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Heavy metal concentrations in soil from abandoned mining area in Barangay Baluno, Zamboanga City, Philippines

Minsarib L. Kalnasa[*1], **Alma N. Abug**[2]

[1]*Department of Environmental Science, College of Forestry and Environmental Studies, Western Mindanao State University, Zamboanga City, Philippines*

[2]*Department of Environmental Science & Technology, College of Science and Mathematics, University of Science and Technology of Southern Philippines, Cagayan de Oro, Philippines*

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Abstract

The study aimed to determine the extent of heavy metal contamination of Copper (Cu) and Lead (Pb) in the soil from the abandoned mining area in Zamboanga City, Philippines using the 2017 EMB Site Characterization Guidelines. Soil samples were randomly collected from 3 meridional blocks at 2 different soil depths, 0-5cm and 20-25cm. Pb and Cu concentrations, organic matter (OM) percentages, pH and Electrical Conductivity (EC) were analyzed using appropriate equipment across sampling sites. The study revealed that heavy metal content in Block 3 exceeded the maximum allowable concentrations based on WHO standard with an average mean of 3,351.00mgkg-1 Pb and 498.67mgkg-1 Cu at 20-25cm soil depth. Moreover, at 0-5cm soil depth, Block 3 had 4176.33mgkg-1 Pb and 494.67mgkg-1 Cu. Furthermore, soil pH was strongly acidic across all blocks with values of pH 5.0 at Block 1; pH 4.7 at Block 2 and pH 4.1 at Block 3. For EC and OM percentages, results ranged from 183.33 µS/cm to 286.67 µS/cm and 1.81% to 4.05%, respectively. Using Analysis of Variance at $P < 0.05$, this study further revealed that there is a significant difference of Pb and Cu concentrations in 3 meridional blocks at 0.001. This indicates that heavy metal concentrations present in the soil varies in the 3 blocks. However, in physico-chemical parameters, only organic matter has significant difference in all blocks at $P \leq 0.01$. Based from the findings, it is recommended that counter measures be undertaken to minimize further retrogressive impacts of mine tailings left in the area specifically in Block 3.

***Corresponding Author:** Minsarib L. Kalnasa ✉ kalnasa.minsarib@wmsu.edu.ph

Introduction

Abandoned mining sites are significant sources of metal pollution even after centuries due to presence of contaminants in the soil. Toxic metals that remain in the soil and tailing ponds have the potential to travel and contaminate environmental habitats such as soil, water, groundwater, and air. It has the potential to alter soil texture, deplete nutrients, penetrate the food chain, create harmful consequences, and destroy ecological habitat and biological variety, including plants (Conesa *et al.*, 2006; Baker *et al.*, 2010; Rashed, 2010).

Soil pollution by heavy metals is a global environmental issue. Heavy metal contaminants represent a health risk to humans through food chain transfer from soils to crops, prompting increased scientific and public awareness of the issue (Alloway 1995; Oliver 1997; Chen and Lee, 1995; Chen *et al.*, 2000) particularly in the areas close to industrial sites and in the vicinity of mining and smelting plants (Pushenreiter *et al.*, 2005). Heavy metal pollution of soils can also be caused by the parent material's high heavy metal content (Huang, 1962; Reeves, 2003). People living in the area may not be aware of the soil pollution, according to Navarrete and Asio (2011), who cautioned that the risk posed by polluted soils is caused by a lack of awareness of people living in the area, who may not be aware of the presence of these pollutants and their health effects.

This study evaluated the concentrations of heavy metals in soil from abandoned mining area in Barangay Baluno, Zamboanga City. Soils in the surrounding mining areas are probably polluted by heavy metals which could possibly pose high health risks to the adjacent community (Li, 2014). The study area has been abandoned for a decade and this study would like to assess the possible contamination of heavy metals in the soil in the present. It was hypothesized that the soils from the abandoned mining area are highly concentrated with heavy metals. The main goal of this study was to determine the concentration of copper and lead in the soils from the abandoned mining area.

Materials and methods

Study Site

The study site is an abandoned mining area which was situated at Sitio Zambales, Barangay Baluno, Zamboanga City, (geographical coordinates at 121^{0}58'30" to 122^{0}00'00" N and 7^{0}00'30" to 7^{0}01'30" E). It has a total land area of 272 hectares with around 40 estimated families living adjacent to the area relying on farming as their primary source of livelihood. Barangay Baluno 28 kilometers away from the City Proper and about 30 minutes to 1hour travel with motorcycle and four wheels' vehicles. The former mining area has been abandoned for more than a decade and it may be suitable for this study.

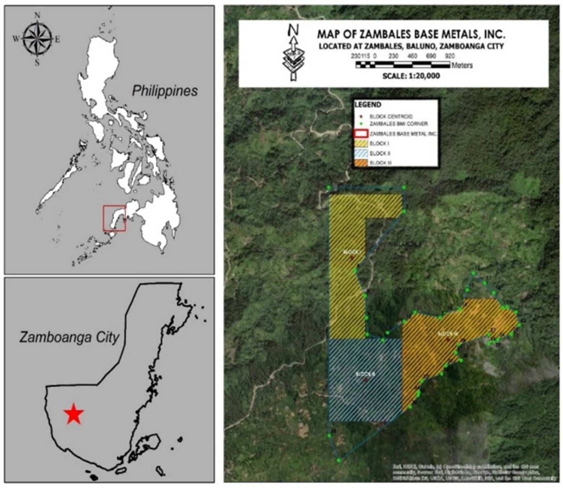

Fig. 1. Location map of abandoned mining site showing the three created meridional blocks.

Sampling Procedure

The abandoned mining area was ground validated for its boundary using the GIS software and created three meridional blocks with a total of 81 has per block. Three sampling stations per block was established using random sampling method set by DENR – EMB Site Characterization Guidelines.

Using an improvised soil auger, soil samples were collected in 3 stations for each block at 0-5cm and 20-25cm soil depth. Collected soil samples from the desired soil depth were placed in the sanitized plastic host or referred as the pre-cleaned zip lock bag and was labeled properly with measurement in centimeters for partition.

Soil Sampling

The improvised soil auger was driven through to 25 centimeters deep for soil samples collection. The soil will be then extracted from the auger and were separated according to its depth (0-5cm and 20-25cm). Extracted soil samples were weighed and only 500 grams of these soil samples will be collected for each 0-5cm and 20-25cm depth (see Fig. 2). Each 500 grams were placed in a zip lock bag and were labeled properly for relevant information such as number of block, number of station and soil depth. Then it was properly placed in an icebox to ensure the integrity of soil samples and was transported to the laboratory for Pb and Cu analysis.

Fig. 2. A-B, Apparatus used to determine the pH and electro conductivity of the soil samples and improvised soil auger during sampling. **C-D**, Soil testing for pH and EC from two soil depths.

Soil Analysis

Soil samples were air dried, and passed through a 2mm sieve prior to the heavy metal analysis. The acidified soil samples (100mL) after filtration with preconditioned plastic Milipore filter unit equipped with a 0.45 µm filter were digested with 1:10 mixture of concentrated HNO2 and 30% H2O2 to concentrate and convert metals associated with particulate matter to the free metal ions. The solutions were then determined for Pb and Cu level using Atomic Absorption Spectrometry (AAS). However, for pH and Electro Conductivity of the soil (Palintest ECO Testr) was used to read the soil pH and soil EC in-situ.

Statistical Analysis

For the interpretation of critical soil total concentration of the heavy metals specifically Lead (Pb) and Copper (Cu) concentration, World Health Organization (WHO) standard were used in the study. In terms of soil the soil samples' pH and Electro-conductivity, Boyer, (1982) was used to interpret the results of the analysis. To determine the significant difference of Pb and Cu concentrations and pH, electro-conductivity, and organic matter percentage in each stations per block, Analysis of Variance (ANOVA) was used to analyse the differences within and among variables in the study.

Results and discussion

The data were gathered for the physico-chemical paratmeters and heavy metals were based on the soil samples taken from abandoned mining site in Sitio Zambales, Upper Baluno, Zamboanga City in one sampling period. The physicochemical was conducted during soil sampling collection and heavy metal were analyzed in the laboratory. The value of the results was compared to the WHO standard.

Table 1. Averages of the Physico-chemical parameters of soil quality according to meridional block.

Parameters	Block 1	Block 2	Block 3
pH	5	4.7	4.1
Electrical conductivity (µS/cm)	260	183.33	286.67
OM (%)	4.05	1.84	1.81

Table 1. shows the result obtained for the physicochemical on soil from the three (3) blocks in the abandoned mining area.

Soil pH averages in all blocks varies from 4.1 to 5. The highest pH value was in block 1 with an average of (5) and followed by block 2 with an average of 4.7. Block 3 has the lowest average pH value (4.1). The averages of soil pH across 3 meridional blocks are strongly acidic (Boyer, J. S. 1982). Low pH accelerates the solubility of heavy metal compounds, resulting in increased pollution in the environment (Nkuli G. 2008). J.P. Anderson et. At, 2000 found that heavy metals' toxicity is determined by their degree of solubility, and they are more harmful at pH levels less than 4.5 because they are more mobile. The pH of the soil is the most critical component among physicochemical parameters. It regulates almost all physical, chemical, and biological processes in soil that affect metal availability, such as metal solid phase dissolution and precipitation, complexation, and acid-base interactions of metal species. Metal availability in soils is often increased when soil pH is reduced (Zhong, X.,.*et al*, 2020).

Furthermore, Average of Soil Electrical conductivity (EC) in all blocks varies from 183.33 µS/cm – 286.67 µS/cm. Block 3 has the highest value of EC with 286.67 µS/cm followed by block 1 which has the value of 260 µS/cm. And Block 3, has the lowest value (183.33 µS/cm) among all blocks. It was observed that the electro conductivity and the heavy metals concentration where directly related to each other. Thus, when EC increases, heavy metal also increases. (Ullman JL et at., 2013), Soil E.C. is an important indicator of soil salinity and a measurement of the salt content of the soil; however, it does not identify the particular salt or ions that may be present. E.C. is effective at detecting salts like sodium, potassium and the like. According to NG Maphula et at., 2021, soil electric conductivity lower than 200 µS/cm has insufficient for the plants and could show a disinfected soil with little microbial activity.

For Organic Matter Percentage, Block 2 and 3 had almost the same average value with 1.84% and 1.8%. However, block 1 got the highest value (4.05%) four times of the value when compared to block 2 and 3. The significant enrichment of heavy metals in particulate organic matter may have an effect on the continued mineralization of soil organic matter. In other words, pollution from soil heavy metals may alter the pace at which soil organic matter is mineralized, affecting the amount and distribution of soil organic matter (Ying Yong Sheng Tai Xue Bao, 2007). Moreover, poor soil structure, a lack of nutrients, and OM, especially for areas contaminated by mining or other industrial operations, cause physico-chemical issues for degraded and/or contaminated soils, which in turn results in low fertility and a low natural attenuation potential of these soils (M.P. Bernal *et al*., 2008).

Table 2. Results of the statistical analysis for physico-chemical properties.

		Sum of Squares	df	Mean Square	F	Sig.
Soil_Ph	Between Groups	.863	2	.432	.429	.659*
	Within Groups	15.077	15	1.005		
	Total	15.940	17			
Electro-Conductivity	Between Groups	34533.333	2	17266.667	.194	.826*
	Within Groups	1338066.667	15	89204.444		
	Total	1372600.000	17			
Organic Matter	Between Groups	19.643	2	9.821	3097.129	.001**
	Within Groups	.048	15	.003		
	Total	19.690	17			

** Significant * Insignificant

Table 2 Presents a significant difference in the Physico-chemical properties of the soil in the abandoned mining site from the 3 categorized meridional blocks in the sampling sites. Data were analyzed using analysis of variance (ANOVA), results reveal that the organic matter exhibits a significant difference between the meridional blocks in the sampling sites with a probability value (p-value) of 0.001 while Soil Ph and Electro-Conductivity display no significant difference showing a p-value of 0.659 and 0.826 respectively. Organic matter percentage were highly evident in block 1 that it compared to block 2 and block 3. This can be a factor that creates a significant difference in the results of the analysis of OM% value for block 1 to block 3 since it was found out in this study that Block 1 location is quite far among the other blocks established in the study.

According to NG Maphula *et al.*, 2021, the physical and chemical properties of the soil are enhanced by organic matter properties by encouraging biological activity and keeping the environment in good condition. Furthermore, increase of heavy metal concentrations in contaminated soil could slow down soil organic carbon's rate of mineralization and increase the amount of organic carbon that is barely biodegradable. As heavy metal pollution increased, particle organic matter and its percentage total soil organic carbon rose, whereas the percentage microbial biomass carbon in total organic carbon fell.

Table 3. Averages of the heavy metal concentrations of the post mining soil based on depth according to meridional block.

Parameters	Block 1		Block 2		Block 3		WHO Standard
	0-5cm	20-25cm	0-5cm	20-25cm	0-5cm	20-25cm	
Lead (mg/kg)	4.04	5.04	30.17	17.03	4,176.33	3,351	Pb (Lead – 85mg/kg)
Copper (mg/kg)	43.07	58.57	56.47	34.63	494.87	498.67	Cu (Copper – 36mg/kg)

Table 4. The one-way ANOVA Results in the analysis of heavy metals in soil samples by depth.

		Sum of Squares	df	Mean Square	F	Sig.
Lead Heavy Metal Concentrations	Between Groups	350680.792	1	350680.792	.064	.803*
	Within Groups	87591671.869	16	5474479.492		
	Total	87942352.661	17			
Copper Heavy Metal Concentrations	Between Groups	3.209	1	3.209	.000	.995*
	Within Groups	1296942.729	16	81058.921		
	Total	1296945.938	17			

** Significant

* Insignificant

Table 3. Shows the averages of the heavy metal concentrations of soil based on depths and compared to the standard set by World Health Organization (WHO) for soil. It is evident concentration of Lead in block 3 exceeded the standard set by WHO from both soil depths (0-5cm and 20-25cm). The average value concentration for Lead (Pb) 44 times higher compared to the standards. However, the average value for Lead in block 1 and block 2 both soil depths (0-5cm and 20-25cm) were within the permissible limit set by WHO.

This means that soil in block 3 were highly contaminated. Maybe, because of the location that block 3 located or close to distance in which the mining and ore processing activities have occurred and where the tailing ponds located compared to location of block 1 and 2 which were a bit farther from the heart of ore processing activities. After a mine is closed, the metals remain in the environment (Rashad and Shalaby 2007) Heavy metals in soil can readily lead to soil contamination; the concentration in soil depends on the quality of the tailing site (El Khali et. 2008). Cu in the other hand, block 3 has the highest average value of Cu concentration in both soil depths 0-5cm (494.87mg/kg) and 20-25cm (498.67mg/kg) respectively.

Average value concentration of Copper (Cu) in block 3 approximately 14 times higher than the standards set by WHO. Further, Block 1 also exceeded the standards in bot soil depths 0-5cm (43.07mg/kg) and 20-25cm (58.57mg/kg). But in block 2 at 20-25cm (34.63mg/kg) the Cu average concentration is within the permissible limit. However, depth 0-5cm (56.47mg/kg) exceeded the standard. Huge amount of Pb and Cu are emitted to the environment during smelting processes (Dudka and Adriano 1997). Because of rapid development in agriculture and industry, as well as disruption of the natural ecosystem due to the tremendous growth in world population, heavy metal poisoning has become a severe threat to the environment and food security (Sarwar *et al*., 2016). Heavy metal pollution, unlike organic pollutants, is undetectable, persistent, and irreversible, and it not only degrades the quality of water bodies, the atmosphere, and food crops, but it also poses a serious threat to organisms' and humans' health and well-being through accumulation in the food chain (Kankia and Abdulhamid, 2014).

The table presents a significant difference between the heavy metal concentration in the abandoned mining sites and the Depth of soil obtained.

Data were analyzed using analysis of variance (ANOVA), results reveal that there is no significant difference between the heavy metal concentrations for Lead and copper and the depth of soil obtained from the abandoned sites showing a probability value of 0.803 and 0.995 respectively.

Table 5. The one-way ANOVA Results in the analysis of heavy metals in soil samples by meridional block.

		Sum of Squares	df	Mean Square	F	Sig.
Lead Concentration	Between Groups	56238989.739	2	28119494.870	13.304	.001**
	Within Groups	31703362.922	15	2113557.528		
	Total	87942352.661	17			
Copper Concentration	Between Groups	804991.241	2	402495.621	12.272	.001**
	Within Groups	491954.697	15	32796.980		
	Total	1296945.938	17			

** Significant

* Insignificant

Table 4 presents a significant difference between the heavy metal concentrations in the abandoned mining sites and the location of the soil sample. Data were analyzed using analysis of variance (ANOVA), results reveal that there is a significant difference between the heavy metal concentration for Lead and copper and the location of the sample in the abandoned mining sites showing both a probability value of 0.001. Lead and Copper concentrations were highly evident in block 3 that it exceeds to the maximum standard set by WHO. This can be a factor that creates a significant difference in the results of the analysis among Lead and Copper concentrations for block 1 to block 3 since it was found out in this study that Block 3 location is the nearest among the other blocks established in the study.

High concentrations of these heavy metals could pose great risk in the soil microorganisms that greatly contributes to soil fertility. Increasing copper concentrations in soil could eliminate the existing invertebrates such as earthworms and oribatid mites (Streit, B. 1984). It can also affect to the growth and composition of plants (Merry RH et, al. 1986) especially to high valued crops (An, Y.J. 2006).

Conclusion

The results of Physico-chemical and heavy metal concentrations in soil samples from the abandoned mining area revealed that the soil contains substantially amount of metals determined (Pb and Cu) due to previous mining activities with no rehabilitation taking place during the closure of the mining company. It revealed in the study that the whole mining area were contaminated with Cu from both soil depths 0-5 and 20-25 respectively. However, for Pb it was evident in block 3 which has the highest concentration value around 5 to 60 times above the standard values set by the WHO standard from both soil depths. So therefore, block 3 were highly contaminated with heavy metals compare to other blocks. Moreover, pH soil across all blocks and stations were acidic and strongly acidic. Metal contamination may lead to a potential danger for the health of the community adjacent to abandoned mining area.

Recommendations

Based on the results of the study, the following were recommended:

a. Coming up with the solution like phytoremediation in the contaminated area to lessen the concentrations of heavy metal in soil especially in block 3 since the concentrations extremely exceed by the given standard. Since the soil parameters were few during this study, it is also good to include other heavy metals aside from the Pb and Cu as additional parameters and to increase the number of samples per meridional block.

b. Given the risk and threats to both environment and human health urgent environmental protection and management such as: Introducing phytoremediation technology to the highly contaminated areas in abandoned mining site.

c. Other heavy metals such as cadmium, mercury and physicochemical properties such as soil type, nitrogen and organic carbon could also be investigated to determine its potential threats.

d. Further studies on the soil fertility assessment, capability to sustain basic crops to sustain the needs of the community in the abandoned mining area.

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