PROFILE OF COPPER, NICKEL AND ZINC ON THREE SELECTED VEGETABLE FARMS AT CABINTAN, ORMOC CITY, PHILIPPINES

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ABSTRACT - The study was conducted to (a) determine the levels of copper, nickel, and zinc on three selected vegetable farms at Cabintan, Ormoc City, Leyte, (b) investigate the distribution of copper, nickel and zinc on the soil profile of the three selected vegetable farms, and (c) evaluate whether the copper, nickel and zinc contents of the vegetable farms are within the standard set by the United States Environmental Protection Agency (US EPA) for agricultural soils. The three heavy metals were analyzed through Flame Atomic Absorption Spectrophotometer at the Central Analytical Services Laboratory of the PhilRootcrops, Visayas State University, Baybay City, Leyte. Results showed that Farm 1 had the highest Cu concentration (0.413 \pm 0.136 ppm) and Farm 3 had the highest Ni and Zn concentrations of 0.058 ± 0.045 ppm and 0.393 ± 0.456 ppm, respectively. The levels of Cu, Ni, and Zn were statistically the same in the surface, subsurface, and subsoil soil layers in each vegetable farms. The soil pH (4.1 \pm 1.6, 4.5 \pm 0.3 and 4.6 \pm 0.2) of the farms which considered the major contributing factor for the heavy metals' vertical mobility was acidic and statistically the same. This study revealed that the levels of the three heavy metals were still below the tolerable limits of US EPA for contaminated agricultural soil. The three selected vegetable farms were considered safe for agricultural use.

Keywords: copper, heavy metal, nickel, soil profile, zinc

INTRODUCTION

Heavy metals are considered toxic to the human body. Chronic exposure can have carcinogenic effects to the nervous, circulatory, and other systems in the human body which can lead to detrimental results. These metals are pollutant elements and cause harmful effects to the ecosystem causing physicochemical alterations to the soil and water, in turn, ultimately affecting the human health. The soil is an important compartment of the environment and in agriculture, the presence of heavy metals puts the ecosystem and its inhabitants at a health risk.

In a relentless pursuit for higher yields, farmers use new forms of fertilizers and pesticides for their crops. The use of metal-enriched chemicals in these fertilizers and pesticides, or organic amendments such as sewage sludge (Salas *et al.*, 1998) greatly contributes to the distribution of heavy metals in the soil and transform them into other forms from the surface soil down to the subsoil layers.

The vegetable farms of Cabintan, Ormoc City, Leyte are considered one of the vegetable baskets in the province. It is an active site for highland agriculture in Leyte for cool vegetables. Some of

the grown vegetables include sweet peppers, cabbage, eggplant, and tomatoes. There is suspicion on excessive use of organic, inorganic fertilizers, pesticides and other chemicals in the farms. Farmers apply mega-Zinc fertilizers as foliar and drench; and not to mention, the site is very close to the geothermal loop in Leyte. The soil in Cabintan has been found by Nierves and Salas (2015) to have very high phosphorus fixing capacity which can be explained by heavy metal interaction. Its acidic and volcanic origin would have some important role in the mobility of heavy metals to nearby water resources.

Without the benefits of soil tests, farmers would apply fertilizers without prejudice and are not aware of nutrient imbalances in the soil and its adverse effect to the environment. Since the soil is the basis of agriculture and all crops for human and animal feed depend upon it, assessing the levels of heavy metals in vegetable farms can be beneficial not only to the farmers but also to the health of the general public. This study aimed to determine the levels of copper, nickel, and zinc on three selected vegetable farms at Cabintan, Ormoc City, Leyte, investigate the distribution of copper, nickel and zinc on the soil profile of the three selected vegetable farms, and evaluate whether the copper, nickel, and zinc contents of the three farms were within the standard set by the Environmental Protection Agency for agricultural soils.

MATERIALS AND METHODS

The planting of vegetable crops such as cabbages, beans, squash, eggplants and tomatoes generally constituted Cabintan's land use. The soil samples were collected immediately after the harvest day from the surface soil (0 to 20 cm), subsurface soil (21 to 40 cm), and subsoil (41 to 60 cm) depth within the immediate area of the selected three vegetable farms under the OK-RANGE of Cabintan, Ormoc City, Leyte. Figure 1 shows the three selected vegetable farms at Cabintan, Ormoc City, Leyte. There were three sampling points randomly assigned per vegetable farm. Farm 1 had a map coordinates of 11°04′26.9"N 124°43′30.8"E, while Farm 2 and Farm 3 had coordinates of 11°04′26.1"N 124°43′28.8"E and 11°04′26.0"N 124°43′31.1"E, respectively.



Figure 1. The map of the vegetable farms located in Cabintan, Ormoc City, Leyte (https://www.google.com.ph/maps/@11.0740147,124.7250463,145m/data=!3m1!1e3?hl=en. Date Accessed: March 23, 2016)

The soil samples were air-dried for a week and pulverized to break down aggregates using an agate mortar and pestle. The samples were then sieved through a 0.01 mm diameter plastic sieve and were stored in clean dry plastic containers at room temperature. The soil pH was determined following the method of SERAS (2002). About 20 mL of ultrapure water was added into each 10 g soil sample and the pH of each soil slurry was then measured using a calibrated pH meter (pH 2, 7, and10). Organic matter present in the soil was determined using the titrimetric procedure of Walkley and Black (1934).

The heavy metals (copper, nickel and zinc) were extracted using the Diethylenetriamine pentaacetic acid (DTPA) extraction method of Reed and Martens (1996). About 10 grams of air-dried soil sample and 20 mL of extracting solution were shaken for 2 hours and then centrifuged for 10 minutes at 2000 rpm. The supernatant was then filtered and analyzed using FAAS at the Central Analytical Services Laboratory, Philippine Root Crops Research and Training Center, VSU, Visca, Baybay City, Leyte. The heavy metal standard (Cu, Ni, and Zn) and the solvent for the extraction process consisted the background standard for the Atomic Absorption Spectroscopic analysis. For the standard blank, the solvent for the extraction process was taken. Each soil sample was analyzed using Flame AAS 200 Series. The selection of sampling sites was done through randomization. One-way nested Analysis of Variance (ANOVA) was used to evaluate the differences in the levels of copper, nickel, and zinc of the three selected vegetable farms. Tukey's Honestly Significant Difference test was used for the significance of copper, nickel, and zinc on the soil profile in each sampling site.

RESULTS AND DISCUSSION

Levels of Cu, Ni, and Zn in the Three Selected Vegetable Farms

Profiling the levels of Cu, Ni, and Zn in the soil of the vegetable farms in Cabintan, Ormoc City, Leyte gives an in-depth toxicity screening on the farms' soil where vegetables are grown, revealing any potential threat of heavy metals to consumers as it goes up the food chain. Results showed that Farm 1 had the highest level of copper $(0.224 \pm 0.164 \text{ ppm})$ while Farm 3 had the highest nickel and zinc concentrations of 0.044 ± 0.017 ppm and 0.194 ± 0.172 ppm, respectively (Table 1). Copper and zinc are considered essential micronutrients for the growth and development of plants. However, high concentration of copper poses a serious threat to agriculture as it bioaccumulates in the plants and also kills active organisms in the soil (Johnston, 1986). Nickel, on the other hand, accumulates readily in plant leaves and seeds (Welch & Cary, 1975), giving it a high potential to enter the food chain. As copper and zinc accumulate in the soil and reach toxic levels, these metals will become phytotoxic and cause metabolic disorder which would lead to a potential threat to human health as they go up the food chain (Chang & Page, 2000).

Table 1. Levels (ppm) of copper, nickel, zinc, % organic matter, and pH in the three selected vegetable farms at Cabintan, Ormoc City, Leyte

Vegetable Farms	рН	% Organic Matter	Cu (ppm)	Ni (ppm)	Zn (ppm)
1	4.1 ± 1.6	4.70 ± 1.98	0.224 ± 0.164	0.037 ± 0.012	0.107 ± 0.108
2	4.5 ± 0.3	3.95 ± 2.35	0.201 ± 0.135	0.038 ± 0.008	0.129 ± 0.140
3	4.6 ± 0.2	4.59 ± 1.41	0.197 ± 0.082	0.044 ± 0.017	0.194 ± 0.172

The soil condition of the three vegetable farms was acidic. This might be due to the decomposing organic matter in the soil which produces humic, fulvic, nitric, and sulfuric acids (Nierves & Salas, 2015). Moreover, the sandy loam soil type of the farms of Cabintan would also facilitate the leaching of basic cations such as Mg^{2+} , Ca^{2+} , and K^+ with the high altitude and intermittent rainfall of the area (Porazo, 2013; Nierves & Salas, 2015).

The organic matter serves as chelates which explains the availability of the metals in the soil. Not only that, the acidic pH made the metals more available by oxidizing them to its divalent ions, Cu²⁺, Ni²⁺, and Zn²⁺, increasing its mobility and solubility (Suave *et al.*, 2000), making it far more available for plants.

Distribution of Cu, Ni, and Zn in the Soil Profile

The distribution of copper, nickel, zinc, and as well as the pH and % organic matter in the surface, subsurface, and subsoil of the three selected vegetable farms is shown in Table 2. In the surface soil of Farm 1, the amount of copper, nickel, and zinc were 0.413 ppm, 0.048 ppm, and 0.232 ppm respectively. Based on the soil fertility factor given by Nachtergaele (2000), the level of copper (> 0.20 ppm) on the surface layer was deemed favorable but level of zinc (< 0.5 ppm) was rather deficient. Furthermore, the pH of the soil surface was also found acidic (pH = 2.3). The acidic condition of the soil surface would cause damage to the root system of the plants making it unfavorable for vegetable production (Harper, 2015).

As the acidic pH makes the metals more mobile and susceptible to leaching (Brock *et al.*, 2005), the metals such as Cu, Ni, and Zn translocated into the deeper layers of the soil. Moreover, the levels of nickel and zinc in the subsoil layer were statistically the same in each soil layers. The results indicated that heavy metals present in the soils of the vegetable farms had already leached into deeper layers of the soil. Not only that, runoff carried by rainwater and through soil erosion can further distribute them to the surrounding environment, which pose a threat not only to the vegetable farms, but also to the water system in the area, as these heavy metals would leach eventually into the groundwater.

The even distribution of organic matter in the soil layers of Farm 1 also contributed to the movement of the metals through the sublayers of the soil. Organic matter plays also an important role in the mobility and distribution of heavy metals (Salas *et al.*, 1998). The humic acid binds the metals while the fulvic acid releases it. The ratio of these two components present in the organic matter generally determines the magnitude of translocation of the metals in the subsurface layers of the soil.

Copper, on the other hand, had a significantly higher level in the surface layer compared to the subsoil layers. However, results on the distribution of copper in the sublayers still indicated the leaching of metal. This observation was in agreement with results of Hooda (2010), Kabata and Pendias (2001), Kabala and Szerszen (2002), that copper was the least mobile heavy metal and its accumulation in soil profile is prominent in the surface layer. Another possible reason for higher copper level in the surface layer would be the application of copper-containing pesticide and the extensive use of chicken dung as one of the fertilizers used in the vegetable farms.

In Farm 2, the levels of copper, nickel, and zinc in the surface soil were 0.357 ppm, 0.047 ppm, and 0.289 ppm, respectively. However, the pH value of 4.1 of the surface soil made it acidic to be considered optimum for plant growth. Farm 2 also exhibited the same trend with Farm 1, with a favorable level of copper (> 0.20 ppm), at the same time, deficient in zinc (< 0.5 ppm) for the optimum growth of

plants. In addition, the distribution of copper, nickel and zinc throughout the soil layers of Farm 2 followed also the same trend with Farm 1, whose copper level was significantly higher in surface layer compared to the soil sublayers, while the nickel and zinc were evenly distributed throughout the soil layers (Table 2). This means that Farm 2 had more or less the same levels of each heavy metals in each corresponding soil layers as Farm 1. This trend was probably due to the comparable organic matter distribution in each of the two farms' soil layers. Although the organic matter in the subsurface layer of Farm 2 is significantly lower than Farm 1 and the same for the surface and subsoil layers, Farm 1 had a significantly acidic pH in its surface soil compared to Farm 2, suggesting a greater leaching of heavy metals into the soil sublayers compared to Farm 2. This would compensate for the significantly lower organic matter in the subsurface layer of Farm 2 which would not hold the metal as strongly as the organic matter present in the subsurface layer of Farm 1. Overall, this would result to the same magnitude of distribution of each heavy metals in each soil layers of both Farm 1 and Farm 2.

Table 2. Average concentration (ppm) of copper, nickel, zinc, % organic matter, and pH in the soil profile of the three selected vegetable farms at Cabintan, Ormoc City, Leyte

Vegetable Farm	Soil Profile	рН	% Organic Matter	Cu (ppm)	Ni (ppm) ^{ns}	Zn (ppm) ^{ns}
1	Surface	2.3 ± 0.3^{c}	6.80 ± 0.00^{a}	0.413 ± 0.136^{a}	0.048 ± 0.000	0.232 ± 0.237
	Subsurface	5.4 ± 0.3^b	4.43 ± 1.40^{a}	0.135 ± 0.011^{b}	0.025 ± 0.007	0.044 ± 0.010
	Subsoil	4.7 ± 0.4^{ab}	2.86 ± 0.60^{ab}	0.124 ± 0.000^{b}	0.039 ± 0.015	0.046 ± 0.006
2	Surface	4.1 ± 0.3^{a}	6.63 ± 0.06^{abc}	0.357 ± 0.012^{a}	0.047 ± 0.008	0.289 ± 0.287
	Subsurface	4.6 ± 0.2^{ab}	2.92 ± 0.45^{c}	0.129 ± 0.003^{b}	0.033 ± 0.004	0.063 ± 0.019
	Subsoil	4.6 ± 0.2^{ab}	2.29 ± 0.48^{abc}	0.116 ± 0.016^{b}	0.035 ± 0.009	0.034 ± 0.000
3	Surface	4.5 ± 0.1^{ab}	6.02 ± 0.65^{c}	0.255 ± 0.007 ^{ab}	0.058 ± 0.045	0.393 ± 0.456
	Subsurface	4.6 ± 0.4^{ab}	4.54 ± 1.88^{c}	0.181 ± 0.062^{b}	0.049 ± 0.019	0.105 ± 0.017
	Subsoil	4.8 ± 0.5^{ab}	3.21 ± 1.65^{bc}	0.139 ± 0.017^{b}	$\begin{array}{c} 0.025 \; \pm \\ 0.006 \end{array}$	0.085 ± 0.061

Values with the same letter are not significantly different from each other at P $<\!0.05$ $^{ns}=$ not significantly different at P $<\!0.05$

The distribution of copper, nickel, and zinc did not significantly vary throughout the soil layers of Farm 3. The copper, nickel and zinc content in the surface soil were 0.357 ppm, 0.047 ppm, and 0.289 ppm, respectively. Just like in Farm 1 and Farm 2, the copper level (>0.20 ppm) in the surface soil was deemed favorable for the growth of plants but the zinc level (<0.50 ppm) was rather deficient for an optimum one. Unlike the first two farms, the distribution of copper in Farm 3 was evenly distributed throughout its soil layers because of the comparable pH and organic matter level in its soil layers. Farm 3 had statistically the same pH value and organic matter content in each of its soil layers. This indicated that the amount of heavy metals the organic matter can hold and the one that leached due to facilitated mobility brought by the comparable acidity of each soil layers, evenly distributed the copper, nickel, and zinc from the surface soil layer down to the subsoil layer of Farm 3. This result simply implied that the soil pH and organic matter were major factors in the mobility, solubility, and sorption of these heavy metals. This leads to the importance of improving the soil pH at agronomic optimum levels for field crops with elevated soil Cu and Zn levels in order to prevent potential toxicity problems.

Even though the presence of nickel in the surface soil may pose a risk to crops such as cabbages, cauliflower, beans, and peas (Kabata-Pendias & Mukherjee, 2007) grown in the vegetable farms in Cabintan, fortunately, the levels of copper, nickel and zinc on the three selected vegetable farms illustrated in Figure 2, were still below the tolerable limits for copper (70 ppm), nickel (38 ppm), and zinc (160 ppm) set by the United States Environmental Protection Agency (US EPA) for contaminated agricultural soils. These in comparison with the levels of copper, nickel and zinc on the agricultural soil of Hong Kong, Croatia, Spain, etc., as depicted in Figure 3, the levels of heavy metals on the soils of the vegetable farms in Cabintan, Ormoc City were significantly very low and exist inherently in the soil only at trace amounts. Therefore, the soil in those three selected vegetable farms at Cabintan is considered safe for agricultural use.

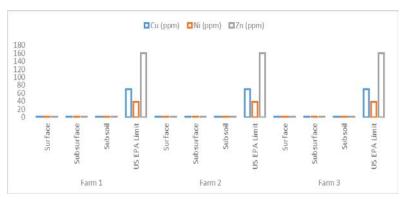


Figure 2. Concentration (ppm) of copper, nickel and zinc in the soil profile of the three selected vegetable farms within the tolerable limits set by the US EPA for contaminated agricultural soil

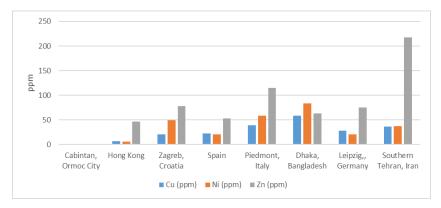


Figure 3. Average concentration (ppm) of heavy metals in agricultural soils from other regions/countries (Du et al., 2014).

CONCLUSIONS

The levels of copper, nickel, and zinc on the three selected vegetable farms at Cabintan, Ormoc City, Leyte were 0.197-0.224 ppm, 0.037-0.044 ppm, and 0.107-0.194 ppm, respectively. In addition, copper, nickel, and zinc had already leached throughout the soil layers of the three farms at a magnitude that the subsoil layer already had comparable heavy metal level as the surface soil layer. Still, the levels of copper, nickel and zinc were way below the limits set by US EPA for contaminated soil. Therefore, the soil in those three selected vegetable farms at Cabintan is considered safe for agricultural use.

RECOMMENDATIONS

Extractable copper, nickel, and zinc levels on the soil profile of the vegetable farms at Cabintan, Ormoc City, Leyte before harvest period should be determined. Total copper, nickel and zinc content (acid digestion), and their fractional forms in the soil profile of the farms should be analyzed to further monitor the impact of heavy metal accumulation. The biological uptake of heavy metals on various plants grown in Cabintan farms should be investigated. Other heavy metals present in the soils of the vegetable farms in Cabintan should be pursued. Improving the soil pH condition at agronomic optimum levels for field crop production via liming is recommended. Studies on the vertical mobility of the three heavy metals with phosphorus content in the soil profile should be done, and the humus and fulvus composition of the organic matter as distributed in the soil profile should be elucidated.

STATEMENT OF AUTHORSHIP

The first author conducted the literature search, prepared the conceptual framework, identified thematic points, formulated recommendations, and undertook the writing up. The second author initiated the concept, identified some issues, formulated recommendations, and reviewed the paper.

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