

Soil Characteristics Interrelationship with Treated Soil Micronutrients in Nigerian Southern

Abstract

We investigated the influence of soil properties on the availability or otherwise of micronutrients in agricultural soils impacted by inorganic and organic manures in the South-South Area of Nigeria. The levels of pH, organic matter (OM), cation exchange capacity (CEC), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) in the understudy soil were examined. The measured pH, OM, CEC, Cu, Fe, Mn and Zn levels revealed: 6.04 ± 0.49 , 17.68 ± 4.78 %, 7.97 ± 0.81 Cmolkg^{-1} , 5.27 ± 0.82 mgkg^{-1} , 232.49 ± 16.01 mgkg^{-1} , 109.30 ± 9.85 mgkg^{-1} , and 8.40 ± 1.15 mgkg^{-1} , for pH, OM, CEC, Cu, Fe, Mn, and Zn, respectively. The values were within the acceptable limits set by national and international standards.

The study revealed variable relationships between the soil properties and micronutrients in the studied soils at $p < 0.05$. Soil pH exhibited a strong negative association with all the micronutrients except Zn. However, a strong positive correlation ($p < 0.10$) was recorded between pH and Zn. OM showed a significant positive correlation ($p < 0.10$) with Fe, a weak positive correlation with Zn, and a non-significant negative correlation ($p < 0.10$) with Cu and Mn at $p < 0.10$. CEC exhibited a fair positive association with Fe and Zn, and a non-significant negative correlation ($p < 0.10$) with Cu and Mn. The principal component analysis (PCA) identified a combination of anthropogenic and natural impact and the impact of agrochemicals applied as the major factors influencing the properties determined in the studied soils. The study concluded that soil properties have a strong influence on the availability or otherwise of micronutrients in the soil.

Keywords: Agricultural soil, Agrochemicals, Micronutrients, Principal component analysis, Soil properties.

1. INTRODUCTION

The soil naturally has some inherent components have little or no impact on the soil quality. However, the introduction of artificial substances such as pesticides, herbicides, inorganic fertilizers, organic manures, wastewater, fungicides etc into the natural soil environment to improve crop yield has elevated these components levels above their recommended limits. Consequently, the soil environment becomes harmful to plants, animals, and humans. Studies have shown that; these agrochemicals in soil tend increase the essential and non-essential substances in the cultivated plants (Benson *et al.*, 2014; Kumar *et al.*, 2016; Orisakwe *et al.*, 2017; Zwolak *et al.*, 2019; Etuk *et al.*, 2022).

The micronutrients which include copper, iron, manganese, zinc, boron, molybdenum, etc are essential for normal plants growths and metabolism (Mathew *et al.*, 2016; Chrysargyris *et al.*, 2022). The deficiency of micronutrients in soil has an unpleasant impact on plants, animal, and humans' health (Shukla *et al.*, 2018; Kihara *et al.*, 2020). Nevertheless, at higher concentrations, negative effects are noticed on the plants and in the underground water quality (Morgan and Connolly, 2013; Zewide and Sherefu, 2021; Nenkam *et al.*, 2022). The availability and lack of these micronutrients depend mainly on the soil properties such as pH, organic matter, cation

exchange capacity, soil texture etc (Chatzistathis, 2018; Grujic *et al.*, 2018; Dhaliwal *et al.*, 2019; Mohiuddin *et al.*, 2022).

Some studies have been carried out in the Nigerian Southern to assess micronutrients levels in the soil and the effect of oil spillage on the micronutrients (Sha'Atoa *et al.*, 2012; Diri and Tate, 2020; Kingsley *et al.*, 2019; Otaiku, 2019). The physicochemical properties of soils including agricultural soils within the Nigeria Southern have been investigated (Ugochukwu *et al.*, 2012; Olorunfemi *et al.*, 2018; Akinde *et al.*, 2020; Joseph and Peter, 2020; Nnaji and Egwu, 2020; Omemu *et al.*, 2022).

The impact of organic manure and inorganic fertilizers on soil properties and fertility has been evaluated (Obi and Ebo, 1995; Ebewore and Emaziye, 2016; Jaja and Barber, 2017; Etuk *et al.*, 2022; Orluchukwu and Amadi, 2022). Nonetheless, information on the relationship between soil properties and micronutrients within the study area is scanty. Hence, this study was undertaken to examine the effect of soil properties on the micronutrients in soils impacted by manures and inorganic fertilizers to provide an adequate concentration of micronutrients for the study (Dhaliwal *et al.*, 2019; Patrick *et al.*, 2013).

The results of this research shall provide information on the correlation between soil properties and micronutrients. It will also assist the farmers to know the type and quantity of manures/inorganic fertilizers to apply in the soil to maintain the soil nutrients. The effect of manures and inorganic fertilizers on soil properties has also been exposed. The gap created by the previous studies on the agricultural soils within the Nigeria Southern has been minimized.

2. MATERIALS AND METHODS

2.1 Study Area

Akwa Ibom State is in the Nigeria Southern where oil exploration activities are carried out. The State is situated between latitudes 4° 32' N and 5° 33' N and longitudes 7° 25' E and 8° 25' E (Figure 1). Akwa Ibom State has two distinct seasons namely: Dry and wet seasons that ranged from November to March and April to October, correspondingly. The yearly temperature of the area varies between 25 °C and 29 °C, whereas the annual rainfall is between 2,000 and 3,000 mm (Afangideh *et al.*, 2005). In the climatic conditions of the study area, agriculture is one of the major activities of the inhabitants. The soil type of the study area is in the Anthrosol category (Ebong *et al.*, 2020).

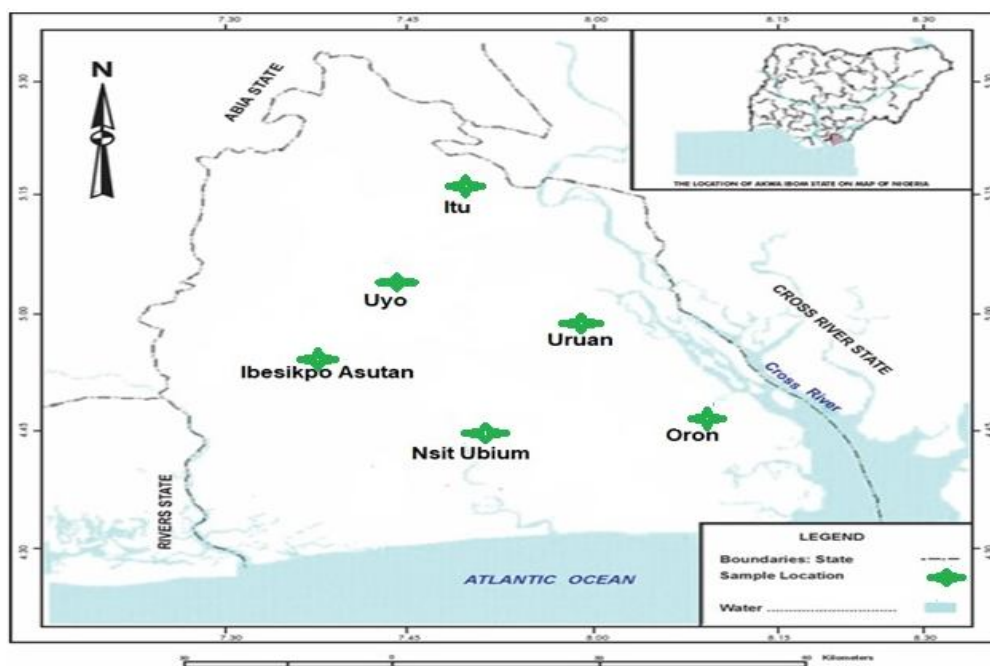


Figure 1: Map of the Study Area within Nigerian Southern.

The studied location, their coordinates and the type of organic and inorganic fertilizers applied are indicated in Table 1.

Table 1: Sites, coordinates and type of manures applied

Site	Coordinate	Type of fertilizer
Ibesikpo Asutan	7° 57' E and 4° 45' N	Organic wastes from poultry and piggery wastes
Itu	7° 59' E and 5° 09' N	Organic wastes from Poultry wastes
Nsit Ubium	7° 56' E and 4° 47' N	Inorganic fertilizer and organic wastes from poultry farm
Oron	8° 14' E and 4° 50' N	Organic wastes from fish and poultry farms
Uruan	8° 05' E and 5° 04' N	Mainly Inorganic fertilizers
Uyo	7° 56' E and 5° 03' N	Organic wastes from dumpsites and organic wastes from fish farm

2.2 Sample collection and treatment

Top soil was obtained at farmlands in Ibesikpo Asutan, Itu, Nsit Ubium, Orn, Uruan, and Uyo within Akwa Ibom State, Nigeria Southern using soil Augar (Figure 1). These samples were obtained during the dry season between December 2017 and February 2018 to avoid leaching. A total of 18 composite samples were obtained. The samples were exposed to the sun for three days, disaggregated and sieved. One gram of the sieved sample was digested with Aqua regia (a 3:1 mixture of HCl and HNO₃) on a hot plate. The filtrates obtained were preserved in polyethylene bottles for the analysis of micronutrients. The concentrations of copper, iron, manganese, and zinc were determined in the filtrate using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent 710 Model) following ISO/IEC 17025 (2017) and Rauret *et al.* (1999).

2.3 Determination of physicochemical properties of the agricultural soils

The pH of the samples was determined in a mixture of the soil with water using a pH meter after Van-Reeuwijk (1993). The organic matter contents of the studied soils were analysed following Walkley and Black (1934). The cation exchange capacity of the agricultural soils was determined by Aprile and Lorandi, (2012).

2.4 Statistical analysis

The statistical analysis of data obtained from this study was carried out with IBM SPSS Statistics 20 (IBM USA) model. Principal component analysis was performed with Varimax Factor analysis on 6 parameters and values from 0.507 and above were considered as significant. Hierarchical Cluster analysis was done with Dendrograms to identify the parameters with familiar properties and source.

3. Results and Discussion

Table 2: Physicochemical properties and essential metals in some agricultural soils

	pH	OM (%)	CEC (Cmolkg ⁻¹)	Cu (mgkg ⁻¹)	Fe (mgkg ⁻¹)	Mn (mgkg ⁻¹)	Zn (mgkg ⁻¹)
Uyo	5.60	23.46	8.72	6.24	256.05	115.30	7.47
Uruan	6.72	15.20	7.72	4.65	214.10	97.29	9.26
Nsit Ubium	5.59	10.14	6.56	6.21	231.08	124.16	6.89
Itu	5.65	18.76	8.43	5.46	246.72	112.45	7.82
Oron	6.26	16.83	7.78	4.58	220.17	104.31	9.43
Ibesikpo Asutan	6.41	21.68	8.61	4.47	226.83	102.26	9.54
Min	5.59	10.14	6.56	4.47	214.10	97.29	6.89
Max	6.72	23.46	8.72	6.24	256.05	124.16	9.54
Mean	6.04	17.68	7.97	5.27	232.49	109.30	8.40
SD	0.49	4.78	0.81	0.82	16.01	9.85	1.15
RSD	8.1	27.0	10.2	15.6	6.9	9.0	13.7

Min is Minimum; Max denotes maximum; SD signifies standard deviation; RSD indicates relative standard deviation.

Results for the physicochemical properties and essential metals of the studied soils are indicated in Table 2. The pH ranged between 5.59 and 6.72. The highest pH was recorded in the Uruan sample while the lowest was in Nsit Ubium. The pH range obtained in this study is consistent with 5.2 – 6.2 recorded in agricultural soils in Nigeria by Ubuoh *et al.* (2019). However, the range is lower than 4.15 – 8.51 reported by Marín-Pimentel *et al.* (2022) in agricultural soils of Colombia. Soil pH controls all the other variables in the soil including the availability and non-availability of essential metals (Oyedele *et al.*, 2008; Neina 2019). Hence, the pH level of agricultural soils should be properly managed to obtain the desired output. The pH levels of the studied soils were acidic and it may favour the bioavailability of soil nutrients (Oseni *et al.*, 2016; Adamczyk-Szabela and Wolf, 2022). The pH values of the agricultural soils at Uyo, Nsit Ubium, and Itu were below the recommended range of 6.0 – 9.0 by WHO (1998). Consequently, this may affect the availability of micronutrients in these farms since low soil pH may lead to low availability of nutrients (Grover *et al.*, 2021). This could be attributed to the impact of agrochemicals applied to these agricultural soils to improve crop yield (Otieno *et al.*,

2018; Etuk *et al.*, 2022). The mean value of pH obtained is within the acceptable range of 6.0 - 9.0 by WHO (1998).

Organic matter (OM) content of the farms investigated ranged from 10.14 to 23.46 %. The highest OM level was obtained on a farm in Uyo while the lowest was reported in Nsit Ubuim (Table 2). The obtained OM range is higher than 5.00 - 8.13 % reported by Bitondo *et al.* (2013) in agricultural soils within Cameroon. OM is another important soil property that can retain or release soil nutrients for plant uptake. It also has a significant influence on the cation exchange capacity, trace metal retention, and buffer capacity. The high OM contents reported in all the farms except Ibesikpo Asutan could be attributed to the application of biodegradable wastes materials as organic fertilizers to these locations. The relatively low OM content in agricultural soils within Ibesikpo Asutan could be attributed to the exclusive application of inorganic fertilizers (Jaja and Barber, 2017). The organic matter contents have no established limit that indicates negative implications.

The cation exchange capacity (CEC) of the studied farms varied from 6.56 Cmolkg^{-1} at Nsit Ubuim to 8.72 Cmolkg^{-1} recorded in the sample from Uyo (Table 2). The reported range is higher than 2.95 - 4.19 Cmolkg^{-1} obtained in Libya by Salem *et al.* (2020). The high mean value of CEC obtained in Uyo could be attributed to the high OM contents due to the application of wastes from dumpsites and wastewater from the fish pond. The CEC of the soil has a strong relationship with the organic matter and soil pH of the soil. CEC indicates the capacity of the soil to hold onto the exchangeable cations. Consequently, CEC has a significant influence on the availability of soil nutrients. Soils with high CEC are less vulnerable to the leaching of essential cations into the sub soil. The mean CEC value obtained ($7.97 \pm 0.81 \text{Cmolkg}^{-1}$) is below the recommended 1000.0 Cmolkg^{-1} for soil by WHO (1998). The low CEC of the studied agricultural soils is an indication of the low capacity of these farms to hold onto the nutrients. This may result in the leaching of the available soil nutrients into the sub soil far away from the plant roots. The levels of CEC reported in the studied agricultural soils are below the acceptable limits of 1000.0 Cmolkg^{-1} by WHO (1998).

Copper (Cu) in the agricultural soils assessed varied from 4.47 to 6.24 mgkg^{-1} (Table 2). The highest concentration was obtained at Uyo while the lowest was reported in the sample from Ibesikpo Asutan. The range recorded is lower than 10.20 - 15.07 mgkg^{-1} obtained by Bahiru and Teju (2019) in agricultural soils within Ethiopia. The high level of Cu obtained in the farm at Uyo could be attributed to the applications of biodegradable wastes and wastewater (Onuoha, 2017). The mean value of Cu obtained ($5.27 \pm 0.82 \text{mgkg}^{-1}$) in this study is below the recommended limit of 100.0 mgkg^{-1} by the National Environmental Standards and Regulation Enforcement Agency (NESREA), (2009). The low levels of Cu reported could be attributed to the OM and pH contents of the studied agricultural soils as reported by (Matijevic *et al.*, 2014). This is corroborated by the negative correlations between Cu and these parameters in Table 3. However, the levels of Cu in the studied agricultural soils are within the high category according to Mehlich, (1984) classifications. Hence, the quantity of Cu in these farms is enough for the proper growth and development of the plants cultivated.

A range of 214.10 - 256.05 mgkg^{-1} was recorded for the concentrations of iron (Fe) between Uruan and Uyo, respectively (Table 2). The obtained range is lower than 2214 - 4820 mgkg^{-1} reported in agricultural soils in Nigeria by Akporhonor and Agbaire (2009). The range of Fe obtained is within the medium class based on the classifications by Mehlich, (1984). The elevated level of Fe in the agricultural soil could be a result of wastewater used (Akhtar *et al.*, 2022). Consequently, the levels of Fe in the studied agricultural soils are not sufficient but are

enough to support normal metabolic activities in plants (Rout and Sahoo, 2015). The mean value of Fe reported ($232.49 \pm 16.01 \text{ mgkg}^{-1}$) in the studied farms is below the recommended 400.0 mgkg^{-1} by Federal Environmental Protection Agency (FEPA), (1999). Accordingly, the levels of Fe in these farms may not pose serious problem to the soil environment and the plants cultivated. The obtained concentrations of Fe in these farms might have been influenced by the soil pH (Celik and Katkat, 2007; Xie *et al.*, 2019). This is based on the negative correlations that Fe exhibited for the soil pH and Zn (Table 3).

Manganese (Mn) concentrations ranged from 97.29 to 124.16 mgkg^{-1} between Uruan and Nsit Ubium agricultural soils, respectively (Table 2). The reported range of Mn is below $73.8\text{--}735.72 \text{ mg kg}^{-1}$ obtained by Rani *et al.* (2022) in agricultural soils within India. The elevated level of Mn obtained in the agricultural soil at Nsit Ubium could be accredited to the agrochemicals applied (Mohammadpour *et al.*, 2016). The obtained range of Mn belongs to the medium class according to Mehlich, (1984). Hence, the levels of Mn in the studied farms can support the cultivated plants to perform their normal enzymatic and catalytic activities (Andresen *et al.*, 2018). However, the mean concentration of Mn ($109.30 \pm 9.85 \text{ mgkg}^{-1}$) is lower than **the** 437.0 mgkg^{-1} recommended for soil by NESREA (2009). Thus, the obtained levels of Mn in the studied farms may not pose **a** serious risk to the soil and plants cultivated. The strong negative correlations displayed by Mn for the soil pH and Zn is an indication of **the** significant negative influence of these parameters on Mn in these farms (Eteng, 2017; Martias *et al.*, 2021; Rolka and Wyszowski, 2021).

Zinc (Zn) in the studied agricultural soils varied between 6.89 and 9.54 mgkg^{-1} at Nsit Ubium and Ibesikpo Asutan farms, respectively (Table 2). The obtained range is below $41.9\text{--}87.4 \text{ mgkg}^{-1}$ obtained by Czarnecki and Düring (2015) in agricultural soils within Germany. The high Zn concentration reported **on** the farm at Ibesikpo Asutan might be caused by the intensive applications of piggery and poultry wastes (Oyewale *et al.*, 2019; Broom *et al.*, 2021). The range of Zn reported in the studied farms is classified as high by Mehlich, (1984). Accordingly, the levels of Zn in the studied farms are sufficient for the usual enzymatic, metabolic and oxidation-reduction processes in the cultivated plants (Hafeez *et al.*, 2013). The reported levels of Zn in the studied farms might have been supported by the soil pH but affected negatively by Cu, Fe, and Mn. This observation is substantiated by the strong positive relationship by Zn for the soil pH but significant negative association with Cu, Fe, and Mn. The mean concentration of Zn obtained ($8.40 \pm 1.15 \text{ mgkg}^{-1}$) is far lower than 421.0 mgkg^{-1} recommended for soil by NESREA (2009). Thus, the level of Zn in the studied agricultural soils may not impact negatively on the soil and plants.

The results indicated the values of relative standard deviation (RSD) otherwise known as **the** coefficient of variation (%) of the parameters as 8.1, 27.0, 10.2, 15.6, 6.9, 9.0, and 13.7 for pH, OM, CEC, Cu, Fe, Mn, and Zn, respectively. Based on the Pimentel-Gomes (2009) classifications of RSD, the pH, Fe, and Mn are in **a** low category, CEC, Cu and Zn belong to the medium class while OM is in the high group. Consequently, the degree of variability of these parameters from one location to the other was high in **the** organic matter **contents** than **in** other soil properties. This could be attributed **to** the variations in the type of manure and fertilizers applied to the different farms (Widowati *et al.*, 2020).

Table 3: Correlation between major soil properties and **micronutrients**

	pH	OM	CEC	Cu	Fe	Mn	Zn
pH	1.000						
OM	0.003	1.000					

CEC	0.076	0.973*	1.000				
Cu	-0.894*	-0.120	-0.222	1.000			
Fe	-0.833*	0.511**	0.456	0.741*	1.000		
Mn	-0.931*	-0.289	-0.390	0.914*	0.618*	1.000	
Zn	0.908*	0.253	0.320	-0.975*	-0.686*	-0.944*	1.000

*Correlation is significant at the 0.10 level, **Correlation is significant at the 0.20 level

Results for the correlation between the major soil properties determined and the micronutrients in the agricultural soils are shown in Table 3. The soil pH correlated negatively and significantly ($p < 0.10$) with Cu, Fe, and Mn however, pH showed a strong positive correlation ($p < 0.10$) with Zn. This shows that, the higher the pH of the soil, the lower the concentration of Cu, Fe, and Mn. This corroborates the reports that low pH favours metals mobility and low availability in soil (Sintorini *et al.*, 2021; Kicińska *et al.*, 2022). This is detrimental to agricultural farms as the levels of the existing soil pH are not encouraging the availability of these micronutrients for plants cultivated. Accordingly, the pH levels of the studied agricultural soils promoted the availability of Zn for plant uptake. Organic matter correlated positively and significantly ($p < 0.10$ and $p < 0.20$) with CEC and Fe, respectively. The result showed that the higher the organic matter contents of the soils, the higher the CEC as reported by Turrión *et al.* (2012) and Masmoudi *et al.* (2020). The CEC of the soils investigated showed a moderate positive association with Fe as reported by Kong *et al.* (2021). This could be attributed to the close relationship between Fe and clay which has high CEC values (Stucki, 2013; Churchman *et al.*, 2018; Kome *et al.*, 2019). Cu exhibited a strong positive relationship with Fe and Mn but, correlated negatively and significantly ($p < 0.10$) with Zn. Hence, a higher level of Cu in these farms may result in corresponding increase in Fe and Mn but, a decrease in Zn. The negative association of Cu with Zn confirms the antagonistic nature of these micronutrients in the soil as opined by Hafeez *et al.* (2013). Consequently, the availability of Zn in the studied agricultural soils could be strongly affected by Cu. Fe correlated positively and strongly with Mn but negatively with Zn at $p < 0.10$. The positive association of Fe with Mn is similar to the report by Alam & Ansari (2001) however, Fe correlated strongly and negatively ($p < 0.10$) with Zn as recorded previously by Zou *et al.* (2019). Consequently, a higher level of Fe may elevate the concentration of Mn but, reduce Zn content in the agricultural soils. Mn showed a strong negative correlation ($p < 0.10$) with Zn similar to the results obtained by Rolka and Wyzkowski (2021). Hence, if the level of Mn in the soil is elevated there may be a decrease in the concentration of Zn and vice versa.

Table 4: Result of principal component analysis demonstrating comparative loading for metals and other properties of the soil investigated

Variable	PC1	PC2
pH	-0.966	-0.142
OM	-0.138	0.980
CEC	-0.223	0.971
Cu	0.973	0.001
Fe	0.765	0.640
Mn	0.966	-0.173

Zn	-0.982	0.111
% Total Variance	63.3	34.0
Cumulative %	63.3	97.3
Eigen value	4.431	2.376

The principal component analysis (PCA) was used for the assessment of the factors accountable for the availability of the soil properties and micronutrients determined in the agricultural soils examined (Kahangwa, 2022). Results for the PCA of the parameters determined in the studied soils are shown in Table 4. The PCA revealed two main factors responsible for the accumulation of these parameters in the studied farms (Table 4). The said factors had Eigen values above one and 97.3% total variance. PC1 (Factor 1) donated 63.3% to the whole variance with strong positive loadings on Cu, Fe, and Mn but a significant negative loadings on pH and Zn (Table 4). This signifies the influence of anthropogenic and natural factors on the natural factor on the studied soils (Chibuike and Obiora, 2014; Zhang and Wang, 2020). PC2 (Factor 2) contributed 34.0% to the total variance with significant positive loadings on OM, CEC, and Fe (Table 4). This could be the impact of agrochemicals applied to the studied agricultural soils (Singh *et al.*, 2010; Ebong *et al.*, 2020).

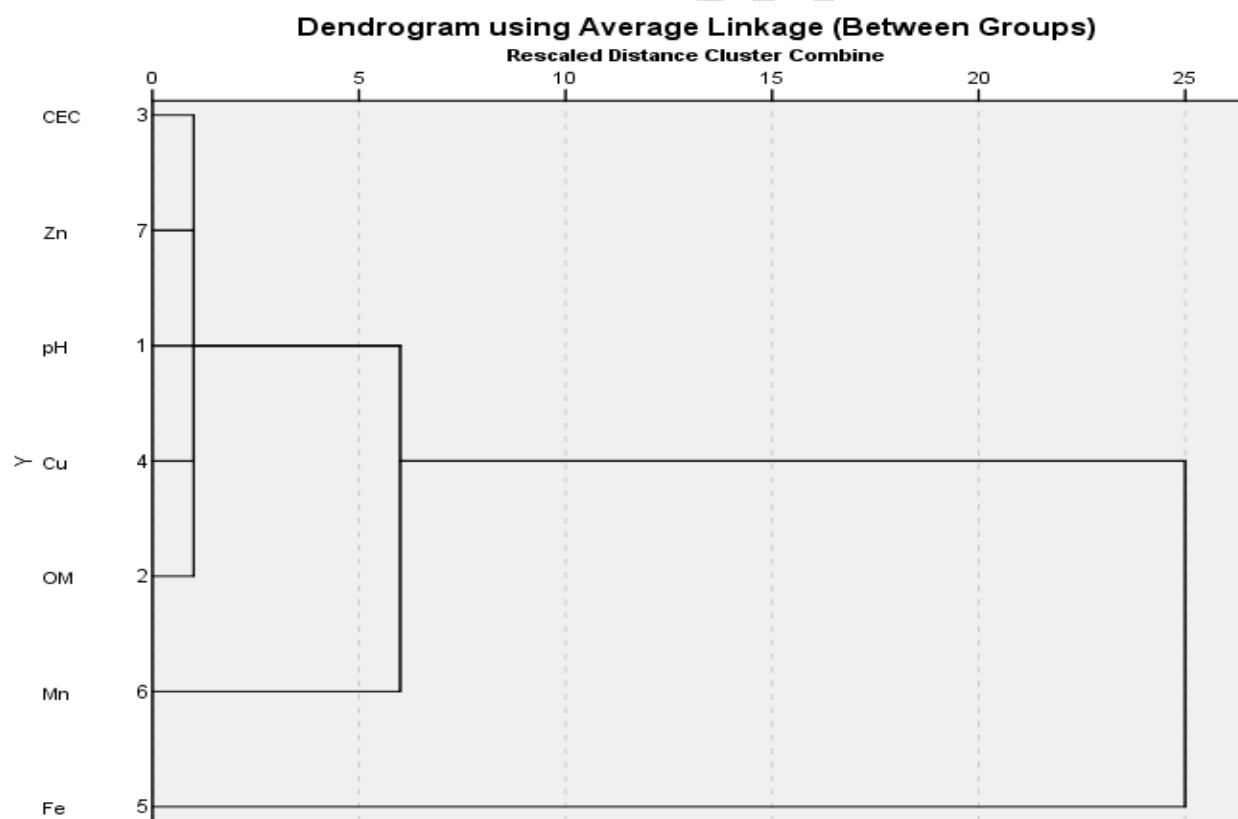


Figure 2: Hierarchical clusters of soil properties determined in the studied agricultural soils.

The hierarchical cluster analysis (HCA) was employed to identify the common source and properties for the parameters determined in the agricultural soils investigated (Sadiq, 2011;

Ebong *et al.*, 2022). Results for the HCA of the parameters in the studied soils are illustrated in Figure 2. The Figure shows three outstanding clusters namely: Cluster one connecting CEC, Zn, pH, Cu, and OM. The second cluster correlates only with Mn while the third cluster links with Fe only. These results showed a common source and character for the parameters in each group (Yang *et al.*, 2011).

Conclusion

The study conclude that, soil properties have a major role to play in the availability of micronutrients in agricultural soils. Consequently, these properties have a strong influence on plant yield and farm outputs. Apart from the natural influence, anthropogenic factor such as agrochemicals can influence the availability of micronutrients for plants uptake. The application of agrochemicals to improve plant yield may impact the soil properties and ultimately render the much-needed micronutrients unavailable for plants.

References

- Adamczyk-Szabela D, Wolf WM. The Impact of Soil pH on Heavy Metals Uptake and Photosynthesis Efficiency in *Melissa officinalis*, *Taraxacum officinalis*, *Ocimum basilicum*. *Molecules*. 2022; 27(15):4671. Doi: 10.3390/molecules27154671
- Afangideh AI, Okpiliya F, Ekanem E. The changing annual rainfall and temperature averages in the humid tropical City of Uyo, Southern Nigeria. *Afr J Environ Pollut Health*. 2005; 4: 54-61.
- Akinde BP, Olakayode AO, Oyedele DJ, Tijani FO. Selected physical and chemical properties of soil under different agricultural land-use types in Ile-Ife, Nigeria. *Heliyon*. 2020; 6(9):e05090. Doi: 10.1016/j.heliyon.2020.e05090.
- Akporhonor EE, Agbaire PO. Physiochemical properties and micronutrients status of farmland soils in Abraka, Nigeria. *African Journal of Pure and Applied Chemistry*. 2009; 3 (7): 131-134.
- Akhtar S, Luqman M, Farooq-Awan MU, Saba I, Khan ZI, Ahmad K, et al. (2022). Health risk implications of iron in wastewater soil-food crops grown in the vicinity of peri urban areas of the District Sargodha. *PLoS ONE*. 2022; 17(11): e0275497. <https://doi.org/10.1371/journal.pone.0275497>
- Alam SM, Ansari R. Influence of Iron and Manganese on the Growth and Contents of Fe, Mn and P in Rice. *Journal of Biological Sciences*. 2001; 1:434-435. DOI: 10.3923/jbs.2001.434.435
- Andresen E, Peiter E, Küpper H. Trace metal metabolism in plants. *J. Exp. Bot*. 2018; 69: 909–954. Doi: 10.1093/jxb/erx465
- Aprile F, Lorandi R. Evaluation of Cation Exchange Capacity (CEC) in tropical soils using four different analytical methods. *J. Agric. Sci*. 2012; 4: 278-289.
- Bahiru DB, Teju E. Levels of some selected metals (Fe, Cu and Zn) in selected vegetables and soil around eastern industry zone, central Ethiopia. *African Journal of Agricultural Research*, 2019; 14(2):78-91. DOI: 10.5897/AJAR2018.13615

- Benson N., Anake WU, Etesin UM. Trace metals levels in inorganic fertilizers commercially available in Nigeria. *Journal of Scientific Research & Reports*. 2014; 3(4): 610-620. <https://doi.org/10.9734/JSRR/2014/7465>
- Bitondo D, Tabi FO, Kengmegne SSA, Ngoucheme M, MvondoZe AD. Micronutrient Concentrations and Environmental Concerns in an Intensively Cultivated Typic Dystrandept in Mount Bambouto, Cameroon. *Open Journal of Soil Science*. 2013; 3: 283-288. <http://dx.doi.org/10.4236/ojss.2013.36033>
- Broom LJ, Monteiro A, Piñon A. Recent Advances in Understanding the Influence of Zinc, Copper, and Manganese on the Gastrointestinal Environment of Pigs and Poultry. *Animals*. 2021; 11(5):1276. <https://doi.org/10.3390/ani11051276>.
- Celik H, Katkat AV. Some Physical Soil Properties and Potassium as an Intensified Factor on Iron Chlorosis. *International Journal of Soil Science*. 2007; 2: 294-300. DOI: 10.3923/ijss.2007.294.300
- Chatzistathis T. (2018). The role of micronutrients in plants metabolism & growth and diagnostic tools to assess micronutrient deficiencies. Bentham Science Publishers, 19: 19 – 37. Doi: 10.2174/9781608059348114010006
- Chibuike GU, Obiora SC. (2014). Heavy Metal Polluted Soils: Effect on Plants and Bioremediation Methods. *Applied and Environmental Soil Science*. 2014: 752708. <http://dx.doi.org/10.1155/2014/752708>
- Chrysargyris A, Höfte M, Tzortzakis N, Petropoulos SA, Di-Gioia F. Editorial: Micronutrients: The borderline between their beneficial role and toxicity in plants. *Front. Plant Sci*. 2022; 13:840624. doi: 10.3389/fpls.2022.840624
- Churchman GJ, Singh M, Marchuk S. Seen as different, soil clays become more important to soils and also beyond soils. *New Zealand Journal of Agricultural Research*. 2018; 61(3): 340 – 346. <https://doi.org/10.1080/00288233.2018.1428204>
- Czarnecki, S. and Duering, R-A. (2015). Influence of Long-Term Mineral Fertilization on Metal Contents and Properties of Soil Samples Taken from Different Locations in Hesse, Germany. *Soil*, 1(1):23-33. DOI:10.5194/soil-1-23-2015
- Dhaliwal SS, Naresh RK, Mandal A, Singh R, Dhaliwal MK. Dynamics and transformations of micronutrients in agricultural soils as influenced by organic matter build-up: A review. *Environmental and Sustainability Indicators*. 2010; 1–2: 100007. <https://doi.org/10.1016/j.indic.2019.100007>.
- Diri KH, Tate JO. Assessing the Macronutrient Status of Some Selected Soils in Bayelsa State, South-South Nigeria. *Advanced Journal of Graduate Research*. 2020; 8(1):105-114. DOI:10.21467/ajgr.8.1.105-114
- Ebewore SO, Emaziye PO. Level of use of organic manure by farmers in Isoko North local government area of Delta State, Nigeria. *International Journal of Agricultural Extension and Rural Development Studies*. 2016; 3(1): 1-11.
- Ebong, G. A., Ettesam, E. S. and Dan, E. U. 2020. Impact of Abattoir Wastes on Trace Metal Accumulation, Speciation, and Human Health–Related Problems in Soils within Southern Nigeria. *Air, Soil and Water Research*, 13. 1–14. DOI: 10.1177/1178622119898430
- Ebong GA, Moses EA, Akpabio OA, Udombeh RB. Physicochemical properties, total concentration, geochemical fractions, and health risks of trace metals in oil-bearing soils of Akwa Ibom State, Nigeria. *Journal of Materials & Environmental Sustainability Research*. 2022; 2(4): 1-18. DOI: <https://doi.org/10.55455/jmesr.2022.009>

- Eteng EU. Soil factors influencing the Availability of Manganese in Soils of Agricultural Land-use System in a Coastal Plain Sands of Umudike. *International Journal of Agricultural Research, Sustainability, and Food Sufficiency*. 2017; 4(5) 218-228.
- Etuk HS, Ebong GA, Dan EU, Udoh HF. Probability of Health Risk, Bioaccumulation, and Geochemical Fractions of Toxic Elements in Soils and Vegetables Impacted by Manures in Nigeria. *Environmental Protection Research*. 2022; 2(2): 75–94.
- FEPA. Federal Environmental Protection Agency (FEPA). Guidelines and standard for environmental pollution control in Nigeria. Federal Ministry of Environment Publications, p. 206. 1999.
- Grover SP, Butterly CR, Wang X, Gleeson DB, Macdonald LM, Tang C. Liming and priming: the long-term impact of pH amelioration on mineralization may negate carbon sequestration gains. *Soil Secur*. 2021; 3 (2021):100007. DOI:10.1016/j.soisec.2021.100007
- Grujic D, Drinic M, Zivanovic I, Cakmak I, Singh BR. Micronutrient availability in soils of Northwest Bosnia and Herzegovina in relation to silage maize production. *Acta Agriculture Scandinavica, Section B- Soil & Plant Science*. 2018; 68(4): 301 – 310.
- Hafeez B, Khanif YM, Saleem M. Role of Zinc in Plant Nutrition- A Review. *American Journal of Experimental Agriculture*. 2013; 3(2): 374-391.
- ISO/IEC 17025. (2017). General Requirements for the Competence of Testing and Calibration Laboratories, 3rd ed. Geneva, Switzerland: ISO; 2017.
- Jaja ET, Barber LI. Organic and Inorganic Fertilizers in Food Production System in Nigeria. *Journal of Biology, Agriculture and Healthcare*. 2017, 7(18): 51 -55.
- Joseph M, Peter KD. Physicochemical properties of soils as influenced by physiography in Gwaara, Khana local government area of Rivers State Southern Nigeria. *Journal of Environment, Earth Sciences and Ecology*. 2020; 02(01):1 -10.
- Kahangwa CA. Application of Principal Component Analysis, Cluster Analysis, Pollution Index and Geoaccumulation Index in Pollution Assessment with Heavy Metals from Gold Mining Operations, Tanzania. *Journal of Geoscience and Environment Protection*. 2022; 10, 303-317. DOI: 10.4236/gep.2022.104019
- Katana C, Jane M, Harun M. Speciation of Chromium and Nickel in Open-Air Automobile Mechanic Workshop Soils in Ngara, Nairobi, Kenya. *World Environment*. 2013; 3(5): 143-154. Doi:10.5923/j.env.20130305.01
- Kicińska A, Pomykała R, Izquierdo-Diaz M. Changes in soil pH and mobility of heavy metals in contaminated soils. *The Electrochemical Society*. 2022; 73(1): e13203. <https://doi.org/10.1111/ejss.13203>
- Kihara J, Bolo P, Kinyua M, Rurinda J, Piikki K. Micronutrients in African soils and the human nutritional nexus: opportunities with staple crops. *Environmental Geochemistry and Health*. 2020; 42: 3015 – 3033. <https://doi.org/10.1007/s10653-019-00499-w>
- Kingsley J, Ayito EO, Akpan-Idiok AU, Effiom OD. Status and distribution of soil available micronutrients along a hillslope at Ekpri Ibami in Akamkpa Local Government Area of Cross River State, Nigeria. *African Journal of Agricultural Research*. 2019; 14(1):40-45. DOI: 10.5897/AJAR2018
- Kome G, Enang R, Tabi F, Yerima B. Influence of Clay Minerals on Some Soil Fertility Attributes: A Review. *Open Journal of Soil Science*. 2019; 9:155-188. Doi: 10.4236/ojss.2019.99010.

- Kong XZ, Li DC, Song XD, Zhang G.L. Quantitative Estimation of the Changes in Soil CEC after the Removal of Organic Matter and Iron Oxides. *Agricultural Sciences*. 2021; 12, 1244-1254. <https://doi.org/10.4236/as.2021.1211079>
- Kumar V, Kothiyal NC, Saruchi. Analysis of polycyclic aromatic hydrocarbon, toxic equivalency factor and related carcinogenic potencies in roadside soil within a developing city of Northern India. *Polycyclic Aromatic Compounds*. 2016; 36(4): 506-526.
- Marín-Pimentel G-E, Saa GR, Flores JCM. Evaluation of physicochemical properties in agricultural soils from Valle del Cauca-Colombia with an emphasis on degradation. *Research Square*. 2022; PPR: PPR535038. DOI: 10.21203/rs.3.rs-1984109/v1
- Martias, Hariyanto B, Purnama T, Nofiarli, Emilda D, Hendri, et al. Critical Level of Manganese in Soil and Leaves: It's Relationship to Fruit Quality of Mangosteen (*Garcinia mangostana* L.). *Annual Research & Review in Biology*. 2021; 36(9): 75-85. DOI: 10.9734/ARRB/2021/v36i930427
- Masmoudi S, Magdich S, Rigane H, Medhioub K, Rebai A, Ammar E. Effects of Compost and Manure Application Rate on the Soil PhysicoChemical Layers Properties and Plant Productivity. *Waste and Biomass Valorization*. 2020; 11:1883–1894 <https://doi.org/10.1007/s12649-018-0543-z>
- Mathew MM, Majule AE, Marchant R, Sinclair F. Variability of Soil Micronutrients Concentration along the Slopes of Mount Kilimanjaro, Tanzania. *Applied and Environmental Soil Science*. 2016: 9814316. <http://dx.doi.org/10.1155/2016/9814316>
- Matijevic L, Romc D, Romc M. Soil organic matter and salinity affect copper bioavailability in root zone and uptake by *Vicia faba* L. plants. *Environ Geochem Health*. 2014; 36(5):883-96. Doi: 10.1007/s10653-014-9606-7.
- Mehlich A. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis*. 1984; 15: 1409–1416.
- Mohammadpour GhA, Karbassi AR, Baghvand A. Origin and spatial distribution of metals in agricultural soils. *Global J. Environ. Sci. Manage*. 2016; 2(2): 145-156. DOI: 10.7508/gjesm.2016.02.005
- Mohiuddin M, Irshad M, Sher S, Hayat F, Ashraf A, Masood S, et al. Relationship of Selected Soil Properties with the Micronutrients in Salt-Affected Soils. *Land* 2022, 2022; 11(6): 845. <https://doi.org/10.3390/land11060845>
- Morgan JB, Connolly EL. Plant-Soil Interactions: Nutrient Uptake. *Nature Education Knowledge*. 2013; 4(8): 2.
- Neina D. The role of soil pH in plant nutrition and soil remediation. *Applied and Environmental Soil Science*. 2019: 5794869. <https://doi.org/10.1155/2019/5794869>
- Nenkam TLLJ, Kringel R, Fantong WY, Nbandah P, Takoundjou AF, Elisabeth Z, et al. Hydrochemistry of nutrients in groundwater under farmland in the Benue River Basin, North-Cameroon. *Environmental Earth Sciences*. 2022; 81:209. <https://doi.org/10.1007/s12665-021-10146-2>
- NESREA. National Environmental Standards and Regulation Enforcement Agency. *Regulations Vol. 96, 65*; the Federal Government Printer, Abuja, Nigeria. 2009.
- Nnaji JC, Egwu AC. Physicochemical Characteristics of Oil Spill Impacted Agricultural Soils in Three Areas of the Niger Delta. *Singapore Journal of Scientific Research*. 2020; 10: 137-144. URL: <https://scialert.net/abstract/?doi=sjsres.2020.137.144>

- Obi ME, Ebo PO. The effects of organic and inorganic amendments on soil physical properties and maize production in a severely degraded sandy soil in southern Nigeria. *Bioresource Technology*. 1995; 51(2-3): 117-123. [https://doi.org/10.1016/0960-8524\(94\)00103-8](https://doi.org/10.1016/0960-8524(94)00103-8).
- Olorunfemi IE, Fasinmirin JT, Akinola FF. Soil physico-chemical properties and fertility status of long-term land use and cover changes: A case study in Forest vegetative zone of Nigeria. *Eurasian Journal of Soil Science*. 2018; 7 (2): 133 -150 . DOI: 10.18393/ejss.366168
- Omemu OS, Abu GO, Onojake MC. Physico-chemical properties of soil samples impacted by hydrocarbons from selected sites in the Niger Delta Region of Nigeria. *Journal of Applied Chemical Science International*. 2022; 13(2):15-21. <https://doi.org/10.56557/jacsi/2022/v13i27457>
- Onuoha SC. Assessment of metal contamination in aquaculture fish ponds south eastern, Nigeria. *World Applied Sciences Journal*. 2017; 35(1):124-127. <https://doi.org/10.5829/idosi.wasj.2017.124.127>
- Orluchukwu JA, Amadi C. Effect of organic and inorganic fertilizers on the growth and yield of cucumber (*Cucumis sativa* L.) in South-South Nigeria. *International Journal of Agricultural Policy and Research*. 2022; 10 (2): 31-37. <https://doi.org/10.15739/IJAPR.22.005>
- Orisakwe OE, Oladipo OO, Ajaezi GC, Udowelle NA. Horizontal and Vertical Distribution of Heavy Metals in Farm Produce and Livestock around Lead-Contaminated Goldmine in Daretu and Abare, Zamfara State, Northern Nigeria. *Journal of Environmental and Public Health*. 2017; 2017: 1 – 12. <https://doi.org/10.1155/2017/3506949>
- Oseni OA, Taiwo AG, Ijaola TO, Yenusa LA. The Effects of pH On the Levels of Some Heavy Metals in Soil Samples of Five Dumpsites in Abeokuta and its Environs. *International Journal of Science and Research*. 2016; 5(9): 1543-1545. DOI: 10.21275/21031604
- Otaiku AA. Effects of oil spillage on soils nutrients of selected communities in Ogoniland, south-eastern Niger Delta, Rivers State, Nigeria. *International Journal of Ecology and Ecosolution*. 2019; 6(3): 23-36. DOI: 10.30918/IJEE.63.18.018
- Otieno HMO, Chemining'wa GN, Zingore S. Effect of Farmyard Manure, Lime and Inorganic Fertilizer Applications on Soil pH, Nutrients Uptake, Growth and Nodulation of Soybean in Acid Soils of Western Kenya. *Journal of Agricultural Science*. 2018; 10(4): 199 -208. Doi:10.5539/jas.v10n4p199
- Oyedele DJ, Gasu MB, Awotoye OO. Changes in soil properties and plant uptake of heavy metals on selected municipal solid waste dump sites in Ile-Ife, Nigeria. *African Journal of Environmental Science and Technology*. 2008; 3(5): 107-115.
- Oyewale AT, Adesakin TA, Aduwo AI. Environmental Impact of Heavy Metals from Poultry Waste Discharged into the Olosuru Stream, Ikire, Southwestern Nigeria. *J Health Pollut*. 2019; 9(22):190607. Doi: 10.5696/2156-9614-9.22.190607.
- Patrick, M., Tenywa, J. S., Ebanyat, P., Tenywa, M. M., Drake N. Mubiru, D. N., Basamba, T. A. and Leip, A. (2013). Soil Organic Carbon Thresholds and Nitrogen Management in Tropical Agroecosystems: Concepts and Prospects. *Journal of Sustainable Development*, 6(12):32-43. DOI: 10.5539/jsd.v6n12p31
- Pimentel-L-Gomes F. *Curso de estatística experimental*. 15^a ed. Piracicaba, FEALQ. P. 451. 2009.
- Rani YS, Jamuna P, Triveni U, Patro TSSK, Anuradha N. Effect of in situ incorporation of legume green manure crops on nutrient bioavailability, productivity and uptake of maize, *Journal of Plant Nutrition*. 2022; 45(7):1004-1016.

DOI: 10.1080/01904167.2021.2005802

- Rauret G, Lopez-Sanchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A., et al. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring*. 1999; 1, 57-61. <https://doi.org/10.1039/A807854H>
- Rolka E, Wyszowski M. Availability of Trace Elements in Soil with Simulated Cadmium, Lead and Zinc Pollution. *Minerals*. 2021; 11: 879. <https://doi.org/10.3390/min11080879>
- Rout GR, Sahoo S. Role of iron in plant growth and metabolism. *Reviews in Agricultural Science*. 2015; 3:1-24. Doi: 10.7831/ras.3.1
- Sadiq N. Principal Component and Clustering Analyses for Seasonal Classification of Karachi. *Pakistan Journal of Meteorology*. 2011; 7(14): 9 – 16.
- Salem MA, Bedade DK, Al-Ethawi L, Al-waleed SM. Assessment of physiochemical properties and concentration of heavy metals in agricultural soils fertilized with chemical fertilizers. *Heliyon*. 2020; 6: e05224. <https://doi.org/10.1016/j.heliyon.2020.e05224>
- Sha'Atoa R, Ajayib SO, Ojanugac AG. Total and extractable copper, iron, manganese and zinc in major agricultural soils in the Lower Benue Valley, Central Nigeria and the concept of extractant efficiency. *Nigerian Journal of Chemical Research*. 2012; 17: 59-82.
- Shukla AK, Behera SK, Pakhre A, Chaudhari SK. Micronutrients in Soils, Plants, Animals and Humans. *Indian Journal of Fertilisers*. 2018; 14 (4): 30-54.
- Singh A, Agrawal M, Marshall FM. The role of organic vs. inorganic fertilizers in reducing phytoavailability of heavy metals in a wastewater-irrigated area. *Ecol Eng*. 2019; 36(12):1733-1740.
- Sintorini MM, Widyatmoko H, Sinaga E, Aliyah N. (2021). Effect of pH on metal mobility in the soil. *The 5th International Seminar on Sustainable Urban Development IOP Conf. Series: Earth and Environmental Science*. 2021; 737 (2021) 012071. Doi:10.1088/1755-1315/737/1/012071
- Stucki JW. Chapter 11 - Properties and Behaviour of Iron in Clay Minerals. *Developments in Clay Science*. 2013; 5: 559-611. <https://doi.org/10.1016/B978-0-08-098258-8.00018-3>
- Turrión MB, Lafuente F, Mulas R, López O, Ruipérez C, Pando V. Effects on soil organic matter mineralization and microbiological properties of applying compost to burned and unburned soils. *J. Environ. Manag*. 2012; 95: 245–249.
- Ubuoh EA, Umezuruike SO, Nworuh BO, Emeka CC. Assessment of Soil pH and Heavy Metal Concentrations in Agricultural Land Impacted with Medical Waste Incinerator (MWI) Flue Ash (FA) in Abia State, Nigeria. *J. Appl. Sci. Environ*. 2019; 23(2): 275–282. DOI: <https://dx.doi.org/10.4314/jasem.v23i2.12>
- Ugochukwu N, Omeke JO, Eshett ET, Ihem EE, Aririguzo BN, Nathaniel OS. Some physico-chemical characteristics of arable soils around selected oil exploration sites in the Niger-Delta Region of Nigeria. *Int. Journal of Agric. and Rural Dev*. 2012; 15(3): 1298 – 1309.
- Van-Reeuwijk LP. Procedures for soil analysis. Wageningen: Technical Paper 9, ISRIC; pp. 16–18. 1993.
- Walkley A, Black IA. An Examination of the Degtjareff method for determining Soil Organic matter and proposed modification of the Chromic Acid titration method. *Soil Science*. 1934; 37, 29–38. <https://doi.org/10.1097/00010694-193401000-00003>
- WHO. Guidelines for Drinking water WHO criteria and other supporting information, WHO, Geneva. p. 130. 1998.

- Widowati, Sutoyo, Karamina H, Fikrinda W. Soil amendment impact to soil organic matter and physical properties of the three soil types after second corn cultivation. *AIMS Agriculture and Food*. 2020; 5(1):150-168. Doi:10.3934/agrfood.2020.1.150.
- Xie X, Hu W, Fan X, Chen H, Tang M. Interactions between phosphorus, zinc, and iron homeostasis in nonmycorrhizal and mycorrhizal Plants. *Front. Plant Sci*. 2019; 10:1172. Doi: 10.3389/fpls.2019.01172
- Yang Z, Lu W, Long Y, Bao X, Yang Q. Assessment of heavy metals contamination in urban topsoil from Changchun City, China. *J. Geochemical Explor*. 2011; 108: 27-38.
- Zewide I, Sherefu A. Review Paper on Effect of Micronutrients for Crop Production. *J. Nutrition and Food Processing*. 2021; 4(7): 1-8. DOI:10.31579/2637-8914/063
- Zhang Q, Wang C. Natural and Human Factors affect the distribution of soil heavy metal pollution: A review. *Water Air Soil Pollut*. 2020; 231: 350. <https://doi.org/10.1007/s11270-020-04728-2>
- Zou C, Du Y, Rashid A, Ram H, Savasli E, Pieterse PJ, et al. Simultaneous Biofortification of Wheat with Zinc, Iodine, Selenium, and Iron through Foliar Treatment of a Micronutrient Cocktail in Six Countries. *Journal of Agricultural and Food Chemistry*. 2019; 67(29): 8096-8106. DOI: 10.1021/acs.jafc.9b01829
- Zwolak A, Sarzyńska M, Szpyrka E, Stawarczyk K. Sources of soil pollution by heavy metals and their accumulation in vegetables: A review. *Water, Air and Soil Pollution*. 2019; 230(7): 164. <https://doi.org/10.1007/s11270-019-4221-y>