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Phytoremediation of Mangrove species exposed to effluents of mining ultramafic soils

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Abstract

The study was conducted to determine the phytoremediation potentials of some mangrove species inside a mine site of Platinum Group Metals Corporation (PGMC) in Claver, Surigao del Norte. For comparison purposes, a separate mangrove forest located at Nasipit, Agusan del Norte (ADN) free from mining activities was also studied. Plant tissues of the three species with the highest SIV in both study sites were analyzed using Microwave Plasma-Atomic Emission Spectrometer and Acid Digestion. *Lumnitzera racemosa, L. littorea* and *Quassia indica* had the highest importance values at PGMC and *Avicennia officinalis, L. racemosa*, and *Ceriops tagal* at Nasipit, ADN. The two sites differ in species composition manifested by low similarity index. *Quassia indica* at PGMC and *C. tagal* at Nasipit, ADN exhibited characteristics of a hyperaccumulator for Molybdenum, Manganese, Lead, Chromium and Nickel. *L. racemosa, L. littorea* and *A. officinalis* were possible excluders of Molybdenum, and *A. officinalis* was a probable indicator of Lead. Salinity is highly encouraged for inclusion in studies of this kind as it also affects species composition, while verification studies should be conducted to validate the results of the study on the phytoremediation potentials of the species examined due to antagonistic and synergistic behaviors of heavy metals.

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Introduction

Environmental issues remain the most serious of all global problems as these pose a major threat to the health and well-being of countless people including global ecosystems. Global warming, climate change and the loss of biodiversity through the extinction of many species are some of its effects (Sintayehu, 2018). UNEP-WCMC (2014) listed pollution of air, water and land, loss of biodiversity, hazardous chemicals and wastes, land degradation, ozone depletion, climate change, and loss of natural and cultural resources as major environmental issues. Appannagari (2017) reported that this "environmental crisis" we are dealing with is a result of a developmental process of the 'economic and technological man.' Though the present century has shown socio-economic, scientific and technological development, it is also plagued by serious environmental problems. This environmental deterioration is caused by several forms such as pollution, uncontrolled exploitation, increasing dependence on fossil fuels, ecologically damaging technologies, loss of habitats due to industrial, urban and agricultural expansion, loss of ecological populations due to excessive use of pesticides and herbicides which has now become a global concern. Furthermore, environmental pollution is now recognized as a major cause of morbidity and mortality in especially in low- and middle-income countries (Suk *et al.*, 2016). According to the World Health Organization (2014), pollution is responsible for 8.9 million deaths around the world each year. The rising environmental pollution by heavy metals, released by industrial and agricultural activities is reported to be a global serious problem. It has evolved as an ecological challenge that threatens primary and secondary consumers and as final point human beings (Mahalakshmi *et al.*, 2017). Heavy metals, as common environmental pollutants, have widespread environmental distribution as it originates from natural and anthropogenic sources. They are non-degradable and remain in the environment; hence, they have received a great deal of concern attributed to their possible health and environmental threats (Arif *et al.*, 2015). Small amounts of heavy metals are considered essential for the survival of many organisms but large quantities are toxic (Harasim & Filipek, 2015). Toxic effects depend on the forms and routes of contact. It interrupts intracellular homeostasis that involves damage to lipids, proteins, enzymes, and DNA by the production of free radicals (Arif *et al.*, 2015). These pollutants are drained from upper vicinities towards the ocean, which tends to accumulate in the coastal sediments (De Wolf *et al.,* 2015). The buildup of these heavy metals in natural ecosystems such as mangrove ecosystems is a real threat to humans and biodiversity because of their persistence and toxicity. Coastal and marine ecosystems are threatened with heavy metal pollution from wastes, agricultural runoffs and industrial sources such as mining (Kholoud, *et al.,* 2017). Physical and chemical processes such as leaching and oxidation can cause these heavy metals accumulated in the soil to be released, meaning, the metals can enter water bodies and be taken up by crops and marine organisms and eventually affect public health through the water supply and the food chain. Heavy metal pollution has not yet been controlled effectively because anthropogenic activities are increasing, especially in developing countries (Xiaolu *et al.*, 2018). The ecological functions of mangroves, on the other hand, are widely acknowledged that includes helping stabilize shorelines and reduce the devastating effects of natural disasters like tsunamis and hurricanes. They also serve as breeding and nursing grounds for marine species that are of high commercial importance. Mangroves and the soil where they grow could sequester huge amounts of carbon each year (Kumar *et al.*, 2015). Mangroves are different types of salt-tolerant plant species, either trees or shrubs, which thrive in intertidal zones of tropical and subtropical sheltered coastlines. The term is used to both the individual plant and the ecosystem. Over the last century, there has been an extensive loss and degradation of mangrove habitats and one of the causes is pollution (UNEP-WCMC, 2014). In mining areas above mangrove ecosystems, heavy metals from upstream are carried by surface runoff during downpours and settle in the sediments where mangroves are then exposed. Currently, phytoremediation has turned out to be an effective and inexpensive technological solution to extract or remove heavy metals from polluted soil. Phytoremediation is the use of plants to clean up contamination from soils, sediments, and water. This technology is environment-friendly and likely cost-effective. Plants with remarkable metal-accumulating ability are known as hyperaccumulator plants (Tangahu *et al.*, 2011). The potential of mangrove species for phytoremediation is also being taken into consideration as Bruno *et al.* (2016) in their study on the potential of mangrove for phytoremediation said that two mangrove species under study could be classified as Pb-hyperaccumulator as indicated in their Shoot-Root Quotient (SRQ) values. Another study by Erakhrumen (2015) suggests that *Rhizophora racemosa* was considered probable hyperaccumulator. It is empirical that a corroborative study in order to give insights if heavy metal, in fact, affects the survival of mangroves and with the phytoremediation of environmental pollutants now receiving wide acclaim as a recent innovative way to deal with these contaminants, it would be necessary to determine which mangrove species that absorb the most of the heavy metal pollutants and distinguish which mangrove species are hyperaccumulators, excluders or indicators of heavy metals.

Materials and methods

The study site

This study utilized two different sites to determine and compare the differences between the variables being studied (Fig. 1). The first study site was in the 15-hectare mangrove forest in the concession area of Platinum Group Mining Company's (PGMC) located at Sitio Kinalablaban, Brgy. Cagdianao, Claver, Surigao del Norte. This mangrove forest constantly receives eroded sand particles and sediments carried by surface runoff during rainstorms from the ultramafic mining site. Generally, the area was exposed to the north-east monsoon, trades, and easterlies (Villarin *et al.,* 2016). The river delta that separates the two creeks inside the mining area was selected as the study site as it received the runoff during a rainstorm including the sediments that are carried with it from the nickel mining activities in the upper vicinities. The area was very much disturbed by the raging waters during rainstorms as manifested by the stunted and swirling of the bole of the older mangroves. The upper surrounding areas where mining activities are carried out consist of soils derived from outcropping ultramafic lithologies with laterite development (GFHI-PGMC Annual Report 2016). Ultramafic soils have high amounts of Mg, Cr, Co and Ni, and low amounts of P, K, and Ca (Ata *et al.,* 2016 and Van der Ent *et al.*, 2015). The other study site was located at Sitio Kabagtokan, Brgy. Ata-atahon, Nasipit, Agusan del Norte, approximately 170 kilometers away from the first study site. The forest is generally situated at the end of a creek and does not receive runoff from areas with mining activities. It was also not affected by raging waters even during heavy rainstorms as compared to the first site. The climatic type of both study sites belong to Type II characterized by a pronounced peak of wet season from November to December without a defined dry season based on the Modified Coronas Classification which is determined by the geographical distribution of the seasonal variation and amount of rainfall. The study was conducted from April 2018 to April 2019.

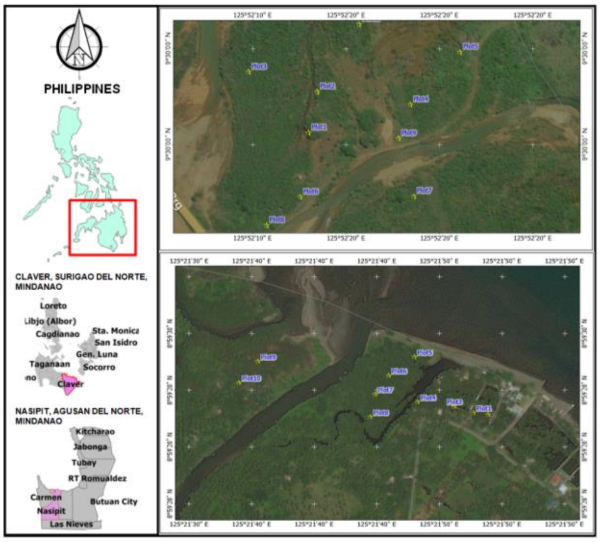

Fig. 1. Location of the study.

Sampling Method

The study used purposive sampling in the gathering of the data in order to get the highest possible representation of the whole area. Purposive sampling is a strategy in which specific settings, persons or events are chosen deliberately to supply important information that cannot be attained from other types of sampling (Taherdoost, 2016). Infrequent species were located and its spot was considered as one sampling site. The sampling method was employed to both study areas. All trees inside the sampling plots with ≥5cm in diameter were recorded. Diameters were measured using a diameter tape and total height was by meter stick.

Identification of Trees

The identification of the species used various approaches such as the use of references that of Primavera (2009) and Tan (2007); taxonomic keys and literature by Fernando (2010), Rojo (1999) and Merrill (1903), and internet method via World Mangrove Database, www.iucnredlist.org, www.stuartxchange.org, and www.phillipineplants.org.

Diversity indices

Diversity indices such as species richness, relative abundance, evenness and Shannon-Weiner diversity index were analyzed using Paleontological Statistical Software Package (PAST) developed by Hammer *et al.* (2001). Diversity values for Shannon-Weiner were categorized based on a scale developed by Fernando (1998) as shown in Table 1.

Table 1. Biodiversity scale (Fernando, 1998).

Relative Interpretation	Shannon's (H') Index	Evenness Index
Very High	>3.5	0.75-1.00
High	3.00 - 3.49	0.50-0.74
Moderate	2.50 - 2.99	0.25-0.49
Low	2.00 - 2.49	0.15-0.24
Very Low	<1.99	0.05-0.14

Vegetation analysis

Vegetation analysis was made to measure the magnitude of species using the parameters density, frequency, dominance, relative density, relative frequency, relative dominance and the importance value following that of Ellenberg and Mueller-Dombois (1974). This type of analysis gives a better index than density alone about the importance or function of a species in its habitat as it also gives order or rank for individual species within the forest community. Species with the highest importance values are considered the most dominant species using the following equations:

$$\text{Dominance} = \frac{\text{Basal area of a species}}{\text{Area sampled}}$$

$$\text{Frequency} = \frac{\text{Number of plots where a species occur}}{\text{Total number ofplots}}$$

$$\text{Density} = \frac{\text{Total number of individual of a species}}{\text{Total number of plots}}$$

$$\text{Relative density of each species} = \frac{\text{Density of each species}}{\text{Density of all species}} \text{ x } 100$$

$$\text{Relative frequency} = \frac{\text{Number of trees per species}}{\text{Total number of trees (N)}} \text{ x } 100$$

$$\text{Relative dominance} = \frac{\text{Basal area of each species}}{\text{Basal area of all species}} \text{ x } 100$$

$$\text{Importance Value} = \text{relative density} + \text{relative dominance} + \text{relative frequency}$$

Heavy Metal Accumulation

A composite sample of the roots and shoots from three (3) species with the highest importance values (IV) were collected from the study sites. Roots and shoots collected were dried, chopped and ground to obtain a representative sample of 250 grams and were analyzed at the Regional Soils Laboratory of the Department of Agriculture (DA), Caraga Region through Microwave Plasma-Atomic Emission Spectrometer Method and Acid Digestion – EPA 3051A (U.S. EPA, 2007). Determination of hyperaccumulator, indicator, and excluder plant species followed the criteria used by Kutty and Al-Mahaqeri (2016) as shown in Table 2.

Sediment Analysis

Sediment samples from both sampling sites were also collected for analyses. Sediment samples collection followed the procedure prescribed by the Department of Agriculture, Caraga Region where sampling points should form a letter “S” inside the areas that are subject to the test. The collected samples were then dried, pulverized, placed in a transparent polyethylene ziplock bags, labeled correctly and were sent to the

Regional Soils Laboratory of DA Caraga Region for Mo, Mn, Pb, Cr, Ni and Cd analyses.

Table 2. Criteria for hyperaccumulator, excluder and/or indicator plants.

Hyperaccumulator	Excluder	Indicator
1. Ratio of heavy metal concentrations of shoot to root must be >1 2. Metal concentration in root/metal concentration in sediments or soil is >1 3. 10–500 times greater heavy metal concentration than the same species found in non-contaminated areas 4. Pb, Cu, Co, Cr, and Ni have >1000 μg/g or 10.000 μg/g of Fe, Mn, and Zn or Cd >50 μg/g in any aboveground tissue in their natural habitat without suffering toxic effects	High levels of heavy metals in the roots but with shoot/root quotients <1	Metal levels in the tissues reflect the levels in the sediments

Data Analysis

Data on heavy metal levels in plant tissues and sediments were analyzed using basic mathematical computations for quotients in the determination shoot-root quotient and sediment-root ratio. Non-metric multidimensional scaling (NMDS) was also performed to determine the species extent and association within study sites. NMDS is an ordination statistical tool that facilitates complicated multivariate data sets to be visualized in a reduced number of dimensions (Dexter *et al.,* 2018). While Bray Curtis analysis was used to determine the similarity index of species of the two study sites.

Results and discussion

Species Importance Values

Among the 17 species found in the mangrove forest at PGMC, *Lumnitzera racemosa, L. littorea* and *Quassia indica* obtained the highest IV of 79.71, 68.31, and 58.50, respectively while the lowest was obtained by *Syzygium brevistylum* with 1.23 (Table 2). On the other hand, the species comprising the sampling plots of Nasipit, Agusan del Norte includes the true mangrove species with *Avicennia officinalis* (78.71)*, L. racemosa* (60.58), and *Ceriops tagal* (40.86) as the species that obtained the highest IV. The dominance of these species is typical for the estuarine mangrove forest ecosystem. Moreover, it further indicates that the sampling area comprises most of the back mangroves species with *Rhizophora mucronata* and *R. apiculata* and other members of Rhizophoraceae which are the seaward species with respect to mangrove zonations obtaining the lowest IV (Table 3).

Table 3. Species and their importance values inside PGMC concession area at Sitio Kinalablaban, Brgy. Cagdianao, Claver, Surigao del Norte.

Species	No.	Sum of Diam	Occur-rence	Freq	Den	Dom	RFreq	RDen	RDom	SIV
Lumnitzera racemosa Willd.	43	347	10	1.0	4.3	0.00946	26.220	26.220	27.270	79.709
Lumnitzera littorea (Jack.) Voigt.	26	402	9	0.9	2.6	0.01269	15.854	15.854	36.600	68.307
Quassia indica Gaertn.	27	336	8	0.8	2.7	0.00887	16.463	16.463	25.569	58.495
Syzygium sp.	17	93	9	0.9	1.7	0.00068	10.366	10.366	1.959	22.691
Vitex parviflora Juss.	8	84	3	0.3	0.8	0.00055	4.878	4.878	1.598	11.354
Avicennia officinalis L.	6	101	4	0.4	0.6	0.00080	3.659	3.659	2.310	9.627
Casuarina equisetifolia Forst.	6	83	3	0.3	0.6	0.00054	3.659	3.659	1.560	8.877
Bruguiera sexangula (Lour.) Poir.	5	36	3	0.3	0.5	0.00010	3.049	3.049	0.294	6.391
Alstonia macrophylla Wall. ex DC.	4	60	3	0.3	0.4	0.00028	2.439	2.439	0.815	5.693
Sonneratia alba (L.) Smith	4	52	4	0.4	0.4	0.00021	2.439	2.439	0.612	5.490
Xylocarpus granatum Koen.	4	45	3	0.3	0.4	0.00016	2.439	2.439	0.459	5.337
Excoecaria agallocha L.	4	40	3	0.3	0.4	0.00013	2.439	2.439	0.362	5.240
Calophyllum inophyllum L.	3	39	2	0.2	0.3	0.00012	1.829	1.829	0.344	4.003
Xanthostemon verdugonianus Naves	3	16	3	0.3	0.3	0.00002	1.829	1.829	0.058	3.717
Heritiera littoralis Ait.	2	24	2	0.2	0.2	0.00005	1.220	1.220	0.130	2.569
Pandanus copelandii Merr.	1	14	1	0.1	0.1	0.00002	0.610	0.610	0.044	1.264

Syzygium brevistylum (C.B. Rob.) Merr.	1	8	1	0.1	0.1	0.00001	0.610	0.610	0.014	1.234

Using the non-metric multidimensional scaling (NMDS), the study revealed that Plots 8 (PGMA site), 11 and 12 (Nasipit, ADN) contains species that were not common to all other plots hence outliers (Figs 2 and 3). Plot 8 which was located inside the mining site was dominated by species that were part of the mining company's enrichment planting which is not a mangrove species. On the other hand, Plot 11 and 12 had more number of *L. racemosa* than the two other found species combined. Bray-Curtis analysis revealed that only 28% of the species comprising both study sites were similar (Fig. 4) as only five species were common to both sites. Moreover, Fig. 5 presents the three mangrove species with the highest importance values found at PGMC and Nasipit, ADN.

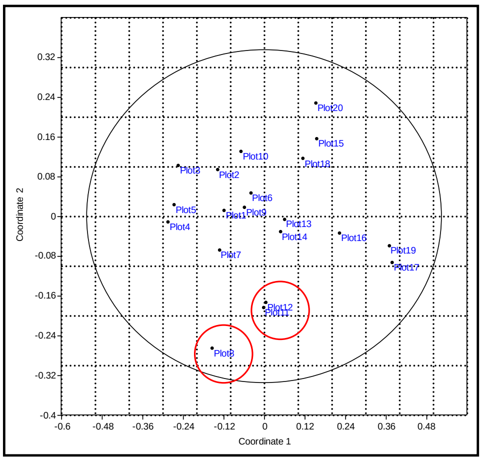

Fig. 2. Non-metric multidimensional scaling of species composition per plot on both study sites on a plot level.

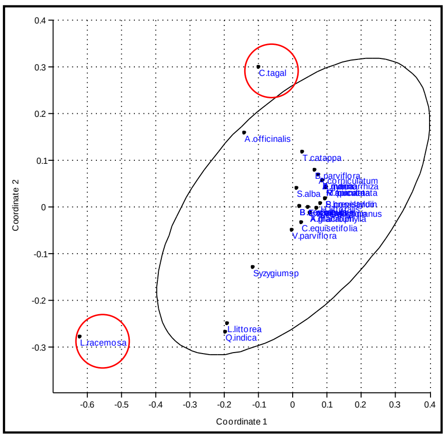

Fig. 3. Non-metric multidimensional scaling of species composition per plot on both study sites on a species level.

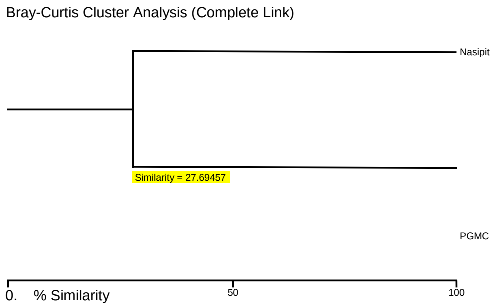

Fig. 4. Similarity index of species of the two study sites using Bray-Curtis analysis.

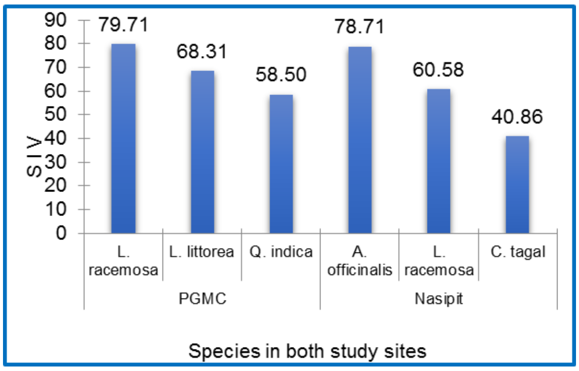

Fig. 5. Three highest importance values of mangrove species at PGMC and Nasipit, ADN.

The species found in the mangrove forest at Nasipit, ADN exhibit similarity to that of the mangrove forest in Pamintayan, Dumanquillas Bay located at Zamboanga Sibugay and Zamboanga del Sur (Bitantos *et al.*, 2017). It also had more or less the same species composition in the mangrove forest assessed by Martinez and Buot (2018) in Manamoc Island for coastal retreat mitigation and that of Relacion *et al.* (2018) in Batasan river in Metro Manila. All stated mangrove forests were free from pollution of mining activities similar to the present study.

Diversity Indices

Using the data on true mangrove species for both sites, Shannon's (H') diversity index revealed that the study site at Nasipit, ADN is more diverse (1.9718) than the PGMC's mining area (1.5299). However, the observed diversity in Nasipit, ADN is way lower compared to that of the mangrove forest at Puerto Princesa Bay located in Palawan Island having 28 true mangrove species, which is one of the most diverse mangrove forests in the country (Dangan-Galon *et al*., 2016).

The higher diversity of the study area at Nasipit, ADN can be attributed to the fact that the area does not experience destructive human activities like mining, aquaculture development, urbanization, settlement, cutting of timber for fuel and charcoal which were the main causes of mangrove forest degradation according to Garcia *et al.* (2013). On the other hand, the lower diversity index of the study site at PGMC could be due to the high concentrations of pollutants that may have changed the structure of the environment and living organisms and render permanent modification in soil and species composition. Moreover, high concentrations of pollutants can also cause a drastic decline in species as a result of adverse effects on the ecosystem (Alzahrani *et al.,* 2018; Numbere, 2018; Ahmed & Shahid, 2015; Bothe, 2011).

Heavy Metal Accumulation Potentials

Fig. 6 shows the levels of heavy metals in the roots and shoots of the three mangrove species with the highest SIV at the PGMC concession area with the following details: Molybdenum was highest in the shoots of *Q. indica* and was lowest in *L. racemosa*. The element was highest in the roots of *L. littorea* and it was lowest in *Q. indica*. Nevertheless, *Q. indica* had an SRQ of 2.250 thereby making it a potential hyperaccumulator of Molybdenum. Manganese was highest in the shoots of *Q. indica* and was lowest in *L. littorea*. It was highest in the roots of *L. littorea* while it was lowest in *L. racemosa*. *Q. indica* had an SRQ of 2.614 making the species a possible hyperaccumulator of Manganese. For Lead, it was highest in the shoots of *L. littorea* and was lowest in *L. racemosa* and *Q. indica*. The heavy metal was found to be highest in the roots of *L. littorea* and lowest in *Q. indica*. All three species had an SRQ of >1 signifying their potential as hyperaccumulator. Chromium was highest in the shoots of *Q. indica* and was lowest in *L. littorea*. It was also the highest in the roots of *L. littorea* and was found to be lowest in *Q. indica*. An SRQ of 1.631 for *Q. indica* which suggests that the species is likely a hyperaccumulator. Finally, Nickel was highest in the shoots of *Q. indica* and was lowest in *L. littorea*. The element was found to be highest in the roots of *L. littorea* and was lowest in *Q. indica*. *Q. indica* had an SRQ of 2.727 which shows that the mangrove species is a potential hyperaccumulator.

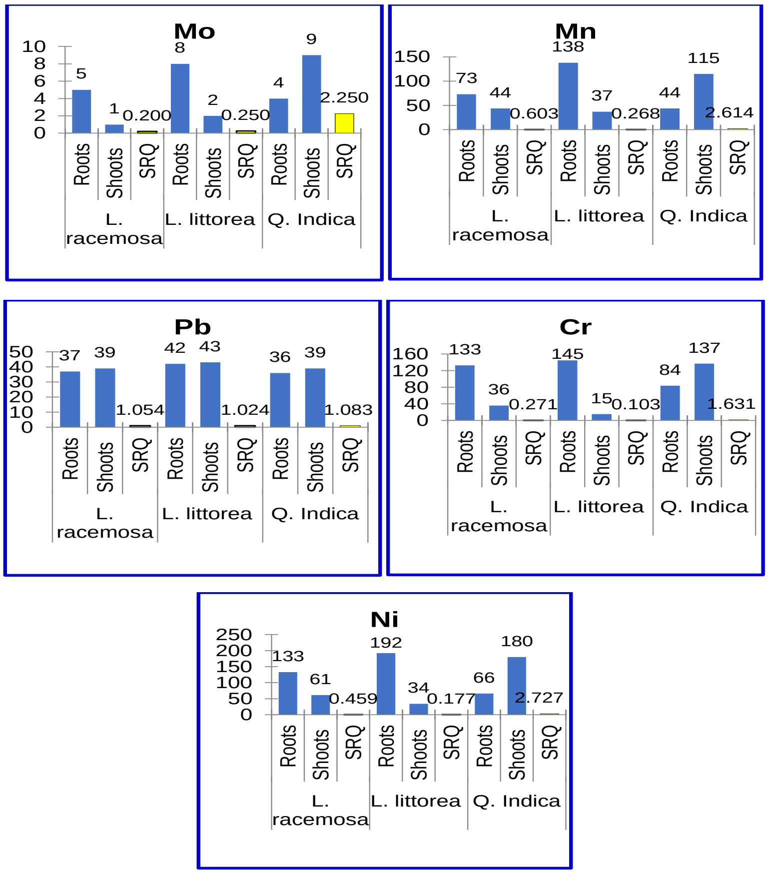

Fig. 6. Heavy metal levels in the roots and shoots of the three mangrove species with the highest SIV at PGMC.

Fig. 7 shows the heavy metal levels in the roots and shoots of the three mangrove species with the highest SIV in Nasipit, Agusan del Norte. Results revealed that Molybdenum was highest in the roots of *L. racemosa*, although all three species were not potential hyperaccumulator of the element as it had an SRQ below one. The Manganese was recorded as highest in the shoots of *A. officinalis* while all three species emerged as potential hyperaccumulator of the heavy metal as indicated by their SRQ of more than one. The Lead was recorded highest in the roots of *A. officinalis* while *C. tagal* had an SRQ of more than one making it a possible hyperaccumulator of the element. Kannan *et al.* (2016) made an effort to test the bioaccumulation of *A. marina* and they found it to have high concentrations in its leaves of Pb. For Chromium, the element was found highest in the roots of *C. tagal*. *A. officinalis* recorded an SRQ of 2.0 which put the species for consideration as a hyperaccumulator of Chromium. Al-Hagibi *et al.* (2018) tested the leaves of the species of the same genus for heavy metal concentrations and found Cr and Pb were higher than the permissible limits set by WHO. Nickel was found highest in both shoots of *A. officinalis* and *L. racemosa* but only *A. officinalis* had an SRQ of more than one which asserts the species could be considered as hyperaccumulator. Table 4 presents the metal uptake in parts per million (ppm) and shoot-root quotient of the three most dominant species in the two mangrove forests.

Soil Properties

From among the six heavy metals assessed, Cr emerged the highest at PGMC while the lowest was Pb. In Nasipit, ADN, the highest concentration was Ni while the lowest was Pb (Fig. 8).

Based on the maximum permissible limits set by WHO and FAO (Table 5) as cited by Chiroma *et al.* (2014), concentrations of Cr and Ni in the sediments in PGMC exceeded to a staggering 4334% and 4234%, respectively while Mn was also way beyond the limit exceeding 43%. Ni and Cr were also way beyond their limits even in the sediments of the mangrove forest outside the mining area exceeding 452% and 234%, respectively.

Table 4. Species and their importance values at Kabagtokan, Ata-atahon, Nasipit, Agusan del Norte.

List of Species	No.	Sum of Diam	Occur-rence	Freq	Den	Dom	RFreq	RDen	RDom	SIV
Avicennia officinalis L.	16	465	5	0.50	1.60	0.01698	13.158	13.158	52.397	78.713
Lumnitzera racemosa Willd.	21	313	7	0.70	2.10	0.00769	18.421	18.421	23.740	60.583
Ceriops tagal (Perr.) C.B. Rob.	22	245	5	0.50	2.20	0.00471	13.158	13.158	14.546	40.861
Sonneratia alba (L.) Smith	4	77	3	0.30	0.40	0.00047	7.895	7.895	1.437	17.226
Terminalia catappa L.	7	128	2	0.20	0.70	0.00129	5.263	5.263	3.970	14.497
Bruguiera parviflora (Roxb.) W&A ex Griff.	4	70	2	0.20	0.40	0.00038	5.263	5.263	1.187	11.714
Avicennia marina (Forsk.) Vierh.	2	48	2	0.20	0.20	0.00018	5.263	5.263	0.558	11.085
Heritiera sylvatica Vidal	2	38	2	0.20	0.20	0.00011	5.263	5.263	0.350	10.876
Bruguiera gymnorrhiza (L.) Lamk.	2	37	2	0.20	0.20	0.00011	5.263	5.263	0.332	10.858
Aegiceras corniculatum (L.) Blanco	3	32	2	0.20	0.30	0.00008	5.263	5.263	0.248	10.774
Azadirachta indica A. Juss.	2	38	1	0.10	0.20	0.00011	2.632	2.632	0.350	5.613
Bruguiera sexangula (Lour.) Poir.	2	34	1	0.10	0.20	0.00009	2.632	2.632	0.280	5.543
Pongamia pinnata (L.) Merr.	1	32	1	0.10	0.10	0.00008	2.632	2.632	0.248	5.511
Excoecaria agallocha L.	1	25	1	0.10	0.10	0.00005	2.632	2.632	0.151	5.415
Rhizophora mucronata Lamk.	1	22	1	0.10	0.10	0.00004	2.632	2.632	0.117	5.380
Rhizophora apiculata Blume	1	19	1	0.10	0.10	0.00003	2.632	2.632	0.087	5.351

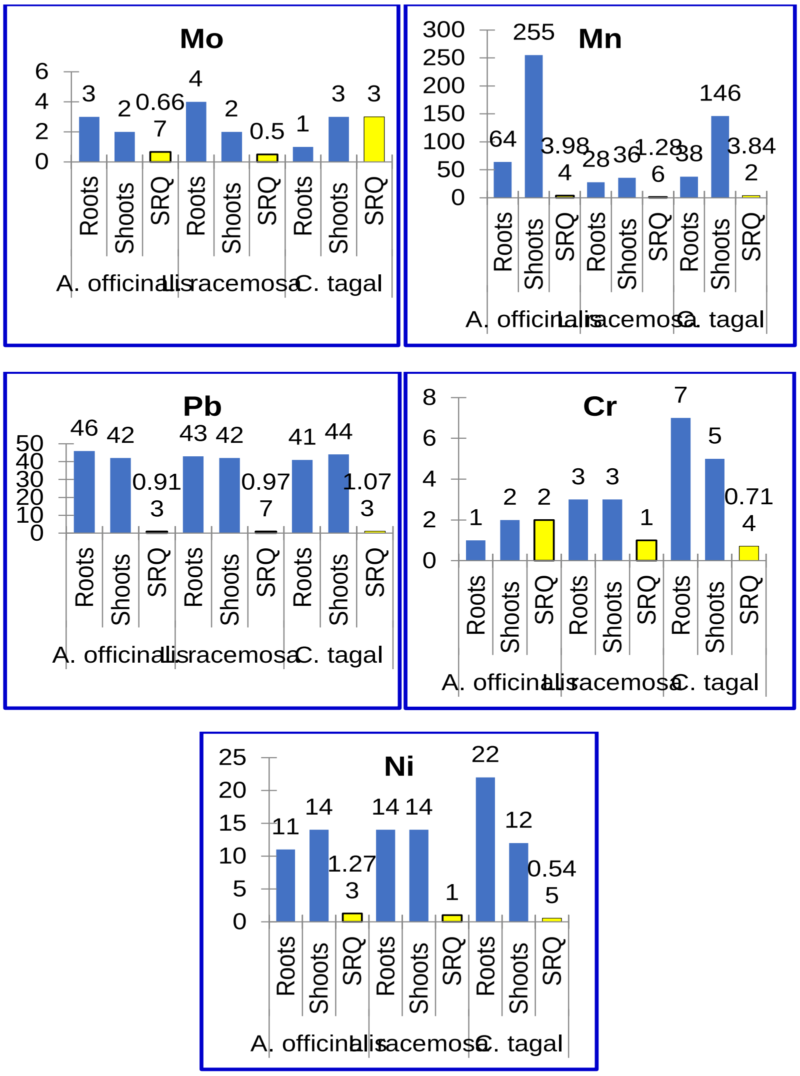

Fig. 7. Heavy metal levels in the roots and shoots of the three mangrove species with the highest SIV at Nasipit, ADN.

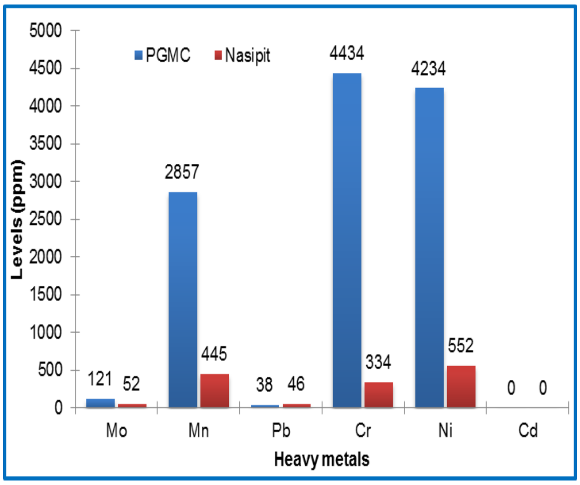

Fig. 8. Heavy metal concentrations on the soil samples from PGMC and Nasipit, ADN in parts per million (ppm).

Pb levels at PGMC and Mn and Pb levels at Nasipit, ADN were within the permissible limit. High concentrations of Ni in the sediments at PGMC was anticipated given that the area is a Nickel mining site while high levels of Cr was probably due to the co-existence of Chromite and Ni as the occurrence of one heavy metal may influence the availability of another in the soil because antagonistic and synergistic behaviors exist between heavy metals (Chibuike & Obiora, 2014). The result also suggests that even mangrove forests which are devoid of detrimental activities like mining, contamination is still a possibility as heavy metals can be transported from distant areas and travel through runoffs and via creeks and rivers and then settle at the mangrove sediments absorbed by mangroves (Vidya & Patil, 2016).

On the species that are potential heavy metal accumulator based on root-sediment ratio, *L. littorea* emerged as a hyperaccumulator for Pb as the metal concentration in the root over the metal concentration in sediments or soil is more than one (Table 6). None of the mangrove species were affected by dose-dependence as despite the high levels of Cr, Ni and Mn in the sediments at PGMC, none of the mangrove species under study showed high concentrations of the heavy metals in their vegetative parts. Dose-dependence was reported by Ugwu *et al.* (2019) that the amount of heavy metal accumulation in the vegetative parts is dependent on the amount of heavy metals found in the sediments.

Table 5. Metal uptake (ppm) and shoot-root quotient (SRQ) of the three most dominant species in the two mangrove forests.

Heavy Metals	PGMC								
	L. racemosa			*L. littorea*			*Q. indica*		
	Roots	Shoots	SRQ	Roots	Shoots	SRQ	Roots	Shoots	SRQ
Mo	5	1	0.200	8	2	0.250	4	9	2.250
Mn	73	44	0.603	138	37	0.268	44	115	2.614
Pb	37	39	1.054	42	43	1.024	36	39	1.083
Cr	133	36	0.271	145	15	0.103	84	137	1.631
Ni	133	61	0.459	192	34	0.177	66	180	2.727
Heavy Metals	NASIPIT, ADN								
	A. officinalis			*L. racemosa*			*C. tagal*		
	Roots	Shoots	SRQ	Roots	Shoots	SRQ	Roots	Shoots	SRQ
Mo	3	2	0.667	4	2	0.5	1	3	3
Mn	64	255	3.984	28	36	1.286	38	146	3.842
Pb	46	42	0.913	43	42	0.977	41	44	1.073
Cr	1	2	2	3	3	1	7	5	0.714
Ni	11	14	1.273	14	14	1	22	12	0.545

Table 6. Permissible limits for heavy metals in soil.

Heavy Metals	Maximum levels (ppm)	Heavy Metals	Maximum levels (ppm)
Arsenic (As)	20	Manganese (Mn)	2000
Cadmium (Cd)	3	Lead (Pb)	50
Cobalt (Co)	50	Nickel (Ni)	100
Chromium (Cr)	100	Selenium (Se)	10
Copper (Cu)	100	Zinc (Zn)	300
Iron (Fe)	50000		

Source: WHO and FAO from Chiroma *et al.* (2014)

L. racemosa, *A. officinalis* and *C. tagal* emerged as potential hyperaccumulator of Cr and Ni based on the third criteria as it was within the 10−500 times greater range of heavy metal concentration of the same species found in non-contaminated area at Nasipit, ADN, while all species under study was found to be hyperaccumulators for Mn as it had 10.000 µg/g of the heavy metal in their shoots without suffering toxic effects. It was also found out that *L. racemosa* is a possible excluder of Mo, while *L. littorea* was found to be a potential excluder for Mo, Cr and Ni and *A. officinalis* a probable excluder for Mo as they had shoot/root quotients of less than one. *A. officinalis* was also found to be an indicator for Pb. Table 7 shows the summary of mangrove species with probability as hyperaccumulator, excluder or indicator based on the four criteria.

Table 7. Root-soil quotient of the three most dominant species in the two mangrove forests.

Heavy Metals	Soil concentrations	PGMC					
		L. racemosa		*L. littorea*		*Q. indica*	
		Roots	SRQ	Roots	SRQ	Roots	SRQ
Mo	121	5	0.041	8	0.066	4	0.033
Mn	2857	73	0.026	138	0.048	44	0.015
Pb	38	37	0.974	42	1.105	36	0.947
Cr	4434	133	0.030	145	0.033	84	0.019
Ni	4234	133	0.031	192	0.045	66	0.016
Heavy Metals	Soil concentrations	NASIPIT, ADN					
		A. officinalis		*L. racemosa*		*C. tagal*	
		Roots	SRQ	Roots	SRQ	Roots	SRQ
Mo	52	3	0.058	4	0.077	1	0.019
Mn	445	64	0.144	28	0.063	38	0.085
Pb	46	46	1.000	43	0.935	41	0.891
Cr	334	1	0.003	3	0.009	7	0.021
Ni	552	11	0.020	114	0.025	22	0.040

Table 8. Summary of mangrove species which are probable hyperaccumulator, excluder or indicator.

Mangrove species	Possible hyperaccumulator for the following heavy metals				Possible excluder for the following heavy metals	Possible indicator of the following heavy metals
	Criteria					
	1	2	3	4		
L. racemosa	Pb, Mn		Cr, Ni	Mn	Mo	-
L. littorea	Pb	Pb		Mn	Mo, Cr, Ni	-
Q. indica	Mo, Mn, Pb, Cr, Ni			Mn		-
A. officinalis	Mn, Ni		Cr, Ni	Mn	Mo	Pb
C. tagal	Mn, Pb		Cr, Ni	Mn		-

Conclusion

The study was conducted to determine the phytoremediation potentials of some mangrove species found inside the mine sites at Claver, Surigao del Norte. For comparison purposes, another site was sampled located at Nasipit, Agusan del Norte. The study was conducted from April 2018 to April 2019. Ten (10) sampling plots with 10x10m dimension were established in both sites. All trees having ≥5cm diameter were measured and recorded. Identification of the species utilizes various approaches such as the use of references, taxonomic keys and literature, and internet method. To determine the heavy metal accumulation potentials, the plant tissues of the three species with the highest SIV were collected and were analyzed using Microwave Plasma-Atomic Emission Spectrometer Method and Acid Digestion. Moreover, sediment samples were also analyzed for heavy metal content. Leaf size indices for the most common species were also determined to verify if there were variations. Results revealed a total of 17 species identified in the mangrove forest inside PGMC with *Lumnitzera racemosa* as the most dominant while a total of 16 species were identified at Nasipit, ADN with *Ceriops tagal* dominates the mangrove forest. *L. racemosa* was found to be a potential hyperaccumulator for heavy metals Pb, Mn, Cr, Ni and a possible excluder to Mo; *L. littorea* emerged as a likely hyperaccumulator for Pb and Mn and a possible excluder for Mo, Cr and Ni; *Q. indica* was discovered to be a possible hyperaccumulator for all heavy metals tested except Cd; *A. officinalis* was found to be a hyperaccumulator for Mn, Ni, and Cr and a possible excluder for Mo and a possible indicator of Pb; while *C. tagal* was found to be a probable hyperaccumulator for Mn, Pb, Cr, and Ni.

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