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Anthropogenic Influence on Soil Quality Dynamics and Potential Ecological Risk in Agricultural Soils of the Nworie River Watershed, Nigeria

Ubuoh Emmanue Attah[1*], Ofoegbu Clara Chinwendu[2], Boise Ekene[3]

Michael Okpara University of Agriculture, College of Natural Resources and Environmental Management,
1&2Department of Environmental Management and Toxicology, Nigeria.
3University of Benin, Benin City, Faculty of Life Sciences, 3Department of Environmental Management and Toxicology, Nigeria.

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Abstract

The study assessed soil nutrients and heavy metals in agricultural soils along Nworie River watershed at three depths: 0 – 15, 15 – 30, and 30 - 45cm. The results indicated that the soil was predominantly sandy with a moderate acidity of 5.2. Except for base saturation, other physicochemical parameters were below the WHO/FAO critical limits. Ratings of soil nutrients in agricultural soils recorded low nitrogen, moderate available P, very low to low exchangeable $K^{+,}$ and low to moderate exchangeable Ca^{+}. Positive and negative correlations exist between physicochemical characteristics and heavy metals. Geo-accumulation (I_{-geo}) ranges from uncontaminated to moderately contaminated. The pollution load index (PLI) recorded ≤ 1 signifying no pollution. The potential risk factors (prf) ranged from low potential to considerably potential risks in order of Cd ≥ Pb ≥ Cu ≥ Zn ≥ Cr. The potential ecological risk index and risk assessment code examined indicated that of the metals sampled, Cd posed the most significant environmental risk associated with complex human activities like indiscriminate application of inorganic fertilizer, waste disposal, and ill-farming practices along the slopes of the watershed. Therefore, anthropogenic sources that degraded agricultural soils within the watershed should be avoided through enforcement of the existing environmental laws.

Keywords: Anthropogenic pollution, Agricultural soils, Toxic elements, Ecological risk, Nworie watershed

1. Introduction

Soil is an important resource for life that provides a variety of goods and services to meet human needs on earth (Garcia-Ruiz et al., 2015; Anache et al., 2017), and is a key factor for sustainable development in the terrestrial world (Ubuoh and Ogbonna, 2018). The improper practices of agriculture could result in anthropogenic impacts on existing natural resources (Zawadzka and Łukowski, 2010), and have become a global environmental issue and concern (Chen et al., 2017; Shao et al., 2018).

The existence of these heavy metals in soil is of great problem due to their potential toxicity (Khan et al., 2015). These metals are indestructible and most of them are categorized as of high toxicity to plants, animals, and humans even at low concentrations (Khan et al., 2015). Environmental factors that govern the transfer mechanism such as soil characteristics have to regulate heavy metal accumulation levels in plants (Velickovic et al., 2016). Noticeably, soil physicochemical characteristics, including pH (Ubuoh et. al., 2019, Ubuoh et al., 2020a), electrical conductivity (EC), organic matter content, and cation exchange capacity (CEC) have been found to affect the absorption of metals in plants (Yu et al., 2014). However, the same soil property can have multiple variant effects on different heavy metal plant systems (Yu et al., 2014). For instance, a study reported that the soil CEC and exchangeable calcium (Ca) are important indices for predicting the critical value of nickel (Ni) in barley and tomato (Rooney et al., 2007), whereas two other reports found that soil pH rather than soil CEC significantly affects the critical value of Ni toxicity in barley or tomato (Zhang et al., 2009; Li et al., 2011). On the other hand, the control of pollution sources is required to minimize their impact, where soils are generally described as geochemical sinks that are normally associated with heavy metals; and also sources for the movement or migration of the metals to other ecological systems (Abbas et al., 2011).

The accumulation effects of heavy metals in drainage basins have been previously investigated at the Pearl River Delta (Zhang et al., 2015), the Luan River (Liu et al., 2009), and the Yangtze River (Yi et al., 2011). However, analyzing soil properties in agricultural soil within Nworie is of great importance in evaluating the safety risks of farmlands for crops safety and farmers' survival void of toxic elements. Its watershed is used for intensive human and industrial discharge of the various pollutants both organic and inorganic in nature (Acholonu et al., 2008), from solid waste dumpsites (Ubuoh et al., 2014). Other activities include emission of automobile exhaust, automobile workshops, building constructions, road construction, destroyed vegetation mostly grasses, and polluted water and sand mining. Recent studies have also shown that the flood plain serves as a waste dumpsite that polluted soils (Ibe et al., 2017).

Meanwhile, regular monitoring and assessment of agricultural soil on Nworie valley slopes are necessary to

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* Corresponding author e-mail: ubuohemmanuel@yahoo.com

assess the impact of human activities on soil quality and the pollution/contamination status (Gotelli and Ellison, 2004). To assess the severity of soil contamination and to distinguish between natural and anthropogenic inputs in the soil, several approaches like Geo-accumulation Index (I_{-geo}), contamination factors (CF), and Pollution Load Index (PLI) have been applied (Manoj et al., 2012; Mohsen and Alireza, 2014).

The study focused on the assessment of the dynamics of soil quality in agricultural and heavy metals in an area prone to human-induced activities using different multivariate approaches and assesses the degree of soil pollution, potential ecological risk, and identifying the local sources of contamination and pollution respectively.

2. Materials and Methods

2.1 Study Area:

Nworie river is about 5km long and it lies between latitudes 5^0 4' and 6^0 3' N and longitude 6^0 15'and 7^0 34' E. It falls within the rainforest zone with an annual rainfall of 2290 mm, relative humidity of 55-85%, and temperature of 27^0C. The river course, however, covers an area of about $5km^2$ from its source to the point where it empties into the Otamiri River to form a confluence (Duru and Nwanekwu, 2012). Currently, human activities exist in the watershed including sand mining, waste disposal, fishing, mechanic workshop, effluent from residential areas and hospitals, and agricultural activities.

2.2 Soil Sampling and preparation

A reconnaissance survey was undertaken to identify the soil sampling sites and indeed familiarize them with human activities within the Nworie River catchment. **The samples were collected during the dry season event.** Soil samples were collected in a randomized method along the valley slope of Nworie River (Figure 1), where human activities were pronounced using an auger-boring instrument at the depths of 0 – 15cm depth (topsoil) and subsoils 15 – 30cm and 30 -45cm according to coordinates (Table 1). The collected soil samples were poured into polythene bags, labeled adequately, and transported to the laboratory immediately for analyses. The soils sampled were air dried at room temperature for sieving. The sampled soil was grounded and sieved with a 2 mm mesh sieve according to standard protocol by the Food and Agricultural Organization (FAO) (2006) and kept for further analysis.

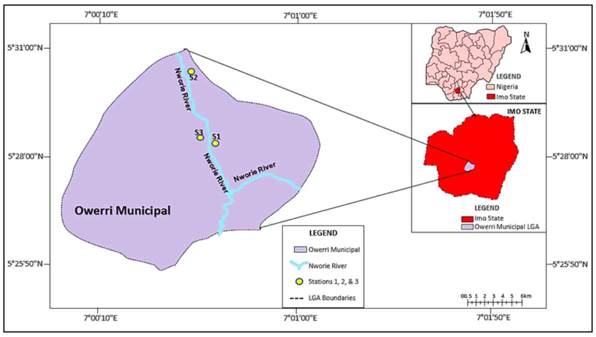

Figure 1. Location map of the study area

Table 1. Soil Sampling Points and Coordinates

Locations	Coordinates	Human activities
Egbeada : SSP_1	N05^{o}29' 10.9" , E 007^o 01'43.5"	Sand mining, Waste dump, erosion, farming, mechanic workshop
Amakohia :SSP_2	N 05^{o}30'56.6" , E 007^o 00'59.2"	Sand mining, Waste dump, farming, runoff
Umezuruike Hospital :SSP_3	N 05^{o}29'16.1" , E 007^o 01'30.0"	Waste dump, hospital effluent discharge, road construction, urban runoff

2.3 Soil physical characteristics:

Particle size distribution expressed in percentage (sand, silt, and clay) was measured by the hydrometer method (Gee and Or, 2002). The soil texture was determined using the soil textural triangle based on the percentages of the different soil particle sizes (Sutherland and Dejong, 1990).

2.4 Soil chemical characteristics:

The soil pH was determined using procedures by Min Liu et al. (2004). The percentage of soil organic carbon was measured using the method by Walkley and Blacks (1965). Percentage soil organic matter is considered the total carbon multiplied by a conversion factor of 1.72 (Chikwendu et al., 2019). Soil Nitrogen was determined using the method by Dhyan et al. (1999). Available phosphorus was determined using the Bray No. 1 extraction method (Bray and Kurtz, 1945). Potassium and Sodium were determined by the flame emission photometer (Pinta, 1970). Calcium and magnesium were determined using the ethylene-diamine–tetracettic-acid (EDTA) method (Allison, 1973). The exchangeable acidity and the exchangeable aluminum were determined by titration as described by Juo (1975). Effective Cation Exchange Capacity (ECEC) was obtained as the summation of exchangeable cations and exchangeable acidity. To calculate the percent base saturation, the sum of the Potassium (K), Magnesium (Mg), Calcium (Ca), and Sodium (Na) (the bases) in Meli equivalent per 100g of soil (Meg/100mg soil) was divided by the CEC and result was multiplied with 100%. Thereafter, the result was compared with the acceptable nutrient standards for soil quality for agriculture by FAO/WHO, and other important environmental standards respectively.

2.5 Soil heavy metals digestion:

Aqua-regia wet digestion was used for the estimation of the selected heavy metals. The extractants were prepared using mixed concentrated HCl with concentrated HNO_3 in 3:1 and the mixture was allowed to mix properly for 5 hours; 10 g of soil samples were taken in acid-washed beakers and 30 ml of aqua-regia was introduced. The mixture was reduced to 10–20 mL by heating at 9^oC on a hot plate according to Enyoh and Isiuku (2020). Accordingly; the mixture reduced was allowed to cool and made to a final volume of 50 mL by addition of de-ionized water, followed by filtration resulting in the filtrate.

2.6 Soil heavy metal determination:

The digested filtrates were used for the total metal quantification using Atomic Absorption Spectrophotometer (Perkin Elmer A Analyst 400). The characteristic wavelengths of metals determined were first set using the hollow cathode lamp, and the digested filtrate samples were aspirated directly into the flame.

2.7 Quality Control and Quality Assurance (QC/QA):

Quality control and quality assurance (QC/QA), accuracy, and precision (A/P) were verified using reference materials sediment-certified samples "GBW07311 (GSD-11) and GBW07366 (GSD-23) of the National Center of China". Equipment for soil analysis was calibrated before soil analysis. The blanks in every set were tested in duplicates using Standard reference material GBW07405 (National Research Center for Standards in China) was used to verify analytical accuracy, and results were presented in mean values of duplicated analysis. For repeat tests, soil samples were picked randomly. All glasses, plastics, and quartz were cleaned and rinsed using 10% HNO_3, and ultrapure water (18.25 $Mohmcm^{-1}$) was used to rinse every time

3. Three Assessments of contamination in agricultural soils

In this study, geo-accumulation index (I-$_{geo}$), contamination factor (), degree of contamination (Cd), ecological risk factor (), and pollution load index (PLI) were calculated to assess the heavy metal contamination levels and associated risk in agricultural soils understudies.

3.1 Geo-accumulation index (I-geo):

Index of Geo-accumulation (I_{-geo}) was introduced to assess metal pollution in sediments and has been applied in recent pollution studies to enable the qualitative assessment of soil contamination by heavy metals (Yaylali-Abanuz, 2011; Bentum et al., 2017). I-$_{geo}$ is computed by:

$$I\text{-}_{geo} = log_{2\left(\frac{Cn}{1.5Bn}\right)} \quad (1)$$

Where;

C_n is the concentration of the element in the tested soil, B_n is the geochemical background value in the average shale of element (Loska et al., 2004), and the constant 1.5 compensates for natural fluctuations of given metal and minor anthropogenic impacts (Taylor and McLennan, 1995). The seven classes of I_{-geo} as proposed by Müller are as follows: $I_{-geo} \leq 0$, uncontaminated (UC) (Class 0); $0 < I_{-geo} \leq 1$, uncontaminated to moderately contaminated (UNC) (Class 1); $1 < I_{-geo} \leq 2$, moderately contaminated (Class 2); $2 < I_{-geo} \leq 3$, moderately to heavily contaminated (MHC)(Class 3); $3 < I_{-geo} \leq 4$,heavily contaminated (HC) (Class 4); $4 < I_{-geo} \leq 5$, heavily to extremely contaminated(HEC) (Class 5); $I_{-geo} > 5$, extremely contaminated (EC) (Class 6).

3.2 Contamination factor (C_f^i) and Contamination degree (Cd):

Contamination factor (CF) is expressed as a ratio of every metal in the present sample to the background values in the same metal. Assessment of soil contamination is performed by the contamination factor (C_f^i) and degree of contamination (Cd) (Table 2):

$$C_f^i = \frac{C_s^i}{C_n^i}, \ \text{Cd} = \sum_i^m C_f^i \quad (2)$$

Where,

SI is the content of metal I, and is the reference value, baseline level, or national criteria of metal i. The contamination factor can be categorized according to their values from 1 to 6 "if CF ≤ 1,low contamination (LC); 1 ≥ CF ≤ 3, moderate contamination ; 3 ≤ CF ≤ 6, considerable contamination ; CF ≥ 6, very high contamination (VHC) (Hakanson, 1979).

Table 2. Classification of Degree of contamination

Classes	Indications	Acronym
Cd<8	Low degree of contamination	LDC
8≤cd<16	A moderate degree of contamination	MDC
16≤cd<32	A considerable degree of contamination	CDC
32≤cd	A very high degree of contaminated	VHDC

3.3 Potential Ecological Risk Index

The Potential Ecological Risk Index, advanced by Hakanson (1980), which represents the toxicity of heavy metals and the extent of pollution of the environment, is defined as:

$$\boldsymbol{R1 = Er^i = \sum(T_i \times C_{i}/B_i)} \quad (3)$$

Where,

R1 is the risk index and calculated as the sum of all six risk factors for heavy metals in soils, *Eri* is the single potential ecological risk factor, T_i is the developed metal toxicity factor. C_i /B_i is the metal pollution factor, C_i is the practical concentration of metals in soil, and B_i is the background value for metals.

3.4 The ecological risk factor (E_r^i)

The ecological risk factor (E_r^i) (Table 3), to quantitatively express the potential ecological risk of a given contaminant also suggested by Hakanson (1980), and expressed mathematically:

$$\boldsymbol{E_r^i = T_r^i C_f^r \quad , \left(C_f^r = \frac{c_0^i}{c_n^i} \right)} \quad (4)$$

Where, the single potential ecological risk factor, is the toxic response factor for a given metal, is the contamination factor, the concentration of metals in agricultural soil, and is the reference value for metals.

Table 3. Descriptive Ecological Risk factor (Eri)

Classes	Indicators	Acronym
Eri≤40	Low potential ecological risk	LPER
40≤ Eri<80	Moderate potential ecological risk	MPER
80≤ Eri<160	Considerable potential ecological risk	CPER
160≤ Eri<320	High potential ecological risk	HPER
Eri≥320	very high ecological risk	

Hakanson (1980),

3.5 Ecological risk index (Ir)

$$I_r = \sum_i^n E_r^i = \sum_i^n T_r^i C_f^i = \sum_i^n T_r^i C_f^i / C_n^i \quad (5)$$

Where the symbols are as described above, Table 4 lists the classes.

Table 4. Descriptive Table for Ecological Risk index (Ir)

Classes	Indications	Acronym
Ir<150,	low ecological risk	LER
150≤ Ir<300	moderate ecological risk	MER
300≤ Ir<600	considerable ecological risk	CER
Ir>600	very high ecological risk	VHER

3.6 Pollution Load Index (PLI)

The pollution load index (PLI) has been used in this study to measure the pollution load of metals from agricultural soils (HIS, 1998). The pollution load index is expressed as the ratio of the metal concentration in the study to the background content of the abundance of chemical elements in the continental crust (Dos Anjos et al., 2000). PLI for the soil samples was determined by the equation below, as proposed by Tomlinson et al. (1980). The PI of each element is classified as either low (PLI ≤ 1), middle (1 < PLI ≤ 3), or high (PLI ≥ 3) (Chen et al., 2005), and mathematically expressed as:

$$\mathrm{PLI}= (\mathrm{CF_n} \times \mathrm{CF_n} \times \mathrm{CF_n} \times \mathrm{CF_n} \times \mathrm{CF_n} \times \mathrm{CF_n})^{\frac{1}{n}} \text{............} \quad (6)$$

Where,

PLI, pollution load index, contaminant factor, n is the observed metal,

3.7 Statistical analytical technique

Analysis of Variance (ANOVA) was used to test for differences between means at a 5%level of significance. Duncan's multiple post hoc test was used to obtain the specific significant differences among the sampling intervals using the GenStat Release 9.2 (PC/Windows), with the inference drawn at a P≤0.05 significant level. Person's correlation analysis was used to establish a relationship between soil quality parameters, while principal component analysis (PCA) was used to determine precise contamination sources (Verla et al., 2020). The factor loadings for heavy metals in the soils were extracted based on Eigen value >1 (Ubuoh et al., 2019).

4. Results and Discussion

The results represented the mean ± standard deviation of the soil physicochemical characteristics of the agricultural land in Tables 5 and 6.

Table 5. Mean ±SD of physical properties of soil in Nworie River watershed.

Sample location	Soil depth (cm)	Sand %	Silt %	Clay %	Textural Class*
Soil sample point (SSP $_1$)	0-15	82.78 ±1.501^a	7.673 ±1.276^a	9.543±0.229^a	Loamy sand (LS)
Upper course (UC)	15-30	82.89 ±1.529^a	7.580±1.251^a	9.530±0.279^a	Loamy sand (LS)
Catchment	30-45	82.55 ±1.297^a	9.017±1.025^a	8.433±0.843^b	Loamy sand (LS)
	Mean	82.74	8.090	9.169	
	%Cv	1.9	15.9	5.8	
	Se	1.550	1.283	0.535	
Soil sample point (SSP$_2$)	0-15	85.12±1.633^b	5.280±0.658^b	9.597±1.032^a	Loamy sand (LS)
Middle course (MC)	15-30	89.28±1.502^a	3.200±1.276^a	7.517±0.229^b	Loamy sand (LS)
Catchment	30-45	87.63±1.160^a	3.470±0.506^a	8.958±0.826^a	Loamy sand (LS)
	Mean	87.35	3.966	8.689	
	%Cv	1.0	13.5	6.6	
	Se	0.872	0.535	0.076	
Soil sample point (SSP$_3$)	0-15	82.78±1.786^a	7.673±1.523^a	9.543±0.266^a	Loamy sand (LS)
Lower course (LC)	15-30	82.55±1.297^a	8.983±0.980^a	8.467±0.809^b	Loamy sand (LS)
Catchment	30-45	82.78±1.786^a	7.673±1.523^a	9.544±0.266^a	Loamy sand (LS)
	Mean	82.71	8.110	9.184	
	%Cv	2.0	16.8	5.6	
	Se	1.640	1.366	0.515	
	Overall CV (%)	1.6	10.4	6	
	Overall mean	84.3	6.7	9.0	

Different letters refer to significant differences between mean + standard deviation of different depths, similar letters refer to the insignificant difference between mean+ standard deviation of different depths Se= standard error, %CV = coefficients of variation.

4.1 Physical Characteristics

Particle size distribution recorded the mean values of 82.74% at the upper river catchment, 87.35% middle river, and Lower River at 82.71% with the overall mean value of 84.3% (Table 5). Except for the soil depth of 0-15cm that recorded a significant difference, other soil depths at the SSP $_{1\text{-}3}$ were significantly the same at *P*≤ 0.05 level. The sand abundance was in the order of UC ≥ MC ≥ LC. The overall mean value of sand being 84.3% in the study is greater than the76.29 % (Challawa,), 75.7% (Eyong and Akpa, 2019) in forested soil in Agoi-Ibami, Cross River State, Nigeria, 80.48% (Jakarta), and 73.41% (Watari) agricultural land in Kano, Nigeria respectively (Dawaki et al., 2013), suspected to be influenced by parent material. Silt recorded the mean values of 8.090 % for the upper course, 3.966% middle course, and 8.110% for the lower course with the overall mean value of 6.7%, with 0.15cm of the middle course (SSP$_2$) being significantly different from others at p ≥ 0.05 level. The silt was in decreased abundance order: UC ≥ MC ≥ LC. The overall mean value of silt is far less than 25.28±11.96 % of silt from anthropogenic sites in Abeokuta, Nigeria (Olayinka et al., 2017), and far below the 30% silt critical value for agriculture (FAO, 2014). Clay recorded mean values of 9.169% in the upper course, 8.689% middle course, and lower course 9.184% with an overall mean value of 9.0%. Clay content at soil depths 30-45cmUC, MC and 15-30cm (LC) were significantly the same and significantly different from others at P ≥ 0.05 levels. The mean clay contents recorded were higher than clays (6–10 Cmol/kg) in the soils of colluvial deposits in Akamkpa, Nigeria (Aki and Ediene, 2018). Kingsley et al. (2020) reported a low CEC to low activity of clay. Clay was in decreased trend of LC ≥ UC ≥ MC. The overall mean value of soil fractions was in decreased trend: Sand ≥ Clay and Silt, with sand dominating, indicating typical soils of the coastal plain sands (Osakwe and Okolie, 2015). The result agreed with the findings of Onweremadu et al. (2011), Osujieke et al. (2016) who reported high sand and low clay in Southern Nigeria. The result is in agreement with World Reference Base (FAO, 2014), which reported sandy clay loamy content as a dominant fraction in agricultural soil, influenced by parent material (Osujieke et al., 2016).

Table 6. Mean ± SD of chemical properties of agricultural soil in Nworie River watershed

Study location/ Soil depth	pH	P (mglkg)	N%	OC%	OM%	Exchangeable bases (cmol/kg)				EA	ECEG	%BS
						Ca (cmol/kg)	Mg^{2+} (cmol/kg)	K (cmol/kg)	Na (cmol/kg)			
SSP_1	Upper course											
0-15 cm	5.2±0.265^{a}	17.3±0.351^{a}	0.1±0.404^{a}	0.9±0.100^{a}	1.5±0.173^{a}	2.7±0.503^{a}	1.7±0.265^{a}	0.2±0.022^{a}	0.1±0.015^{a}	0.9±0.202^{a}	5.6±0.421^{a}	83.1±2.403^{a}
15-30 cm	4.5±0.557^{a}	13.3±0.818^{b}	0.6±0.012^{b}	0.4±0.091^{b}	0.7±0.157^{b}	2.7±0.321^{a}	1.1±0.115^{b}	0.1±0.022^{b}	0.1±0.005^{b}	1.1±0.129^{a}	5.0±0.315^{a}	78.5±1.263^{a}
30-45cm	4.9±0.321^{a}	8.9±0.404^{c}	0.05±0.010^{b}	0.5±0.126^{c}	0.8±0.183^{b}	2.6±1.155^{a}	1.2±0.152^{b}	0.1±0.010^{c}	0.1±0.003 ^{b}	1.1±0.092^{a}	5.1±0.978^{a}	78.1±4.660^{a}
Mean	4.869	13.19	0.068	0.592	1.021	2.7	1.333	0.1	0.114	1.038	5.3	79.92
Cv%	8.5	4.8	21.1	17.3	17.4	27.1	14.1	13.7	10.3	9.5	13.5	3.6
Se	0.414	0.627	0.015	0.103	0.177	0.723	0.187	0.017	0.012	0.099	0.714	2.871
SSP_2	Middle course											
0-15 cm	5.6±0.127^{a}	21.6±1.273^{a}	0.3±0.021^{a}	0.9±0.035^{a}	1.6±0.037^{a}	3.5±1.273^{a}	1.7±0.707^{b}	0.1±0.032^{a}	0.1±0.017^{a}	1.0±0.778^{a}	6.6±0.261^{ab}	84.6±8.860^{a}
15-30 cm	5.0±0.177^{a}	9.9±0.212^{b}	0.05±0.010^{a}	0.4±0.033^{b}	0.8±0.064^{b}	4.6±0.728^{b}	1.7±2.05^{b}	0.2±0.019^{ab}	0.1±0.006^{a}	0.9±0.707^{a}	7.4±2.085^{a}	88.1±12.49^{a}
30-45cm	5.4±0.247^{a}	9.2±0.884^{b}	0.04±0.020^{a}	0.5 ±0.042^{b}	0.8±0.078^{b}	1.3±0.707^{c}	3.4±0.778^{a}	0.1±0.014^{c}	0.1±0.049^{b}	0.9±0.212^{a}	5.8±1.336^{c}	83.7±3.189^{a}
Mean	5.3	13.60	0.1	0.6	1.0	3.1	2.3	0.2	0.1	0.938	6.6	85.4
Cv%	8.0	7.7	164.5	15.0	14.9	14.9	17.6	14.6	11.7	21.7	8.9	3.8
Se	0.500	1.051	0.232	0.091	0.156	0.468	0.400	0.022	0.014	0.204	0.588	3.27
SSP_3	Lower course											
0-15 cm	5.0±0.085^{a}	23.7±1.473^{b}	0.1±0.016^{b}	1.3±0.625^{a}	2.2±1.078^{a}	3.6±0.451^{a}	1.3±0.503^{a}	0.1±0.018^{b}	0.1±0.012^{b}	0.8±0.132^{a}	5.9±0.411^{b}	86.8±1.348^{b}
15-30 cm	5.2±0.200^{a}	27.2±2.002^{a}	0.2±0.025^{a}	2.3±0.626^{a}	4±1.079^{a}	4.2±0.764^{a}	2.5±0.473^{a}	0.2±0.013^{a}	0.2±0.022^{a}	0.8±0.127^{a}	7.8±1.009^{a}	90.03±0.88^{a}
30-45cm	5.5±0.500^{a}	7.4±0.557^{c}	0.03±0.006^{c}	0.2±0.081^{b}	0.4 ±0.141^{b}	5±0.917^{a}	2.5±0.503^{a}	0.1 ±0.015^{c}	0.1±0.008^{b}	0.8± 0.136^{a}	8.5±1.080^{a}	90.8±0.710^{a}
Mean	5.2	19.4	0.1	1.3	2.2	6.0	2.1	0.1	0.1	0.8	7.4	89.2
Cv%	6.0	7.6	17.5	40.6	40.7	17.3	23.4	10.6	11.9	16.8	11.9	11.1
Se	0.315	1.479	0.018	0.513	0.885	0.736	0.493	0.015	0.015	0.132	0.886	1.017
Overall mean	5.15	15.4	0.1	0.82	1.41	3.9	1.9	0.14	0.12	0.92	14.4	86.2
Overall CV	7.5	6.7	17.9	24.3	24.3	19.7	18.3	13	11.3	15.9	11.4	6.2

Different letters refers to significant differences between mean + standard deviation of different depth, similar letters refers to insignificant difference between mean+ standard deviation of different depths Se= standard error, CV% = coefficients of variation, P= phosphorous, N= nitrogen, OC= organic matter, OM= organic matter, Ca= calcium , Mg= magnesium, K= potassium, Na= sodium, EA= exchangeable acidity, ECEC= cation exchangeable capacity, BS=base saturation.

4.2 Chemical properties of soils

The Soil pH ranged from 4.5 (strongly acidic) at SSP_1 to 5.6 at SSP_3 (moderately acidic) across the stations and depths, indicating no significant difference at $P \geq 0.05$ (Table 6). The result is consistent with the finding of Hazelton and Murphy (2007) who reported moderately acidic soils in Wouri River due to human activities (Tening et al., 2013), and high amounts of rainfall on soils dominated by acidic cations in parent material from which the soils are derived (Ahukaemere et al., 2015; Ubuoh and Ogbonna, 2018; Osujieke et al*.,* 2016; Ubuoh et al*.,* 2020^{a}).

The mean values of available phosphorus ranged between 13.2-19.4 mg/kg^{-1}, with the overall mean value of 15.4 mg/kg and Cʋ of 6.7%, with SSP_1 recording the lowest value and the highest being SSP_3 followed by SSP_2, with significant different at $P>0.05$ level, at various soil depths and locations. However, the overall mean available phosphorus was <20 critical limits (Landon, 1991). The available phosphorus significantly varied across the depths at $p<0.05$ level, suspected to be due to excessive rainfall through the leaching of sandy soil (Ubuoh et al., 2013; Ubuoh and Ogbonna, 2018; Ubuoh et al., 2020b).

The mean nitrogen of the soils varied from 0.07-0.14%, with the overall mean value of 0.1% and Cʋ 17.9% respectively, with SSP_1 being the lowest and SSP_2 recording the highest followed by SSP_3, < 1.5 critical limit of N described as low in content (Esu, 1991), and ≤ 2.0 critical levels of N for soils of the humid tropics (Adeoye and Agboola, 1984), due to high rainfall (Brady and Weil, 2008). The total nitrogen significantly decreased down the soil depths at all the sample locations at $p>0.05$ level, which may be due to leaching. However, the total nitrogen of all sites recorded a low value compared to the rating of soils of southeastern Nigeria (Ubuoh et al*.,* 2010). Organic matter ranged from 1.0 -2.1%, with a mean value of 1.4% and Cʋ of 24%, with $SSP_1 \leq SSP_3 \geq SSP_2$. The organic matter content significantly varied across the depths at $p \geq 0.05$. The result of OM in the study is within 0 to 3.9%, which was rated low (Enwezor et al*.,* 1989). Organic carbon ranged from 0.6-1.3%, having an overall mean value of 0.82% and overall Cʋ of 24.3%, with OC in order: $SSP_1 \leq SSP_3 \geq SSP_2$. The result of OC is less than (≤ 10%) critical value for agricultural soil (Esu, 1991). The low OC is suspected to be caused by poor soil management in the area and the sloppy land toward the River (Lal, 2018), and unsustainable farming activities along the slopes (Omuto and Vargas, 2018).

Exchangeable bases are Ca^{+}, Mg^{+}, Na^{+} and K^{+} (Ubuoh et al*.,* 2020^{a}; Ubuoh et al*.,* 2020^{b}). The mean result of calcium varied from 2.6 - 6 cmolkg^{-1}, having an overall mean of 3.9 cmolkg^{-1} and an overall means Cʋ of 19.7%, with $SSP_1 \geq SSP_3 \geq SSP_2$. The overall mean value of Ca is within 2-5 soil critical limit (Esau, 1991), which may be due to organic materials from solid wastes (Tanimu et al., 2013). The result is against the findings of Edosomwan et al. (2001), Emmanuel et al. (2018) who reported low levels of Ca in most Nigerian soils, due to low decomposition of organic matter and slow release of chemical elements into the soil (Brady and Weil, 2008).

The mean of magnesium ranged from 1.3-2.3, with an overall mean of 1.9 and 18.3% Cʋ, with SSP_1 having the lowest value and the SSP_2 with the highest value ≥ SSP_3. The magnesium of the SSP_2 and SSP_3 showed a significant increase with depths while SSP_1 recorded a significant decrease. Generally, the Mg^{2+} was higher than the critical level of 0.5cmolkg^{-1} soil across the sample points (Landon, 1991), suspected from organic wastes (Tanimu et al., 2013), and against the finding of Emmanuel et al. (2018) who reported low Mg^{2+} in Nigerian soils.

The mean value of potassium varied from 0.12-0.2 cmolkg^{-1}, with the overall mean of 0.14 cmolkg^{-1}, having 13% Cʋ respectively, with the mean order: $SSP_1 \leq SSP_2 \geq SSP_3$. The exchangeable potassium (K^{+}) significantly varied across the soil depths at $P \geq 0.05$, with the overall mean of K^{+} less than ≥0.6 cmol/kg critical limit (Landon,1991). The result is a variant of the findings of Edosomwan et al. (2001), Emmanuel et al. (2018) that reported low K^{+} in the tropical soil due to the high tropical rainfall and low decomposition of organic matter soil. The mean sodium varied from 0.114-0.126 cmolkg^{-1} having the mean value of 0.12 cmolkg^{-1} less than 1cmolkg^{-1} soil critical limit (Landon, 1991), having 11.3%Cʋ, with location order: $SSP_1 \leq SSP_3 \geq SSP_2$. The exchangeable sodium content varied significantly across the soil depths at $P \geq 0.05$.

The mean Exchangeable acidity as acid cation (H^{+} AL^{3+}) varied from 0.8-1.0 cmolkg^{-1}, with the overall mean value of 0.9 cmolkg^{-1}, less than 1.1 cmolkg^{-1} obtained from farmland in Kano (Adamu *et al*.,2014), with 15.9% Cʋ with the mean order: $SSP_3 \leq SSP_1 \leq SSP_2$, having no significant differences across the soil depths and locations at $P \geq 0.05$. Low EA may result in an increase in soil acidity that results in toxicity in soil (George, 2009).

The effective cation exchange capacity (ECEC) of the soils ranged from 5.1-8.5 cmolkg^{-1} across the three stations and soil depths, greater than 3.7-4.9 cmol/kg ECEC rated low (Benton, 1999), 4.31 cmolkg^{-1} ECEC in soils around River Wouri in Cameroun (Norbert et al., 2018). However, the cation exchange capacity values obtained in this study were below the value of 20 cmol/kg-^{1} reported as being suitable for crop production (FAO, 1995). Meanwhile, where the cation exchange capacity of the soil is ≤ 5, such soil is inherently infertile (Christian and Beniah, 2020), due to leaching through excessive rainfall (Njoku, 2017).

The base saturation of the soils ranged from 78.1–to 90.8% across the three-course streams and depths. Base saturation had mean values of 86.2% for the study catchment was greater than the FMEnv/WHO limits of 80% at some stations (FMEnv, 1991). Generally, the base saturation is relatively high in moderately weathered soils that formed from the basement complex (Draft Report, 2016). Based on the classification of Cʋ variations by Lian et al. (2019), pH, phosphate, potassium, ECEC, and base saturation Cʋ were below Cʋ ≤ 15%, an indication of low, nitrate, organic matter and carbon, calcium, manganese, sodium, and EA fall within 15% ≤ Cʋ ≤ 36% that indicate medium variation in soil respectively.

Table 7. Comparison of soil nutrients with agricultural soil in Nworie River Catchment.

Soil nutrients	Ratings of soil nutrients: Loganathan, 1987					The study: Nworie River	Remark
	Very low	Low	Moderate	High	Very high		
(Total N, %)	<0.05	0.05–0.15	0.15–0.20	0.20–0.30	>0.30	0.068 - 0.140	Very low –low
(available P, Bray and Kurtz No.1, ppm)	<3	3 – 10	10 – 20	20 – 30	> 30	13.19 - 19.42	Moderate
(exchangeable K, meq/100g)	<0.2	0.2–0.3	0.3–0.6	0.6–1.0	> 1.0	0.124 - 0.150	Very low
(exchangeable Ca meq/100g)	<2	2 – 5	5 – 10	10 – 20	> 20	2.667 - 6.000	Low- moderate
(exchangeable Mg, meq/100g)	<0.3	0.3–1	1 – 3	3 – 8	> 8	1.333 - 2.26	Moderate

From the comparison of rating of the selected soil nutrient values in agricultural soils by Loganathan (1987) to Nworie River catchment agricultural, soil (Table 7). The total N of the study was recorded low, which is in tandem with the finding of Enwezor et al. (1988) who reported low to medium total nitrogen (0.15 – > 0.20%) in Nworie River agricultural soil, available P (moderate), as Enwezor et al. (1988) reported low, moderate and high available P in Nworie soil. Exchangeable K (very low), exchangeable Ca (low - moderate), and exchangeable Mg (moderate) agreed with the finding of Isirimah et al. (2003). Low to moderate nutrient values in agricultural soil in Nworie River catchment were recorded along the slopes toward the river course, reflecting the impact of human activities on soil nutrients.

Table 8. Mean ±SD of heavy metals of soil in Nworie River Catchment.

Location	Depth(cm)	Heavy metals (mg/kg^{-1})					
		Cd	Cr	Cu	Fe	Pb	Zn
SSP$_1$	0 – 15	0.25± 0.067^{a}	0.012± 0.012^{a}	0.37± 0.038^{c}	16.67 ± 0.332^{a}	0.95± 0.067^{a}	8.83± 0.216^{a}
Upper course	15 – 30	0.04± 0.210^{b}	0.03± 0.102^{a}	0.68± 0.167^{b}	13.85 ± 0.225^{b}	0.76± 0.104^{b}	6.33± 0.276^{b}
	30 – 45	0.09± 0.032^{b}	0.08± 0.022^{a}	1.31± 0.169^{a}	12.80 ± 0.166^{c}	0.92± 0.090^{ab}	4.89± 0.020^{c}
	Mean	0.125	0.044	0.786	14.44	0.878	6.683
	%Cʋ	34.5	139.0	17.7	1.7	9.9	10.6
	Se	0.043	0.061	0.139	0.239	0.087	0.700
SSP$_2$	0 – 15	0.04± 0.012^{b}	0.02± 0.014^{a}	0.61± 0.125^{a}	12.47±0.053^{ab}	2.25± 0.210^{a}	3.96± 0.078^{c}
Middle course	15 – 30	0.14± 0.067^{a}	0.02±0.010^{a}	0.4± 0.163^{ab}	8.83± 0.237^{c}	0.78± 0.151^{b}	5.83± 0.216^{b}
	30 – 45	0.04± 0.006^{b}	0.03± 0.016^{a}	0.47± 0.065^{c}	14.93± 0.117^{a}	1.09± 0.185^{a}	8.02± 0.306^{a}
	Mean	0.072	0,021	0,462	12.08	1.373	5,937
	%Cʋ	54.0	61.8	26.9	1.3	13.4	3.7
	Se	0.039	0.013	0.124	0.155	0.183	0.220
SSP$_3$	0 – 15	0.05± 0.006^{b}	0.05± 0.035^{a}	0.22± 0.120^{b}	11.43 ± 0.147^{c}	0.94± 0.080^{b}	6.35± 0.150^{b}
Lower course	15 – 30	0.23± 0.074^{a}	0.02± 0.002^{a}	1.04± 0.173^{a}	17.64 ± 0.195^{a}	1.41± 0.137^{a}	9.58± 0.204^{a}
	30 – 45	0.03± 0.013^{b}	0.01± 0.013^{a}	0.23± 0.083^{b}	14.95 ± 0.127^{b}	0.717 ± 0.273^{b}	9.35± 0.575^{a}
	Mean	0.10	0.03	0.50	14.7	1.02	8.42
	%Cʋ	42.9	84.9	26.4	1.1	17.8	4.3
	Se	0.043	0.021	0.130	0.159	0.182	0.363
OCV		43.8	95.2	23.7	1.4	13.7	6.2
Omv		0.10	0.03	0.6	13.7	1.1	7.0

Different letters refer to significant differences between mean + standard deviation of different depths, similar letters refer to the insignificant difference between mean+ standard deviation of different depths.SSP- Soil sampling point, OCV- Overall coefficient value, OMV-Overall mean value

4.3 Heavy metal concentration in soil

Table 8 presents the summary of the heavy metals in agricultural soil samples from the study locations. The mean cadmium (Cd) ranged from 0.07–0.125 mgkg^{-1}, SSP$_2$ recording the lowest value and SSP$_1$ with the highest value ≥ SSP$_3$, less than cadmium concentrations in soil that ranged between 0.25 - 1.64 mg/kg-^{1} in Accra (Fosu-Mensah et al., 2017). The overall mean of Cd (0.10) in all agricultural soil falls below the WHO/FAO (2001) permissible limit of 3 mg/kg for soils. The level of cadmium concentration decreased with depth and varied significantly across the soil depths and study locations at $P \geq 0.05$ level. The level of Cd in this study was found to be lower than values obtained in soils of Malaysia (Yap et al., 2003), and within the range of results obtained in Lagos, Nigeria (Okereke et al., 2019), less than 1.8 mgkg^{-1} in agricultural soils near a dumpsite in Umuahia, Abia State, Nigeria (Ubuoh et al, 2019).

The mean chromium (Cr) ranged from 0.02 -0.04 mgkg^{-1}, with SSP$_2$ ≤ SSP$_1$ ≥ SSP$_3$, with the overall mean value of 0.03 mg kg^{-1} less than the range of 22.4-102.04 mg kg^{-1} by Mohammed et al. (2015). The result of Cr is far less than Cr ranging from 2.28 mg/kg at S$_3$ to 56.00 mg/kg at S$_1$ with a mean value of 11.55 mg/kg-^{1} in e-waste dumpsite in Accra (Fosu-Mensah et al., 2017), and the high contents of Cr recorded may come from solid wastes deposition

(Fosu-Mensah et al., 2017). The Cr recorded no significant difference between the study locations and soil depths at $P \geq 0.05$. The overall mean of Copper (Cu) in soil samples was recorded at 0.6 mg/kg^{-1} and ranges from 0.462 - 0.495 mgkg^{-1}, with SSP_1 being the lowest and SSP_3 being the highest $>SSP_2$, and far above the Cu (202.99 mg/kg) in soils at Korle Lagoon area in Accra, Ghana (Fosu-Mensah et al., 2017), with the overall mean value of Cu in the soil below the WHO/FAO (2001) permissible limit of 100 mg/kg^{-1} for soils, but above 0.2 (Esu, 1991). The copper concentration increased significantly with soil depths and locations at $P \geq 0.05$. The variations in the concentration of Cu in the stations may be due to vehicle flow, household and medical waste materials as copper is commonly found in electrical wirings, engine wear, brake linings, and some medical materials (Manno et al., 2006).

The iron (Fe) content varied from 12.08 - 14.67 mg kg^{-1} with $SSP_2 \leq SSP_3 \leq SSP_1$, having an overall mean value of 13.7 mg kg^{-1}, less than Fe mean of 29.1 mg kg^{-1} in agricultural soils in Northern China· (Yushu et al., 2013), and far below the average Fe (10351.83 mg kg^{-1} in agricultural soils of Siling Reservoir Watershed in Zhejiang Province, China (Naveedullah et al., 2013). The Fe concentration decreased significantly with depths and locations at $P \geq 0.05$ level. It is reported that Fe between 0.1 to 50–100 µg/g in soil within a few weeks, can a be a problem in lowland acid soils suffering from weathering (FAO, 2006), and in toxicity is mostly associated with highly acidic soil leading to nutrient deficiencies like SOM, N, P and K (FAO, 2006). Lead (Pb) concentration varied from 0.9 - 1.4 mg kg^{-1}, in order of $SSP_1 < SSP_2 > SSP_3$ with the mean value of 1.1 mg kg^{-1}greater than Pb in soils 0.0001-1.41mg/kg (Mohammed and Folorunsho, 2015), and less than 25.76 mg/kg in agricultural soil in Buriganga riverbank (Rahaman et al*.,* 2016). Significant variations of Pb were observed across the depths and locations at $P > 0.05$ level. The mean value of Zinc (Zn) ranged from 5,937 - 8.424 mg kg^{-1}, in order: $SSP_2 < SSP_3 > SSP_1$, with the overall mean value of 7.0 mg kg^{-1}, less than the mean value of 8.68 mg/kg in agricultural soil (Fosu-Mensah et al*.,* 2017), 75.6 mg kg^{-1} Beijing (Wu et al., 2010) respectively. The mean value of Zn of the study was below the WHO/FAO (2001) permissible limit of 300.00 mg/kg for soils. The presence of zinc in soil could be attributed to municipal wastes (Bai et al., 2011; Ubuoh et al., 2014).

Table 9. Comparison of heavy metals in agricultural soil with existing standards (mg/kg) globally

Standard	Cr	Cu	Zn	Cd	Pb	Fe
CCME[a]	64	63	200	1.4	70	-
Dutch intervention value[b]	180	190	720	13	530	-
USEPA[c]	-	30	-	-	10	-
WHO	-	4	50	0.3	20	47,200
FAO	-	0.2	2.0	0.01	5	-
Present study	0.1.0	0.03	0.6	13.7	1.1	7.0

[a] Canadian soil quality guidelines for the Protection of Environment and Human Health, 2007

[b]VROM 2009

United State Environmental Protection Agency

WHO World Health Organization, FAO Food, and Agriculture Organization (United Nations)

To understand the status of heavy metal concentrations in agricultural soils in the Nworie River catchment, a comparison of the results obtained in the study with other studies in agricultural soils from different regions of the world was made (Table 9). The mean concentration of Cr, Cu, Zn, Pb, and Fe (WHO/FAO) only in soil samples are under the Dutch intervention value (180, 190, 720, 13, and 530 mg/kg respectively). These values were below the standard of the world guidelines recognized by World Health Organization (WHO/FAO) limits. Accordingly, the concentrations of Cr, Cu, Zn, and Pb in samples are lower than the Canadian quality guidelines for agricultural soils (CCME) (Table 9). Meanwhile, the obtained value of Cd exceeds the standard value (1.4 mg/kg) recommended by the Canadian soil contamination, CCME, and WHO/FAO guidelines, suspected to be from industrial and domestic wastes (Bohn et al., 1985). The result is in consonant with the finding of Oumenskou et al. (2018) who reported the exceedance of Cd in agricultural soils from Beni Amir in Tadla plain, Morocco. It is reported that Cd is toxic even in small concentrations in soil (Oumenskou et al., 2018), resulting in changes in the size, composition, and activity of soil microbial community (Liao et al., 2005).

Table 10. Correlation coefficients between different heavy metals in the soil around Nworie River catchment

Soil sample point		Cd	Cr	Cu	Fe	Pb	Zn
SSP$_1$	Cd	1.000					
(Upper course)	Cr	-0.309	1.000				
	Cu	-0.515	0.013	1.000			
	Fe	0.816	-0.162	-0.856	1.000		
	Pb	0.603	0.005	0.185	0.319	1.000	
	Zn	0.681	-0.236	-0.916	0.940	0.062	1.000
SSP$_2$	Cd	1.000					
(Middle course)	Cr	0.208	1.000				
	Cu	0.139	0.039	1.000			
	Fe	-0.789	0.237	-0.172	1.000		
	Pb	-0.508	-0.132	0.716	0.298	1.000	
	Zn	-0.028	0.459	-0.672	0.442	-0.675	1.000
SSP$_3$	Cd	1.000					
Lower course	Cr	-0.280	1.000				
	Cu	0.968	-0.350	1.000			
	Fe	0.742	-0.603	0.804	1000		
	Pb	0.860	-0.091	0.832	0.547	1.000	
	Zn	0.458	-0.682	0.545	0.913	0.207	1.000

SSP-Soil sample point. Correlation is significant at the 0.01 level (two-tailed).

4.4 Correlation Matrix of Heavy Metals in the Soil

To obtain more reliable information about the relationships among the variables, factor analysis was applied (Bartolomeo et al., 2004). Regression values for the relationship were characterized as negative when – 1 ≤ 0 and positive when ≥ 0 ≤ 1 (Verla et al., 2020). The correlation identifies the source and movement of metals among heavy metals (Wang et al., 2017). Pearson's correlation coefficients among heavy metals in the studied agricultural soil along the valley slopes of Nworie River are presented in Table 10. Many metal pairs had positive correlations ($P<0.01$) in soils along Nworie River catchments. The correlation relationship in SSP$_1$ indicates that Cd is negatively correlated with Cu (r^2: -0.515), and positively associated with Fe (r^2: 0.816), Pb (r^2: 0.603), Zn (r^2: 0.681) respectively. Cu is negatively associated with Fe (r^2: -0.856), Zn (r^2: -0.916) respectively and Fe is positively associated with Zn (r^2: 0.940). At SSP$_2$, Cd is negatively associated with Fe (r^2: -0.789) and Pb (r: -0.508). The Cu is positive with Pb (r^2: 0.716) and negative with Zn (r^2: -0.672). At SSP$_3$, Cd is positively associated with Cu (r^2: 0.968), Fe (r^2: 0.742), Pb (r^2: 0.860) respectively, Cr negative with Fe, Zn (r^2: -0.603; -0.682) respectively. Copper was positively correlated with Fe (r^2: 0.804), Pb (r^2: 0.832), Zn (r^2: 0.545). Fe indicates a positive association with Pb (r^2: 0.547) and Zn (r^2: 0.913) at $p< 0.01$, in soil within the Nworie River catchment. This observation is in line with the finding of Lian et al. (2019), who reported a highly positive correlation among metals from the same source. The sources of metals in agricultural soils of the study are in agreement with the findings of Enyoh and Isiuku (2020), and Ubuoh et al. (2020^c) who observed that the mixed sources like artisanal activities, metal processing works, surface run-off, vehicle emissions, and agricultural activities may be responsible for soil pollution in flood basin in Amakohia, Owerri, Nigeria. Previous studies have also shown that these sources play a major role in introducing metals into the environment (Verla et al., 2017; Verla et al., 2020; Isiuku and Enyoh, 2020).

Table 10. Comparison of heavy metal concentrations in the soils from other regions of the world with this study

Author	Cr	Cu	Zn	Cd	Pb	Fe	Location
This study	0.03	0.6	7.0	0.19	1.1	13.7	Nworie River (agric. Soil)Nigeria
Rodríguez Martín et al. (2013)	29.6	25.7	65.7	0.4	25.6	-	Almería (Spain)
Sun et al. (2013)	49.7	18.9	58.9	-	35.4	-	Dehui (China)
Cai et al. (2012)	27.61	16.74	57.21	0.10	44.66	-	Huizhou (China)
Nanos and Martin (2012)	20.53	11.01	42.42	0.159	14.06	-	Duero basin (Spain)
Acosta et al. (2011)	17.6	11	18.4	0.22	48.9	-	Murcia (Spain) medians
Parizanganeh et al. (2012)	-	67.68	299.31	1 .4	58.18	-	Zanjan Province (Iran)
Huang et al. (2007)	77.2	33.9	98.1	0.3	35.7	-	Yangzhong District (China)
Zhao et al. (2007	58.6	40.4	112.9	0.14	46.7	-	Wuxi (China)
Li et al. (2009)	64.65	24.0	162.6	0.28	58.0	-	Guangzhou (China)
Benlkhoubi et al. (2015)	7.81	37.61	105.56	7.81	26.71	-	Sebou basin-Kenitra (Morocco)
Tomgouani et al. (2007)	5.25	10.91	20.12	0.21	29.66	-	Settat (Morocco)
Oumenskou et al. (2018)	57.0	25.9	294.7	1.8	33.3	-	Beni Amir perimeter (Morocco)

Table 11 lists the contents of heavy metals sampled in soil within Nworie River catchment were lower than areas compared with, except Cadmium (Cd) and Fe in some cases. The Cd (0.19 mg kg^{-1}) in soil within Nworie River catchment was slightly higher than 0.10 mg kg^{-1} Huizhou (China) (Cai et al., 2012), 0.159 mg kg^{-1} Duero basin (Spain) (Nanos and Martin, 2012). Iron (Fe) with 13.7 mg kg^{-1} recorded the highest, while compared locations recorded none. The factor that might influence the higher concentration of Cu, Cd, and Mn in agricultural soil in Nworie River catchment is an anthropogenic activity from the surrounding area (Owanda et al., 2018). The mean result of Cr, Cu, Zn, and Pb in the agricultural soil of Nworie River catchment are far less than soils from different regions of the world indicated in Table 11.

Table 12. Rotated Loading Matrix of the physicochemical characteristics and heavy metals in agricultural soil

	Principal component (PC) as factorial loading					
Soil Quality as Item	PC_1	PC_2	PC_3	PC_4	PC_5	PC_6
Physical soil tracer						
Sand	-0.118	-0.977	0.037	0.129	-0.004	-0.015
Silt	0.212	0.916	0.053	-0.147	-0.112	0.207
Clay	-0.208	0.611	-0.264	-0.01	0.323	-0.526
Chemical soil tracer						
pH (H_2O)	-0.053	-0.166	0.184	0.64	0.496	-0.086
Phosphorous (Avail. P)	0.818	0.22	0.026	-0.129	0.414	-0.183
Nitrogen (avail. N)	0.211	0.053	0	0.023	0.74	0.067
Org. C. (OC)	0.889	0.24	0.079	0.093	0.139	0.008
OrgM (OM)	0.889	0.24	0.079	0.092	0.139	0.008
Calcium (Ca)	0.079	0.038	0.97	-0.124	0.015	-0.023
Magnesium (Mg)	0.036	-0.197	0.016	0.823	-0.044	-0.227
Potassium (K)	0.779	-0.24	0.155	-0.044	0.37	-0.114
Sodium (NA)	0.828	-0.077	0.245	0.195	0.169	0.202
Exch A (EA)	-0.2	-0.027	-0.388	-0.118	0.242	0.682
Exch C	0.107	-0.093	0.869	0.356	0.032	-0.079
Base saturation (BS)	0.263	-0.098	0.771	0.22	-0.045	-0.486
Heavy metals						
Iron	0.337	0.557	-0.199	0.642	-0.101	-0.011
Zinc	0.27	0.254	0.148	0.676	-0.428	-0.345
Lead	0.339	-0.049	-0.022	0.053	0.847	0.077
Copper	0.268	0.178	-0.093	-0.12	0.007	0.832
Cadmium	0.735	0.062	0.002	0.151	-0.32	0.228
Chromium	-0.053	0.164	-0.267	-0.554	-0.173	-0.186
Total Eigenvector	4.737	2.922	2.788	2.62	2.394	2.082
% of Variance	22.6	13.914	13.276	12.478	11.399	9.916
Cumulative %	22.556	36.47	49.746	62.224	73.623	83.539

P(0.05)

4.5 Principal Component Analysis (PCA)

Principal component analysis (PCA) has been used to infer the hypothetical source of heavy metals (natural or anthropogenic) (Li et al. 2009; Yi et al. 2011). In this study, heavy metals were grouped into a six-component model, which accounted for 83.5 % of all the data variation (Table 12). The initial component matrix indicated that the first PC (PC_1, variance of 22.6 %) included 25 variables. Meanwhile, out of twenty-five variables, Phosphorous, organic carbon, organic matter, magnesium, sodium, and cadmium were positively loaded as anthropogenic components and may originate from similar pollution sources (Ghrefat and Nigem, 2006; Shan et al., 2013; Lian et al., 2019). The only metal (Cd) may have originated from farming practices (Atafar et al. 2010; Xue et al., 2014), like commercial phosphate and inorganic fertilizers applications (Nziguheba and Smolders 2008).

The component (PC_2), with a variance of 13.9% was negatively loaded with sand and positively loaded with silt and clay respectively. The result is in tandem with the finding of Moss et al. (1975), and Lautridou and Ozouf (2016) who reported that soil fractions originated from a variety of physical processes; involving chemical weathering of rock and physical weathering processes.

The PC_3 with the variance of13.3% was positively loaded with exchangeable cation and percentage basic saturation. The positive loading between CEC and base saturation was observed by Gaspar (2019) who reported that Mg content in crops and plants increased as Mg saturation of the CEC increased. Meanwhile, Dassenakis et al. *(*2003), Yuan et al. (2004), Ubuoh et al. (2021) have used the concentrations of the exchangeable fraction as an indicator of anthropogenic impact on the environment. The PC_4 with a variance of 12.5% was positively loaded with Mn, Fe, and Zn. It has been reported that Zn can be associated with Fe and Mn oxides of the soil or sediments (Ramos et al., 1999), and Zn can originate from farming practices, which is in agreement with the finding of Shan et al. (2013). The PC_5 with a variance of 11.4% was positively loaded with Pb. The lead and zinc in soil may have originated from vehicles tire wear and solid wastes (Shan et al*.,* 2013), signifying anthropogenic sources (Ghrefat and Nigem, 2006) while PC_6 with a variance of 9.9% was positively loaded with exchangeable acidity and cadmium, which indicate that positively loaded metals in soils may be influenced by terrestrial inputs (Benoit et al., 1994; De Souza Machado et al., 2016).

4.5 Pollution assessment indices for the heavy metals in the soil

Table 13. Geo-accumulation index (I-$_{geo}$) of heavy metals of soil in Nworie River watershed

Stations	Cd	Cr	Cu	Fe	Pb	Zn
SSP_1	0.768	7.5	0.019	0.217	0.026	0.056
SSP_2	0.444	3.7	0.011	0.182	0.041	0.050
SSP_3	0.629	4.3	3.9	0.221	0.031	0.071
Mean	0.613	1.5	0.011	0.206	0.033	0.059
Remark	UM: $0 \le I_{-geo} \le 1$.	Mc: $1 \le I_{geo} \le 2$	Mc: $0 \le I_{-geo} \le 1$	UM: $0 \le I_{-geo} \le 1$.	Mc: $0 \le I$-$_{geo} \le 1$	Mc: $0 \le I$-$_{geo} \le 1$

UM: Uncontaminated-moderate, MC: Moderately contaminated.

4.6 Geo-accumulation index (I_{-geo})

Soil quality was measured using the I-geo index of classification proposed by Muller (1981) (Table 13). The mean I-geo Index values of agricultural soil samples within Nworie River watershed are indicated and the calculated I_{-geo} values of Cd ranged between approximately 0.4 to 0.8, with the mean value of 0.6 as uncontaminated to moderately contaminated ($0 \le I_{-geo} \le 1$), Cr (3.7 to 7.5), with the mean of 1.5 as moderately contaminated ($1 \le I_{-geo} \le 2$), Cu (0.011 to 3.9), with the mean value of 0.011, Fe (0.182 to 0.221) with the mean of 0.21, Pb (0.03 to 0.041), with the mean 0.033 and Zn (0.050 to 0.071), with the mean of 0.059, indicating uncontaminated to moderately contaminated ($0 \le I_{-geo} \le 1$) respectively. Thus, the I_{-geo} results of the sampled heavy metals in soils classified as uncontaminated to moderately contaminated according to Müller (1969) classes, are suspected to be due to human activities like agricultural practices and mining. The heavy metals responsible for the geo-accumulation in the soils are in a decreased sequence of: Cr ≥ Cd ≥ Fe ≥ Zn ≥ Pb ≥ Cu, constituting 61.93%, 25.31%, and 8.51%, 2.44% 1.36%, and 0.45% with a percentage of Cr dominating. Chromium had been in the parent materials of soils with little temporal and spatial variation in worldwide rural soils (Wu et al., 2010). Chromium toxicity can induce alterations in growth, photosynthesis, gas exchange attributes, and yield formation in crops (Anjum et al., 2016) and adversely affect soil microorganisms (Adriano 2017). From an environmental pollution perspective, Zn is often considered a toxic element, but very insoluble and very rare (Alloway, 1990). On the other hand, Cd has no essential biological function and is a highly toxic metal to plants and animals (Chen et al*.,* 2019).

Table 14. Contamination Factor, degree of contamination, and pollution load Index of heavy metals in the soil of Nworie River watershed

Stations	Contamination factor (cf)						C/degree	PL1
	Cd	Cr	Cu	Fe	Pb	Zn		
SSP_1	3.826	3.7	0.094	1.083	0.132	0.280	5.419 (39.21%)	0.225
SSP_2	2.214	1.9	0.055	0.906	0.206	0.251	3.634 (26.31%)	0.107
SSP^3	3.133	2.1	0.019	1.101	0.153	0.356	4.764(34.47 %)	0.117
Mean	3.058	2.6	0.056	1.030	0.164	0.296	4.606	0.150
Remark	3 <cf< 6 (CC)	1<cf<3 (MC)	cf< 1 (LC)	1<cf<3 (MC)	cf< 1 (LC)	cf< 1 (LC)	< 8 (LDC)	0.150 ≤ 1 (NP)
Percentage (%)	42.4	36.0	0.7	14.2	2.2	4.1	13.82	0.449
CC: Considerably contaminated, LC: Low contamination, MC: Moderate contamination, LDC: Low degree of contamination, NP:No pollution								

4.6 Contamination Factor (CF), Degree of Contamination (CD), and Pollution Load Index (PLI)

Table 14 lists the contamination factor of heavy metals in soil is between CF<1 which indicates low contamination, 1<CF<3 indicating moderate contamination, and 3<CF<6 indicating considerably contaminated. The degree of contamination in the table is <8, which indicates a low degree of contamination. While the pollution load index (PLI) is ≤ 1 indicates no pollution. The contamination factor, degree of contaminant and the pollution load of the heavy metals from the soil of Nworie River at SSP_1- SSP_3 are in Table 14. The table showed that at the three stations, cadmium (Cd) and iron (Fe) had contamination factors that ranged from 2.214 – 3.826 and 0.906 – 1.101 which were ≥ one (1), as categorized by Hakason (1980). The result showed that the soil had considerable contamination of Cd, which agrees with the finding of Chai et al. (2014) who reported the highest Cd having anthropogenic origins in Bohai Bay, China. The Cr and Fe recorded moderate contamination, while Cu, Pb, and Zn were ≤ zero (0) at SSP_3, indicating that the soils of the Nworie River are low contaminated, with the percentage of contamination factors ranging between approximately 0.7-42.4% in decreasing order of Cd ≥ Cr ≥ Fe ≥ Zn ≥ Pb ≥ Cu. The degree of contaminant (CD) ranges from 3.634 - 5.419 with SSP_1 having the highest degree and SSP_2 having the lowest in the soil of Nworie which was ≤ 8 degrees of contaminant stipulated by (Hakanson, 1980). The percentage of contamination degree of sampling points was in a decreased sequence of $SSP_1 \geq SSP_3 \geq SSP_2$, constituting 39.21%, 34.47 %, and 26.31% respectively.

The table showed that pollution load ranged from 0.225 in SSP_1 to 0.107 in SSP_3, in a decrease sequence of $SSP_1 \geq SSP_3 \geq SSP_2$, with the overall mean PLI recording 0.150≤ 1 with approximately 0.45% indicating no pollution by Tomlinson et al. (1980). This implies that the soil at the different course streams was not polluted by the heavy metals (Ubuoh et al., 2016), with the source being geogenic.

4.7 Ecological risk assessment

Table 15. Ecological Risk Factor and Risk Index of Heavy Metals in the soil of Nworie Riverwatershed

Stations	Ecological Risk Factor (Er)					Risk Index (Ir)
	Cd	Cr	Cu	Pb	Zn	
Station 1: (SSP_1)	97.80	$7.4x10^{-3}$	0.470	0.660	0.280	99.217
Station 2: (SSP_2)	66.42	$3.8x10^{-3}$	0.275	1.030	0.251	67.980
Station 3: (SSP_3)	93.99	$4.2x10^{-3}$	0.095	0.765	0.356	95.210
Mean	86.07	$5.1x10^{-3}$	0.280	0.818	0.296	87.47
Remarks	CPER	LPER	LPER	LPER	LPER	Low ecological risk

The following categories were used to describe the risk factor: E*ri* < 40 = low potential ecological risk (LPER) , 40 ≤ E*ri* ≤ 80 = moderate potential ecological risk; 80 ≤E*ri* ≤ 160 = considerable potential ecological risk (CPER), 160 ≤ E*ri* ≤ 320 = high potential ecological risk and E*ri* 320 > =very high ecological risk at hand for the substance in question (Tesleem et al., 2018). The ecological risks of Cd in soils at (SSP_1) (97.80) and SSP_3 (93.99) were ≥ 80 while in SSP_2 recorded the ecological risk of 66.42 ≥ 40 but, ≤ 80. The ecological risk values indicate that Cd has a considerable potential ecological risk to the soil in SSP_1 and SSP_3 while the moderate potential ecological risk to the soil at SSP_2, with Cd posed a high-risk factor (Table 15). The result is also in line with (Ke et al. 2017; Saravanan et al., 2018), who reported Cd as the metal with a potential risk factor. The values of Pb, Cu, Zn, and Cr were below 40, indicating low potential ecological risk. The ecological risk indices of the heavy metals were in decreasing order: Cd ≥ Pb ≥ Cu ≥ Zn ≥ Cr, with the Cd accounted most of the total risks. The overall potential ecological risk as risk index (Ir) of heavy metals ranged from 67.980 in SSP_2 to 99.21 in $SSP_1 \leq 150$ indicating low potential ecological risk (Tesleem et al., 2018), with the overall mean risk index being approximately 87.5 ≤Ir<150 which signifying low ecological risk for the entire Nworie River agricultural soil. Ultimately, the results of the ecological risk factor are in agreement with Ghrefata and Nigem (2006) who reported that Zn posed a low environmental risk, whereas Cd posed a medium environmental risk in sediments in Wadi Al-Arab Dam, Jordan respectively.

4.8. Summary and Conclusion

The results of this study revealed that agricultural soils were predominantly sandy and moderately acidic, with cadmium above the WHO/FAO critical limit for agricultural soil. Agricultural soils recorded low nitrogen, moderate available phosphorous, very low exchangeable K and low-moderate exchangeable Ca. A correlation existed between physicochemical characteristics and heavy metals in soils depicting the same sources. Positively loaded variables are associated with human activities while negatively loaded variables are associated with lithogenic factors. The results suggested that agricultural soils were uncontaminated to moderately contaminated. Contamination factors indicated considerably contaminated moderately contaminated, and low contaminated. The contamination degree recorded a low degree of contamination, with no pollution. The ecological risk indices were in decreasing order: Cd ≥ Pb ≥ Cu ≥ Zn ≥ Cr. The potential ecological risk index and risk assessment code determined indicated that of the heavy metals examined, Cd posed the most significant ecological risk in the Nworie River watershed in agricultural soils studied. Therefore, human activities such as indiscriminate application of inorganic fertilizer, and disposal of solid waste along the slopes of Nworie River valley should be avoided within the upper, middle, and lower areas of the watershed. This will help in eliminating the ecological risk associated with Cd pollution in the watershed.

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