing Agusan River showing the three sampling sites (A-C).

Soil sample analysis

Bottom sediment (BS) samples were collected by wet screening of river bed sediment through a 150 µm sieve, using a minimal amount of water to avoid the loss of fine silt and clay fractions. Samples were sealed in plastic containers to avoid evaporative losses and oxidation and were transported in an ice chest. The Atomic Absorption Spectrometer (PerkinElmer, Inc., Shelton, CT) was used in the study. The determination of total mercury in solid samples using the principles of thermal decomposition, amalgamation and atomic absorption described in EPA Method 7473 (5) (US EPA, 1997).

Plant sample analysis

The SMS 100 mercury analyzer (PerkinElmer, Inc., Shelton, CT) was used for the study. This is a dedicated mercury analyzer for the determination of total mercury in solid and liquid samples using the principles of thermal decomposition, amalgamation and atomic absorption described in EPA Method 7473 (5) and ASTM Method 6722-016. The SMS 100 uses a decomposition furnace to release mercury vapour instead of the chemical reduction step used in traditional liquid-based analyzers. Both solid and liquid matrices can be loaded onto the instrument's auto sampler and analyzed without acid digestion or sample preparation prior to analysis. Because this approach does not require the conversion of mercury to mercuric ions, lengthy sample pre treatment steps are unnecessary. As a result, there is no need for reagents such as highly corrosive acids, strong oxidizing agents or reducing chemical.

Results and discussion

Concentration of mercury in soil sediments

Among the three sampling sites, site 1 had the highest level of mercury contamination for soil sediments. Site 3 obtained the second highest level of contamination, while the site 2 had the lowest (Table

1). The results confirmed the recent study conducted by Cabuga *et al*. (2016) and Velasco *et al*. (2016), that the sediments in Agusan River were contaminated with heavy metals as well as in the muscles of some fishes, although the result are still fit for human consumption, they are still endangers human life through bio-accumulation.

Table 1. Mean concentrations of Mercury in Plant samples and soil sediments from Lower Agusan River Basin Butuan City, Agusan Del Norte. Philippines.

Samples	N	Mean Hg (mg/kg) /site			F-value	P -value	WHO -Recommended Safe Limits (mg/kg)
		Site 1	Site 2	Site 3			
P. stratiotes	3	0.23	0.08	0.18	1.434	0.0001*	0.002
Soil Sediments	3	0.26	0.17	0.20	1.768	0.002*	0.1

(0.02 detection limit of AAS) *α = 0.05.

One-way ANOVA shows that the mean concentrations of mercury in sediments across three sampling sites were significantly different. Based on the results, mercury concentrations in sampling site 1 were higher than those of site 2, and the results exceeded the permissible amount of concentration set by World Health Organization (WHO). This finding qualified the sediments in the river to a polluted category.In the aquatic environment, sediments act as reservoirs or important sinks for metals and other aquatic pollutants. Sediment contamination by heavy metals affect water quality and could lead to bioaccumulation of heavy metals to aquatic organisms including plants which results to potential long-term implication on human health and ecosystem (Macnair,2003).

Results of the study also revealed that mercury from soil and water samples from Agusan River were extremely turbid as a result of discharges from artisanal mine workings and mineral processing plants upstream which uses mercury in the process of amalgamation to separate gold from the soil sediments and other discharges from industrial and residential facilities making the Agusan river as their waste collector.

These high concentrations have potential risk of bioaccumulation to humans and other aquatic organisms in the area with frequent exposure to contaminants.

The present study confirmed this result and further indicated clear evidence of Hg deposition in sediments.

Concentration of mercury in P. stratiotes

Results revealed that among the three sites, Sites 1 and 3 have the highest mercury levels while site 2 obtained less the detectable limit. Analysis of variance revealed that there is no significant difference between the mercury accumulation of plant samples and soil samples. These results signified that aquatic plants specifically *P. stratiotes* (Fig. 2) can accumulate heavy metal contamination from soil sediments and they were potential for phytoremediation. Aquatic plants are among the most indicative factors in aquatic system for estimating heavy metal pollution and risk potential to human health (Tokeshi, 2002). This was also confirmed in the study of Roa (2010) that there is an alarming level of Hg in some plant and fish species in Agusan River.

This report is significant because it gives an idea to the mechanism of accumulation of heavy metals through aquatic plants in the contaminated river. This plant is potential for phytoaccumulation (Reeves, 2000). In view of these findings strict method of waste disposal control should be adopted to ensure the safety of the environment and safeguard our aquatic life.

Ingesting mercury-contaminated food for years, even at small doses will threatens human health. This is because mercury becomes toxic through a process called bioaccumulation by which organisms, including humans, can take up contaminants more rapidly than their bodies, thus the amount of mercury in their body accumulates over time. Mercury is easily absorbed by the respiratory tract that can result to permanent health damage, particularly brain damage (Boyd, 2007).

Fig. 2. Habit of *P. stratiotes* Lam.(Water Cabbage).

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