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Baseline Profile of Soil Samples from Suawan River Watershed

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Abstract

The study was conducted to determine the quality and fertility of the soil samples taken from Suawan River Watershed of Davao, Philippines. Its objectives were to determine the pH, organic matter, cation exchange capacity, macronutrients (N, P, K, Ca, Mg), micronutrients (Fe, Mn, Zn) and Pb as a pollutant indicator of the twenty soil samples. Based on soil fertility guidelines set by the Bureau of Soils and Water Management, soil's pH, cation exchange capacity, organic matter, phosphorous, potassium and calcium generally ranged from moderately to adequately favorable. Nitrogen level was moderate while magnesium content for all soil sampleswasvery high. Low levels for iron, manganese and zinc. Lead content ranged from below the detectable limit to 1.9551 ppm which was below the level that can be considered as environmental contaminants. Results of this study can be a productive and effective contribution to agricultural sector for a better crop yield. This will also help Mines and Geosciences Bureau Region XI to have a comprehensive data for the purpose of mapping out Davao's aquifer and City Government of Davao for its local assessment, conservation management planning and sustainable development.

<i>Keywords:</i> soil quality; fertility; Suawan River Watershed; macronutrients; micronutrient	S

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1. Introduction

Conserving the soil and its vegetative cover is one way of protecting the watershed. The type and amount of vegetation and the plant community structure can greatly affect the storage capacity of a watershed as well as prevent soil from eroding. This could only be achieved if all the soil nutrients needed by the plants are accessible and readily available for a healthy growth [1].

Recently, Davao City has been expanding and growing in terms of its economic and industrial sphere. It becomes truly a haven of so much opportunity for all. This fact coupled with the rise of population and the influx of people to the region resulted to inevitable exhaustion of the local natural resources. With the advancement of the region, polluted runoff from commercial, urban and agricultural areas, erosion from development and other activities, and flood and drainage impacts all threaten the watersheds [2].

The local government unit of Davao City spearheaded by the Mines and Geosciences Bureau (MGB) – Department of Environment and Natural Resources, Region XI and City Planning Office with its desire to have a comprehensive soil analysis, is currently undergoing Geoscientific research of the whole Davao City Watershed. A study was done by the MGB on Suawan Watershed, a part of Davao City Watershed area which includes some physical test only. Thus, this study was envisioned to provide baseline information of some chemical properties of the soil samples taken from different barangays of Suawan River Watershed. Specifically, this study focused only on the determination of the levels of pH, organic matter, cation exchange capacity, macronutrients (N,P,K,Ca,Mg), micronutrients (Fe,Mn,Zn) and the concentration of lead as a possible environmental contaminant of the soil samples provided by the MGB- Region XI. The results were then compared to the standards set by the Bureau of Soils and Water Management.

2. Materials and Methods

The soil samples from Suawan River Watershed were collected randomly by the MGB XI staff. Sample preparationincludes drying, sieving, homogenizing and packing.

2.1 Potentiometric Determination of Soil pH

Three grams of initially prepared soil sample was weighed analytically and placed into a 50 mL beaker, in which 20.00 mL of distilled water was added. The suspension was thoroughly stirred using magnetic stirrer for 30 minutes and was left standing for 1 hour. The pH of the suspension was determined using the pH meter that was previously calibrated with standard buffer solution of pH 4.0 and 7.0 [3].

2.2 Organic Matter (Graham Colorimetric Method)

The Graham Colorimetric Method involved the oxidation of readily oxidizable soil organic matter by potassium dichromate solution and measuring reduced chromium ions colometrically. The reaction between carbon and

K₂Cr₂O₇ carried out in sulfuric acid solution is represented by the equation below:

$$3C + 2Cr_2O_7^{2-} + 16H^+$$
 \longrightarrow $3CO_2 + 4Cr^{3+} + 8H_2O$

Ten mL of 0.167 M potassium dichromate solution was added to a 1.0 gram of air-dried sample in a 250 ml-flask. The solution was swirled for 15 minutes after the addition of 20.00 mL 18 M sulfuric acid and allowed to stand for 30 minutes. The solution was diluted with 60.00 mL water, swirled again and was left to stand overnight for a complete settling of soil particles.

The suspension was subjected to decantation. The decanted liquid was centrifuged and the centrifugate was used for absorbance reading of UV-Vis spectrophotometer at wavelength 589.1 nm. A third sample treated with the same procedure was spiked with a solution of known concentration [3].

2.3 Cation Exchange Capacity

Cation exchange capacity in soils is a reversible chemical reaction. All of the cations held on surface of soil minerals and within the crystal framework of some mineral species plus those which are part of certain organic compounds can be reversibly replaced by those of salt solutions and acids [3].

The sample was shaken with 0.5 M HCl to remove bases and to saturate sorption. Excess HCl was removed and absorbed H⁺ is replaced with acetate of barium. The amounts of cations adsorbed were determined by titrating it with NaOH using phenolphthalein indicator and calculated to mequivalent per 100 g air dried soil [4].

Two grams sample of soil was used for CEC analysis. It was analytically weighed in a 250 mL Erlenmeyer flask and treated with 100.00 mL of 0.5 M HCl. The flask was stoppered to prevent spilling and was shaken vigorously for 30 minutes in a mechanical shaker. The mixture was filtered and the residue was washed with 10 mL portions of water until the last washing showed no more precipitate with 3.00 mL of 1% silver nitrate. The filtrate was discarded and the residue was transferred to a 250 mL Erlenmeyer flask using spray from wash bottle containing 100 mL of 0.25 M barium acetate. The flask was stoppered and shaken for 30 minutes. It was then filtered, washed with three 100 mL portions of water. The soil was discarded and the filtrate was titrated with standard 0.0917 M NaOH using 3 drops of phenolphthalein indicator until the first pale pink end point was reached [5].

2.4 Total Nitrogen Content (Kjeldahl Method)

Kjeldahl method is very important for analyzing samples containing nitrogen consisting of organic and ammonium forms. This is a wet oxidation procedure using sulfuric acid for the digestion. For the distillation of ammonium, the solution is made alkaline. The distilled ammonium is then received in boric acid and titrated with a standard acid [3]. These steps can be summarized by the chemical reactions below [5]:

- a. Pre-reduction
- b. Digestion

Organic (C, H, O, N)
$$\longrightarrow$$
 CO₂ + H₂O + NH₄HSO₄

c. Distillation

$$2OH^{-} + NH_{4}HSO_{4}$$
 \longrightarrow $NH_{3}(g) + 2H_{2}O + SO_{4}^{2-}$
 $NH_{3} + H^{+}$ \longrightarrow NH_{4}^{+}

A soil sample of 0.80 to 1.00 gram was weighed analytically and transferred in a Kjeldahl flask. Fifteen grams of powdered potassium sulfate, 0.7g HgO, and 25.00 mL of concentrated sulfuric acid were added to the sample. The mixture was heated in an inclined position to convert organic nitrogen to ammonium sulfate. The digestion was stopped only after black color disappears and became clear. After cooling the mixture, 200 mL of water was then added.

A steam distillation set-up was constructed after the digestion. The Kjeldahl flask, in a tilted position, was attached to a condenser and a 250 mL erlenmeyer flask was placed at the other end for distillate collection. A 100 mL of 40% NaOH solution was poured slowly without agitation. The tip of the condenser was immersed in the receiver flask which contained 50.00 mL of 0.1011 M standardized HCl with 5 to 7 drops of the phenolphthalein indicator. The distillation was stopped until the receiver flask contained a total volume of 150.00 mL. The distillate was then titrated with standard 0.0893 M NaOH until a faint-pink end point color was reached [3].

2.5 Available Phosphorous Content (Troug Method)

Troug method involves the removal of adsorbed phosphate from the soil by an extracting solution. In acidic solution, reduction of soluble phosphates with molybdates resulted to the formation of a blue-colored soluble complex known as heteropolymolybdophosphoric acid complex. This is the basis for the colorimetric determination of phosphates concentration.

Reactions:

$$H_3PO_4 + 12H_2MoO_4$$
 \longrightarrow $H_3P(Mo_3O_{10})_4 + 12H_2O$ \longleftrightarrow Blue product

A one gram of soil sample was measured accurately in a 250 ml Erlenmeyer flask and exactly 100.00 ml of Troug solution was added. The solution was shaken for 30 minutes using mechanical shaker and then filtered. Exactly 25.00 ml aliquot was placed into a 125 ml Erlenmeyer flask and added with 2.00 ml molybdate reagent. Two drops of SnCl₂ was placed and mixed immediately before reading the sample in the UV-VIS spectrophotometer. The reading was done within 12 minutes after SnCl₂ was added.

The UV-Vis spectrophotometer was set at 700.31 nm wavelength in determining the concentration of phosphorous. Third sample was spiked with standard solution of phosphorus. This was used to calculate the percent recovery.

2.6 Potassium, Calcium and Magnesium Content (AAS Method)

The exchangeable cations, K, Ca and Mg, are extracted with ammonium acetate and then evaporated to dryness. Addition of nitric and hydrochloric acid and ignition at 390°C will destroy the organic matter and the ammonium salts present in the sample. The residue then is dissolved in nitric acid and the exchangeable cations are determined directly in separate aliquots [3].

One gram of soil sample was treated with 10.00 mL of 1M ammonium acetate in a 100 mL beaker. The mixture was stirred for a few minutes and then covered with watch glass and allowed to stand overnight. The mixture was filtered using 50.00 mL volumetric flask as receiver. The residue was washed again with ammonium acetate. It was noted that the soil had not become dried and cracked. The filtrate was then diluted to the mark with ammonium acetate which became the ammonium extract.

The ammonium extract was then transferred to a 150 mL beaker and evaporated to about 20 mL on a hot plate, allowed to cool and covered with watch glass. Slowly the extract was added with 5.00 mL concentrated nitric acid and 1.00 mL concentrated HCl. The solution was heated moderately until no more brown fumes were emitted. The watch glass was rinsed with distilled water allowing the rinsing to drain to the beaker. After then, the solution was evaporated to dryness. These was cooled down again and treated with 3.00 mL of 1:1 HCl. Again, the solution was heated and evaporated to dryness on a steam bath. After cooling down, the residue was diluted to 50.00 mL with 0.1 M HNO₃ using volumetric flask. Then, it was filtered [3].

The filtrate then was ready for K, Ca, and Mg determination using Atomic Absorption Spectrophotometer. Since Ca and Mg were affected by the presence of phosphate and sulfates, the analysis was done separately. A 1.00 mL aliquot was taken with 5.00 mL of 2% SrCl₂ and diluted to 50.00 mL volumetric flask with 0.1 M HNO₃. For the determination of K, 1.00 mL aliquot was pipetted into a 50 mL volumetric flask and diluted to mark with 0.1 M HNO₃. A third sample was treated the same procedure was spiked with a standard solution of known concentration in order to solve for the percent recovery.

2.7 Total Fe, Mn, Zn, and Pb Content (AAS Method)

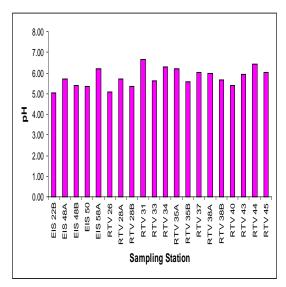
About 0.5 grams of soil sample was weighed in 100 mL beaker and treated with 10.00 mL aqua regia. A watch glass was used as a cover. The solution was allowed to stand overnight. The solution was heated to half of its volume. It was cooled, transferred quantitatively into a 100.00 mL volumetric flask and diluted to mark. The solution was filtered and the filtrate was used for AAS analysis for Fe, Mn, Zn, and Pb. For the determination of Fe, 1.00 mL aliquot was diluted to 100.00 mL volumetric flask with water as the diluent. Further dilution was made by taking 5.00 mL of the later dilution and diluted volumetrically to 50.00 mL with water. Manganese and zinc on the other hand were analyzed separately by taking 5.00 mL and 25.00 mL respectively from the original

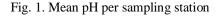
solution and diluted with water to 100.00 mL volumetrically. Analysis of lead was done on the original solution. All dilutions were shaken 36 times to ensure homogeneity of the solution.

3. Results and Discussion

3.1 pH

Figure 1 shows the mean pH of the twenty soil samples from Suawan River Watershed Area. The pH reading ranged from 5.05 to 6.67. RTV 31 soil sample had the highest pH of 6.67. Significant source of the soil sample's acidity, considering Suawan River Watershed is not far from the city and it's large industrial complexes, has been acid rainwater. The acidity in the atmosphere is generated from oxides of nitrogen and sulfur coming mostly from the combustion of coal, gasoline and other fossil fuels. When combine with water vapor, HNO₃ and H₂SO₄ are formed resulting to rainwater with pH value of 4.0 to 4.5. Although its concentration may not change the pH drastically, however, over a period of time, the addition has a decided acidifying effect. Furthermore, leaching encourages acidity by replacing bases from the colloidal complex through removal of metallic cations. On the other hand, EIS 22 B with the lowest pH is planted with pine trees. Result of a study showed that the degree of acidity goes up as the precipitation increases especially on soils under pine forest than soils under grassland [6]. Other soil samples with lower pH values were covered with grass and a settlement area. Figure 2 shows the difference in pH among the sampling sites based on the general guidelines for the fertility rating of soil. Fertile soil generally has a pH of 6.3 to 6.8 [7]. Soil samples with pH under both extreme conditions may lack nutrients even if the fertilizers have been applied. As soil alkalinity increases the amount of available nitrogen together with some minor elements like Fe, Mn, Co, Zn correspondingly decreases. Whereas, when the soil is very acidic, it is generally lacking in Ca, Mg and P [8].





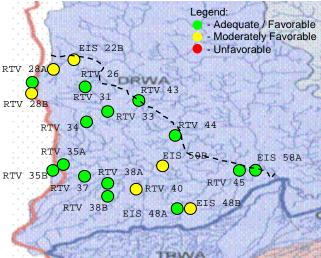


Fig. 2. Map of mean pH per sampling site

3.2 Organic Matter (%)

Organic matter improves the soil by improving aeration, drainage and moisture retention. Also it provides some soluble nutrients in the soil. The mean % organic matter of the twenty soil samples from Suawan River Watershed Area is shown in Figure 3. EIS 48A had the highest % OM while EIS 48B had the lowest % organic matter. This contrast of result was attributed mainly on its depth. The EIS 48B was taken 30 cm from the A horizon which contains a mixture of organic matter and inorganic matter. While EIS 48A was taken 10 cm from the O horizon (topsoil) which contains mostly of organic matter. The same is true with RTV 28 A (25 cm) & B (150 cm) as well as RTV 38 A (25-50 cm) & B (50-150 cm). The rest of the soil samples were moderately favorable in their % organic matter content. Using the fertility guidelines, Figure 4 shows the differences of the organic matter content on the soil samples.

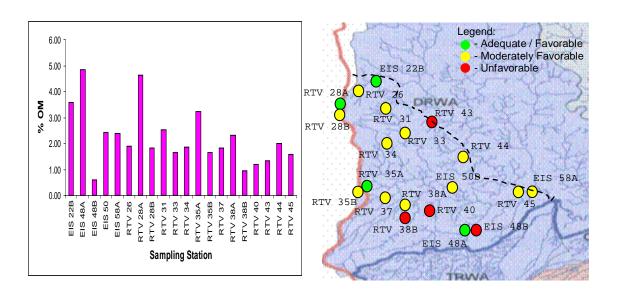
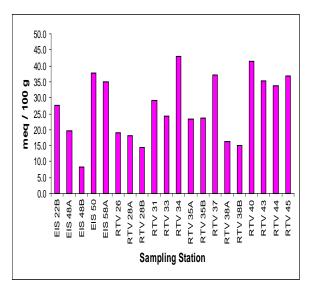


Fig. 3. Organic matter per sampling station

Fig. 4. Map of mean % OM per sampling site

3.3. Cation Exchange Capacity (meq/100g)

The cation exchange capacity (CEC) of a soil is a measure of the amount of cations that can be held by it. The exchange capacity is directly dependent on the kind and amount of colloids the soil contains. Figure 5 shows the mean CEC of the twenty soil samples from Suawan River Watershed Area. Soil sample RTV 34 had the highest CEC value. Most of the soil samples with pH value of 6 and higher exhibit high CEC values. This result is in agreement with its pH value since CEC in most soils also increases with pH [7]. Also, this is in accordance with [3] that a soil higher in clay or with fine texture and organic matter has high CEC value. Hence, there will be minimal leaching of nutrients.



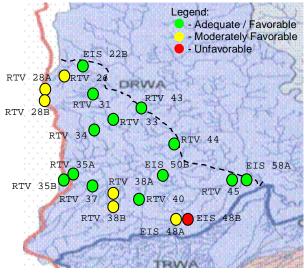


Fig. 5. C.E.C. per sampling station

Fig. 6. Map of mean CEC per sampling site

3.4 Total Nitrogen (%)

Figure 7 shows the mean % total nitrogen of the twenty soil samples from Suawan River Watershed Area. Based on the standard guidelines for the fertility rating of soils as shown in Figure 8, all soil samples are moderately favorable in its nitrogen content. Soil found in the Philippines are generally low in nitrogen. Thus, N must be applied in almost all soils in the country that would be planted, especially in soils low in organic matter. Organic matter is the native source of nitrogen. Low organic matter is indicative of low nitrogen levels in the soils. Thus, increasing nitrogen level means increasing the organic matter content of the soil. These can be done by the application of organic matter sources such as compost and organic fertilizer. These do not only supply nitrogen and trace elements, but also contains "humus", whose importance cannot be underestimated since it improves the soil's physical, chemical and biological properties [3].

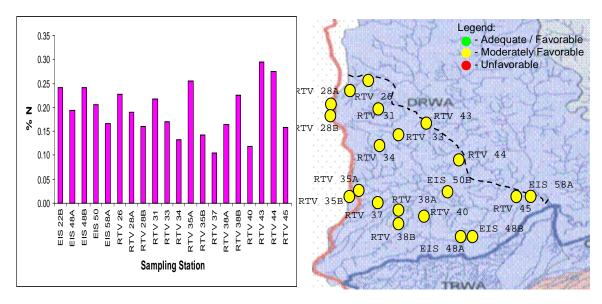


Fig. 7. % Nitrogen per sampling station

Fig. 8. Map of % N per sampling site

3.5 Total Phosphorus (ppm)

Figure 9 shows the mean ppm phosphorus of the twenty soil samples from Suawan River Watershed Area. Almost all of the soil samples had adequate amount of phosphorus based on the general guidelines for fertility rating of soils (Figure 10). Soil sample EIS 50B had the highest value with a mean of 24.6712 ppm. This maybe attributed to the fact that subsoil contains greater phosphorus than in the surface and greater in the poorly drained than well drained soil [9]. While RTV 45 had the lowest value of 6.6850 ppm.

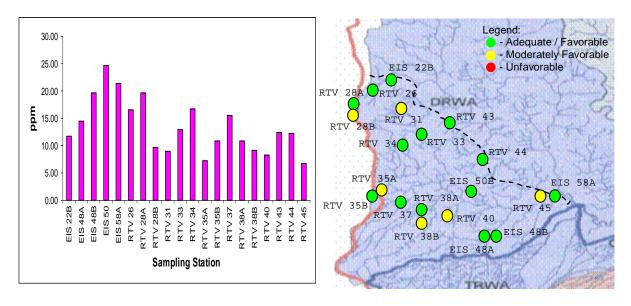


Fig. 9. Phosphorous per sampling station

Fig. 10. Map of P per sampling site

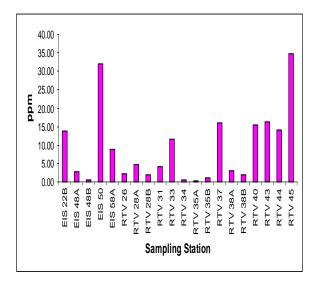
3.6 Potassium

Potassium is present in most soils, but is often unavailable to plants. It is also one of the few nutrients that is not an inherent component of organic molecules, though some organic materials contain substantial amounts. Organic matter improves potassium availability mainly by raising the soils cation exchange capacity (CEC) [11].

Figure 11 shows that RTV 45 had the highest potassium content while RTV 35A had the lowest value of 0.02181 ppm. Moreover, soil sample EIS 48 B illustrates the principle that low organic matter gives low cation exchange capacity and eventually decreases the potassium level [10].

3.7 Calcium (ppm)

From Figure 13, the mean calcium of the twenty soil samples from Suawan River Watershed Area is presented. Soil sample EIS 50B had the highest calcium content. There were only two soil samples that has moderate calcium content namely RTV 28B and RTV 38B. Based on the fertility guidelines as shown in Figure 14, all sample contains calcium ranging from moderate to adequate amount.



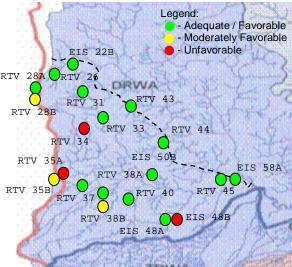


Fig. 11. Potassium per sampling station

Fig. 12. Map of ppm Potassium per sampling site

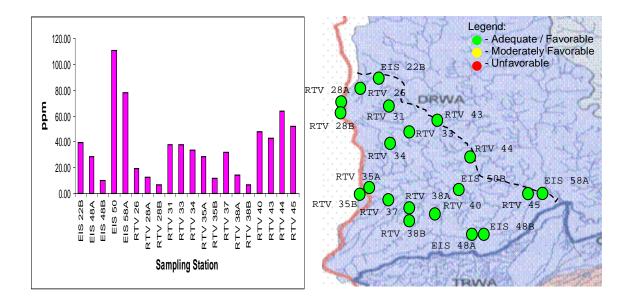
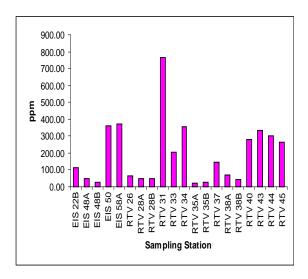


Fig. 13. Calcium per sampling station

Fig. 14. Map of ppm Calcium per sampling site

3.8 Magnesium (ppm)

Figure 15 shows the mean magnesium of the twenty soil samples from Suawan River Watershed Area. RTV 31 had the highest magnesium content with a value of 359.39 ppm. On the other hand RTV 35A had the lowest value, yet all of these soil samples are still adequately favorable for plant growth in terms of magnesium content based on the standard guidelines for fertility rating of soil samples (Figure 16).





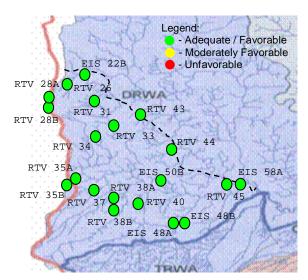


Fig. 16. Map of Magnesium per sampling site

3.9 Micronutrients (ppm)

Micronutrients are minerals which are important in very small amounts for the proper functioning of biological systems. The desired amount in soil for Fe, Mn and Zn are 25,000 ppm, 2,500 ppm and 100 ppm respectively [10]. Most of the results were somehow very low compared to the desired amount.

The availability of the micronutrient is greatly influenced by soil type, organic soils, intensive cropping, extreme pH and eroded soils. Strongly leached, acid, sandy soils are low in micronutrients. At high pH values, availability of all the micronutrients is unfavorably affected. Manganese and zinc levels decreases as the pH rises. Furthermore, soil erosion can influence micronutrients availability. Erosion of topsoil carries away considerable soil organic matter in which much of the potentially available nutrients are held. Also, removal of topsoil exposes subsoil horizon that are often higher in pH than the topsoil a conditions that leads to deficiencies of some micronutrients such as zinc [10]. Figures below show the differences in the mean concentration of the three micronutrients.

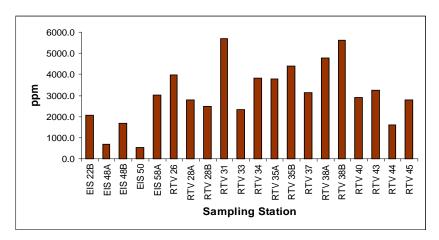


Fig. 17. Distribution of Fe for the different sampling sites

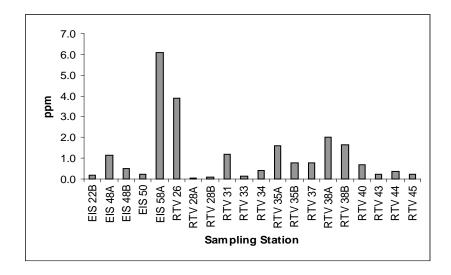


Fig. 18. Distribution of Mn for the different sampling sites

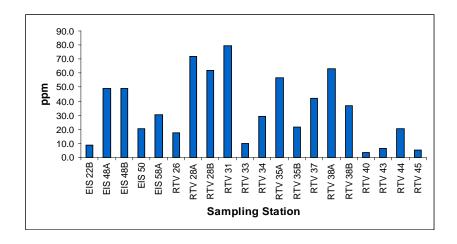


Fig. 19. Distribution of Zn for the different sampling sites

3.10 Lead (ppm)

Figure 20 shows the lead concentration of the twenty soil samples which ranges from below the detection limit to 1.9511 ppm. RTV 35A soil sample had the highest lead content. Considering its location which is near the roadway, lead content may come primarily from airborne lead, from automobile exhaust, from paint chips and dust fromwoodmark coated with old lead pigmented paints. However, these values were still below the concentration of lead in soil that can be considered an environmental contaminants that ranges from 2 to 200 ppm of lead [7].

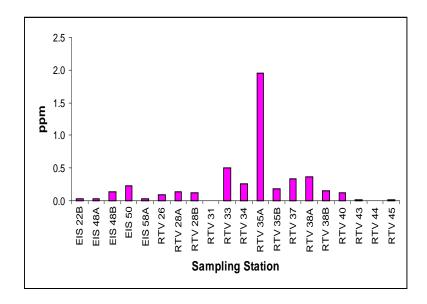


Fig. 20 Distribution of Pb for the different sampling sites

4. Conclusion

Based on soil fertility guidelines set by the Bureau of Soils and Water Management, soil's pH, cation exchange capacity, organic matter, phosphorous, potassium and calcium generally ranged from moderately to adequately favorable. Nitrogen level was moderate while magnesium content for all soil samples was very high. Though there are no standard values for micronutrients but basing on the desired amount, all soil samples had low iron, manganese, and zinc level. Lead content ranged from below the detectable limit to 1.9551 ppm. Concentrations were still below the level that can be considered an environmental contaminants.

Results of this study can be a productive and effective contribution to agricultural sector for a better crop yield. This will also help Mines and Geosciences Bureau Region XI to have a comprehensive data for the purpose of mapping out Davao's aquifer and to the City Government of Davao for its local assessment, conservation management planning and sustainable development.

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