Distribution of heavy metals, soil microbial enzymes and their relationship in Kano, Northwestern Nigeria

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Abstract: The increase in population and industrial growth has led to increased production of industrial and domestic waste which contain heavy metals in various forms. Therefore, affect the diversity and activities of soil microbes and subsequently affect environmental sustainability. This research aimed at assessing the distribution of heavy metals, soil enzymes, and evaluate the functional relationship if any. The study area was divided into two locations as contaminated and control; thus, each location one square kilometre was demarcated and divided into 25 small square (grid). A Sample was collected in each grid from 0 – 15 cm depth using point composite sampling technique. The properties investigated are heavy metals, enzymes, pH, and soil temperature. The results of the analyses were subjected to statistical analyses to undertake one-way analysis of variance, and a t-test of means at α value of <0.05, also correlation, and regression at a P<0.05 significant level. The results revealed that there is a gradual accumulation of all heavy metals and the concentration is higher in the contaminated than control locations. The soil is potentially polluted with Cd is clean from Cr, Fe, Mn, Zn, Pb, and Cu. High values of heavy metals were discovered in the dry season than the wet season due to rainfall which enhanced the dissolution, leaching, and runoff of heavy metals which is capable of removing the metals from the subsurface. High pH and temperature in the contaminated location influenced the toxicity and microbial activity respectively, this results in high enzymatic activity in the contaminated location. Favourable environmental conditions in the wet season led to the higher activity of the enzymes than the dry season. The finding also revealed that phosphatase and urease were negatively correlated with Cd and Ni. Inversely, dehydrogenase was negatively correlated with Ni and Zn. It was concluded that the determination of the heavy metals and enzymes reflects the microbial activities in soils and is considered as soil quality indicators.

Keywords: soil enzymes, contamination, soil microbes, biological indicator, soil quality

1. Introduction

Soil is an incarnate, multidimensional system, non-renewable resources, the mediocre of life, and the underpinning of human existence. Its conditions and functions are vital for food and fiber production, and for sustaining the global environmental quality (Donaji et al., 2018). Soil serves as a medium through which plant grows, the habitat of various forms and types of living organisms and almost all living organisms on the earth depend either directly or indirectly on the resources provided by the soil. However, its multifaceted system has been affected by numerous biochemical processes involve the soil microbes which affects the soil quality and services provided to the ecosystem (Brady & Weil, 2015).
Heavy metals are an assemblage of high-density metals and are toxic when the threshold limit exceed. These metals are dispersed into the environment mostly by natural and human activities such as industrial operation, automobile, and domestic waste discharge (Nkununowo et al., 2020). The occurrence of heavy metals in the soil ecosystem is a serious issue of concern globally due to its adverse effect to the environment, thereby posing a great risk to organisms via ingestion, absorption by plant, alteration of soil reaction and other chemical content of the soil which reduces soil quality for sustainable agricultural production. (Masindi & Muedi, 2018). The heavy metals contamination is a threat to the quality of soil worldwide, and therefore, change the diversity and population of soil microbes (Xie et al., 2017). Heavy metals also alter soil characteristics predominantly it a microbial and biochemical parameter, thus, generating devastation in the alterations and exchange of nutrients in the soil ecosystem (Wyszkowski, 2019).

The disposal of industrial effluent is a problem of increasing gravity throughout the world. In Kano metropolis, huge amounts of effluents are generated from Bompai industrial area which is discharged into the Getsi River. The effluent/wastewater has an important role to play in irrigated agriculture in view of the scarcity of freshwater resources for the purpose. Besides being a useful source of soil nutrients, these effluents often contain a high amount of various organic and inorganic materials as well as toxic heavy metals (Mohammed, 2016; Bichi & Bello, 2013). Subsequently, these toxic heavy metals may have a detrimental effect on the environment such as the contamination of surface and groundwater, as well as soil which would interfere with key biochemical processes in the soil such as the decomposition of organic materials, enzymatic activities and reduction in microbial diversity and activities and consequently affect the soil health (Donaji et al., 2018).

The soil enzymes are essentially microbial sources resulting from the intercellular activities related to the physiological processes of beings. Enzymes are direct intermediaries for the catabolism of the biological components of the soil. Therefore, these catalysts provide an eloquent assessment of reaction rates of vital processes occurring in soil. The activity of soil enzymes is used as a direct measurement of microbial activity, soil productivity, and the effects of reticence due to the presence of microbial activity. Soil microbes react rapidly to alterations in the environment with modification in metabolic activity, biomass, and assembly of the community. Generally, enzymes have been anticipated as indicators for the monitoring of soil quality and variation of microbial activity in the soil (Donaji et al., 2018).

Dian (2018) reported that increases in heavy metals in soil reduces the soil enzymes due to direct interface between the enzymes and the heavy metals which is not connected with a decline in soil microbes. Heavy metals have abundant and undeviating effects on soil enzyme activity by the destruction of the longitudinal configuration of the lively assemblage of the enzymes. Additionally, the duplication and growth of soil microbes are subdued, consequently, falling the synthetic and breakdown of soil microbial enzymes.

Dibofori-Orji & Edori (2015) assessed the concentrations of heavy metals in crops irrigated with wastewater and discovered a high concentration of heavy metals in the crops grown in the area. Also, Audu & Idowu (2015) and Haruna et al. (2019) assessed the levels of heavy metals in water used for irrigation and the results revealed a high concentration of heavy metals in the soil of the area. The limitation of these studies is in their scope because they only considered heavy metals level in crops and water respectively; however, the heavy metal and enzymes in soil and their relationship were not coopted.

In spite of the large scale of industrial activities in Kano Nigeria, an insufficient attempt has been made on the assessment of the distribution of heavy metals, enzymes, and their relationship in the area. Even some studies by Wiatrowska et al. (2014); Egejuru et al. (2014); Eremasi et al. (2015) were carried out outside the Sudano – Sahelian region of Nigeria and some of these studies stimulated the contamination of their soil samples artificially in the laboratory which makes their results not sufficiently valid when information on a specific area is required. Even though some attempts were made by Haliru et al. (2014); Imam et al. (2015) to examine the concentrations of the heavy metals in the soils of the region, the studies were limited in scope because the distribution of enzymes and their relationship with heavy metal on seasonal bases were not considered. That is, the data was limited to the concentration of heavy metals which is not sufficiently comprehensive in determining the soil quality.
In order to achieve soil sustainability and enhance productivity, it is important to understand the distribution of heavy metals, enzymes and, clarify the regulatory role of soil microbial communities on these processes and identify the functional relationship that exists between heavy metals, and some soil enzymes. Furthermore, since the rate of soil contamination and microbial activities tends to vary seasonally, it is very pertinent to conduct an empirical investigation for the area, on seasonal bases. Which generated and update the appropriate database used for decision making with respect to environmental quality and sustainable soil management. The objectives of the research are to assess the distribution of heavy metals and soil enzymes (dehydrogenase, urease, and phosphatase), evaluate the pollution status of the heavy metals and determine the association of heavy metals with soil enzymes in the area.

2. Methodology

2.1. Study Area

The study conducted in irrigated land around Getsi River valley which passed through Bompai industrial area, situated in the Northeastern part of the Kano city, located between latitude 12° 10’ N to 12° 12’ N and longitude 8° 33’ E to 8° 35’ E (Fig. 1) and covers the radius of 6 – 8 km from the city (Mohammed, 2017). The climate of the area is tropical wet and dry type, coded as AW by Koppen, although climatic change is believed to have occurred in the past (Ayoade, 1983; Adamu, 2014). The rainfall is a very important element because of its deficiency during the dry season in a normal year which affects soil microbial processes in the area.

![Figure 1. Study area and sampling locations (control location and contaminated location)](image)

Rainfall in the area starts around June, reaches its maximum around August, and ceases around October (Buba, 2014) which favors the activities of soil microbes and thereby enhances the carbon input, rapid mineralization rate, dilution and mixing of soil minerals (Brady & Weil, 2015). This also facilitates the leaching and run-off of the dissolved minerals in the soil of the area.

The materials used in this work include a Global Navigation Satellite System (GNSS), soil auger and spade for soil sample collection, polyethylene bags, marker, pH meter, and Atomic Absorption Spectrophotometer (AAS, 210 VGP American Model). The sampling was carried out at effluent
affected location (where farmers used wastewater directly from contaminated stream to irrigate their lands) as contaminated location and an adjacent control location (where farmers use less contaminated groundwater from boreholes and hand-dug wells for irrigation).

Google Earth was used as a base map whereby 1 square kilometre was demarcated, divided into 25 small squares (grids), and superimposed on each study location (Contaminated and control). The Soil sample was collected in each grid using composite sampling techniques from 0 – 15 cm depth. The soil samples collected were placed into polyethylene bags, labelled appropriately, air dried, and then taken to the laboratory for further analysis.

2.2. Laboratory Procedures

The laboratory procedures for the determination of heavy metals, dehydrogenase, urease, phosphatase, and pH was presented.

2.3. Determination of Heavy Metals

The soil was digested through the wet digestion methods as described by Anderson (1974). Weighted ten grams of soil in a clean 300 ml calibrated digestion tube and 5 ml of concentrated sulphuric acid (H₂SO₄) was added in the fume hood, swirled gently. Five Milles of tri-acid mixtures (HNO₃, H₂SO₄, and HCL) were added and then heated to 240 °C for further one hour. Then filtered through Whatman No. 42 filter papers and stored in pre-cleaned polyethylene bottles for further analysis. The AAS was set up at a wavelength for each analyte as Ni (232 nm), Pb (220 nm), Cd (229 nm), Fe (260 nm), Zn (214 nm), Mn (280 nm), Co (229 nm) Cr (358 nm), and Cu (325 nm). The readings were dispensed on the readout unit of AAS.

2.4. Determination of Enzymes

The dehydrogenase activity was analyzed using triphenyl tetrazolium chloride as a substrate as described by Thalmann (1968) in the modification described by Nannipieri et al. (2003). 20 grams of air-dried soil were mixed with 0.2 g of CaCO₃ and 6 g of the mixture was placed into the three test tubes set. 1 ml of 3 % aqueous solution of Triphenyl tetrazolium chloride (TTC) and 2.5 ml of deionized water were added and the samples were incubated at 36 °C for 24 hours. Ten milliliters of methanol were added, twirled, and filtered. The red color intensity was measured at 485 nm wavelength using a spectrophotometer and the result is expressed in microgram µm of H g⁻¹ soil h⁻¹.

Alkaline phosphatase was determined using p-nitrophenyl phosphate as described by Nannipieri et al. (2003). One gram of soil was mixed with 0.2 ml of toluene, 4 ml of modified universal buffer at pH 11, and 1 ml of p-nitrophenyl phosphatase solution in a flask. The flask was placed in an incubator at 36 °C for 1 hour, 1 ml of 0.5 M CaCl₂, and 4 ml of 0.5 M NaOH were added and the soil suspension was filtered through a filter paper. The yellow color intensity was measured at 400 nm wavelength using a spectrophotometer.

The urease activity was determined spectrometrically at a wavelength of 410 nm, following the modified methods of Zantu & Bremner (1975) described by Nannipieri et al. (2003). 5grams of moist soils were placed into a 50 ml volumetric flask. 0.2 ml of toluene and 9 ml tris buffer were added and mixed. 1 ml of urea solution was added and mixed again for 10 – 40 seconds. The flask was stopped and incubated for 2 hours at 37 °C. After the incubation, 35 ml of KCl-Ag₂SO₄ solution was added, swirled for 10 – 45 seconds, and then cooled at room temperature. KCl-Ag₂SO₄ (50 ml) solution was added and mixed thoroughly. This procedure was repeated for the control sample, but 1 ml of 0.2 M urea solution was added after the addition of 35 ml of KCl-Ag₂SO₄ solution. The ammonia released was estimated by 5 ml of boric acid indicators pipetted into Erlenmeyer flask and also 20 ml of resultant soil suspension was placed into 100 ml distilled flask and then 0.2 g MgO, and distilled thereafter 30 ml was collected into Erlenmeyer flask and was titred with 0.005 M H₂SO₄ and 1 ml of H₂SO₄ (Sarkar & Haldar, 2005).

2.5. Data Analysis

Statistical analyses were performed in spreadsheet software, i.e. MS Excel and SPSS. The one-way analysis of variance (ANOVA) was conducted to determine the variability among the three soil enzymes considered in the study at α values of 0.05 significant level. Student t-test was computed to determine
whether there are significant differences in mean values of enzymes and heavy metals between contaminated and control location, as well as between the dry and the wet seasons at \( \alpha < 0.05 \) significant level. Furthermore, the relationship between heavy metals and enzymes activities were determined using Pearson’s correlation and also regression was used in clarifying the response of enzymes under different values of heavy metals at \( P < 0.05 \).

The association can be identified from a coefficient \((r)\) value which portrays the level of the relationship between enzymes and heavy metals. Where \( r \) is more than 0.7 between 0.4 and 0.7, or if it is less than 0.4, the quantified variables would have high, moderate, and weak relationships. The single pollution index (equation 1) evaluation methods was used to evaluate the level of soil pollution by heavy metals in the area (Hong – Gui et al., 2013).

\[
P\_{ij} = \frac{C\_{ij}}{S\_{ij}}
\]

Where, \( P\_{ij} \) is the pollution index of heavy metal in the j – the functional area of soil, \( C\_{ij} \) is the measured contaminant value of heavy metal j in the j – the functional area and \( S\_{ij} \) is the background contaminant value of heavy metal j, the grading level is \( P\_{ij} < 1 \) clean, \( 1 \leq P\_{ij} < 2 \) Potential pollutions, \( 2 \leq P\_{ij} < 3 \) slightly pollution and \( 3 \leq P\_{ij} \) heavily polluted.

3. Results and Discussion

3.1. Distribution of Heavy Metals

The mean values and standard deviation of heavy metals in the dry and wet seasons are evaluated and presented in Table 1 which shows that there is spatial variability in the concentration of each individual heavy metals among the study locations. This depicted that the concentration of Fe, Cu, Mn, and Ni, are higher in the study locations, contrariwise, low concentration of Zn, Co, Mo, and, Cd was recorded. The variability of the individual heavy metals in the area is probably attributed to the fact that the concentration of heavy metals in the soil varies from one metal to another because Fe and Mn are relatively common in the earth crust, while Cd and Pb are rare and can be toxic even at low concentration and also the variation in the anthropogenic activities and geological composition of the soil (Ebong et al., 2020). The value of heavy metals obtained in this research is higher than the values obtained by Abdullahi & Mohammed (2019); Amalo et al. (2019). This implies that there is a gradual accumulation of these heavy metals in the area.

| Study locations | Seasons | Statistics | Co  | Cr  | Cd  | Fe  | Mn  | Mo  | Ni  | Zn  | Pb  | Cu  |
|-----------------|---------|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                 |         |            | Mean| ±SD | Mean| ±SD | Mean| ±SD | Mean| ±SD | Mean| ±SD |
| Bompai          | Dry     | CV%        | 76.6| 64.8| 4.4 | 55.5| 125.3| 25.9| 191.9| 60.6| 43.6| 118.3|
|                 | Wet     | CV%        | 12.2| 15.6| 13.7| 9.5 | 12.2| 9.3 | 11.6| 11.1| 8.6 | 8.6 |
|                 |         | CV%        | 12.7| 17.9| 12.6| 29.4| 60.3| 18.1| 30.7| 117.3| 11.8| 53.1|
|                 |         | CV%        | 4.2 | 7.0 | 3.4 | 14.0| 9.2 | 5.5 | 6.9 | 29.6 | 3.4 | 5.8 |
|                 |         | CV%        | 33.1| 39.4| 27.1| 47.7| 15.3| 30.2| 22.5| 25.3 | 28.7| 10.9|
| Bompai          | Wet     | CV%        | 38.6| 18.7| 3.6 | 45.5| 74.8| 17.0| 171.5| 19.0| 32.0| 45.4|
|                 |         | CV%        | 1.1 | 1.5 | 0.9 | 6.0 | 3.3 | 3.0 | 12.1| 1.3 | 3.0 | 3.0 |
|                 |         | CV%        | 2.7 | 7.9 | 23.3| 13.2| 4.4 | 17.7| 7.0 | 6.8 | 9.4 | 6.6 |
| Bompai control  | Wet     | CV%        | 13.2| 23.3| 9.7 | 9.5 | 13.0| 29.5| 46.0| 26.7| 33.5| 29.5|

SD = Standard deviation, CV% Coefficient of variability and \( n = 25 \)
Figure 2 shows that a high concentration of heavy metals was found in contaminated location than the control location. This is probably attributed to the industrial and domestic waste released into a contaminated location which contributes in contaminating or increasing heavy metals load into the soil. This is contended by Kausar et al. (2019) who explained that the major causes of the presence and increases of heavy metals in soil could be attributed to discharge of industrial and domestic waste, sewage sludge, and effluent. This is further supported by the fact that Bomapai contaminated location is affected by both industrial and domestic waste from city abattoir, Sabon Gari, and Brigade quarters as well as heavy traffic flow along airport road which finally contaminates the stream (Figure 1).

Dawaki & Alhassan (2008) reported that Bompai location is contaminated from wastewater released from industries, domestic sewage sludge from densely populated part of the city center, Sabon Gari and Brigade quarters and the location is considered the busiest location in term of traffic flow compared to control location. The concentration of heavy metals in the soil of the area is in order Ni>Mn>Cu>Co>Cr>Zn>Fe>Pb>Mo>Cd. This implies that the soil accumulated more of essential heavy metal (Ni, Mn, Cu, and Cu) than toxic heavy metals which may be attributed to discharged of domestic waste with high concentration of these essential metals. This is in line with the findings of Ebong et al. (2020) who discovered high concentration of essential heavy metals Zn, Cu and, Ni than toxic one and attributes it to abattoir waste discharged into area.

The student t-test analysis show that there is a significant difference in the mean values of all heavy metals between the contaminated and the control location at \(\alpha<0.05\) significant level. This depicts the impact of industrial and domestic waste discharged into the contaminated location on increasing the level of heavy metals in the soil (Al-Edresy et al., 2019).

### 3.2. Pollution Level of Heavy Metals in Soil of Sharada and Bompai Area

Table 2 shows the comparison of heavy metals with the international standard which revealed that the mean values of Cd and Mo were higher than European Union Regulatory Values (EURV), conversely, the values of Co, Cr, Fe, Mn, Zn, Ni, Pb, and Cu were below EURV. This implies that based on this research the soils of the area could not be at risk of being polluted by Co, Cr, Fe, Mn, Zn, Ni, Pb, and Cu since their values are below the threshold level that may cause any immediate toxicological effects. Nevertheless, the soil could be at risk of being polluted by Cd and Mo if there is continues accumulation of heavy metals in the soil especially Cd, Mo and may pose a great ecological risk and health problem due to the bioaccumulation of crops grown in the area.
The pollution index (Table 3) shows that the soil is potentially polluted with Cd and slightly polluted with Ni at all locations, while at contaminated location the soil is potentially polluted with Co only. Conversely, the soil of the area is clean with respect to Cr, Fe, Mn, Zn, Pb and Cu.

### Table 3. Pollution Index of Heavy Metals in the Area

| Heavy metals (Mg/kg) | Co  | Cr  | Cd  | Fe  | Mn  | Mo  | Ni  | Zn  | Pb  | Cu  |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Bompai contaminated  | 76.6| 64.81| 4.37| 55.54| 125| 25.94| 191.9| 60.63| 43.61| 118.28|
| Bompai control       | 38.6| 18.72| 3.95| 45.5 | 74.8| 17.01| 171.5| 19.02| 32.05| 45.4 |
| EU Values (mg/kg)    | 140 | 180 | 3   | 1500| 200 | 8   | 75  | 300 | 300 | 140 |

The pollution level of soil with Co, Cd, and Ni in the study locations may be attributed to the used of effluents containing a high amount of Cd, Co and Ni generated from industrial and domestic sources, and through the use of sewage sludge containing a high amount of these metals as manure in the area (Mohammed, 2017). This is explained by Lal (2006) that, the concentration of Cd and Ni in irrigated soil are increased by applications of sewage sludge and industrial effluent.

### 3.3. Seasonal Variability of Heavy Metals

Figure 3 (a) and (b) show the seasonal variability of heavy metals between the wet and dry seasons which revealed that the mean values of all heavy metals were higher in the dry season than the wet season except Cd and Zn in a contaminated location which is higher in the wet season. The low mean values of heavy metals in the wet season may be attributed to the effect of rainfall which facilitates the dilution of metals, oxidation reaction, leaching, and runoff which are capable of removing heavy metals from the subsurface soil. Conversely, the high mean value of Zn in the wet season is due to its high reactivity and low bioavailability in a moist conditions. This is contended by Osakwe et al. (2012) who reported that the reactivity nature of Zn as lattice-bound metals makes it very difficult to mobilized and be available in the soil and thereby dissolution, leaching of dissolved Zn is minimal.
This is further supported by Delbari & Kulkarni (2011) who explained in their finding that high concentration of heavy metals in the dry season is due to fact that in the wet season there are rapid changes in redox reaction due to abundance moisture, the occurrence of runoff and leaching of dissolved heavy metals which are eased by rainfall, thereby dissolved heavy metals can easily be mobilized and remove out from soil subsurface. Conversely, in the dry season low moisture in the soil reduces the rate of a redox reaction, dissolution of metals, and low rate of leaching and runoff, this results in accumulation of high concentration of heavy metals in the dry season. Also, Lal (2006) explained that seasonal variation of heavy metals influenced by runoff and leaching of dissolved heavy metals is expedited by rainfall.

The seasonal variability of heavy metals was statistically evaluated using student t-test analysis which revealed that there is a significant difference in the mean values of all heavy metal between the wet and the dry seasons at $\alpha<0.05$ significant level except Pb where no significant difference in the mean value between the wet and the dry seasons was observed.

### 3.4. Distribution of Soil Enzymes

Table 4 shows the distribution of enzymes, pH, and temperature which indicates that all the enzymes were found to be higher in the contaminated location where all the heavy metals are higher than their control counterpart, thereby nitrogen cycle and hydrolysis of organic phosphorus to inorganic form is higher in contaminated location due to high activities of the soil enzyme (Fazekasova & Fazekas, 2020). This is ascribed to the fact that the concentration of heavy metals recorded in contaminated locations does not reach the level that inhibits the activity of soil enzymes. This is probably an evident that the soil is clean from Co, Cr, Fe, Mn, Zn, Ni, Pb, and Cu based on the pollution index.

This result is contrary to the results of Gang et al. (2017); Tang et al. (2019) who revealed significant inhibition of soil enzymes by increases of heavy metals. Furthermore, high temperature and pH at contaminated locations encourage soil microbial activities and influence the solubility, availability, and toxicity of heavy metals to soil microbes respectively, thus, decrease the effect of heavy metals on the biochemical reaction in the soil. This is explained by Brady & Weil (2015) that soil microbial activities nearly ceases at low temperature (below 5 °C) and increases more than double for every 10 °C rise in temperature up to an optimum of 35 °C to 40 °C.
Table 4. Distribution of Soil Microbial Enzymes, Temperature and pH

| Enzymatic activities | Phosphatase (μg of p-nit. phenol soil h\(^{-1}\)) | Urease (μg of NH\(_4\) soil h\(^{-1}\)) | Dehydrogenase (μm of H g\(^{-1}\) soil h\(^{-1}\)) | Temperature (°C) | pH (KCl) |
|----------------------|---------------------------------|---------------------------------|---------------------------------|----------------|---------|
| **Seasons**          | **Statistics**                  | **Bompai Contaminated Location** | **Bompai Control Location**     |                 |         |
| Dry                  | Mean                            | 0.117                           | 0.02                             | 0.005           | 24.74   | 7.65    |
|                      | Range                           | 0.105-0.13                      | 0.013-0.026                      | 0.003-0.0075    | 24.1-25.52 | 6.9-8.2 |
| Wet                  | Mean                            | 0.038                           | 0.0215                           | 0.021           | 25.55   | 7.32    |
|                      | Range                           | 0.036-0.04                      | 0.020-0.022                      | 0.021-0.022     | 24.6-27.0 | 7.3-9.1 |

This is also evident that contaminated location where the mean values of enzymes activities are higher recorded higher pH than control location where the mean values of enzymes are low. This is explained by Utgikar et al. (2003) that soil with high pH and temperature may contain high heavy metal without any sign of toxicity to the soil microbe. This is supported by Lal (2006) that the toxicity of heavy metals to soil microbes depends on the pH and temperature level which in turn affect the enzymatic activities.

The correlation analyses between heavy metals and phosphatase activity (Table 5) shows that phosphatase was negatively correlated with Cd and Ni, and was positively correlated with Co, Cr, Fe, Mn, Mo, Zn, Pb, and Cu. However, there is a significant relationship between phosphatase and Cr, Fe, Mo, Pb, and Cu at P<0.05 probability level.

Table 5. Relationship of Phosphatase with Heavy Metals

| Heavy metals | Correlation coefficient (r) | p-value |
|--------------|-----------------------------|---------|
| Co           | 0.2066                      | 0.2005  |
| Cr           | 0.3914                      | 0.0125* |
| Cd           | -0.225                      | 0.1611  |
| Fe           | 0.4472                      | 0.0038* |
| Mn           | 0.2050                      | 0.2043  |
| Mo           | 0.3766                      | 0.0165* |
| Ni           | -0.0920                     | 0.5720  |
| Zn           | 0.2321                      | 0.1493  |
| Pb           | 0.3913                      | 0.0125* |
| Cu           | 0.4478                      | 0.0037* |

* Significant at P< 0.05

The regression equation shows that for every one-unit increase in Co, Cr, and Pb there would be a decrease in phosphatase activities because they are heavy metals with negative b-values, while for every one unit increase in Cd, Fe, Mn, Mo, Ni, Zn, and Cu there would be an increase in phosphatase since they are heavy metals with positive b-values. However, the variation in phosphatase was best to be accounted for (32% and 45% for dry and wet season respectively) by heavy metals leaving the remaining (68% and 55%) percentage to be explained by other factors (Table 7). This implies that the heavy metals in the area have less inhibition effect on soil phosphatase, this is probably because the concentration of heavy metals is up to the level that may inhibit the phosphatase activities in the area.
The relationship between some heavy metals and urease activity (Table 6) show that urease was negatively correlated with Cd and Ni, and was positively correlated with Co, Cr, Fe, Mn, Mo, Zn, Pb, and Cu.

| Heavy metals | Correlation coefficient (r) | p-value |
|--------------|-----------------------------|---------|
| Co           | 0.436                       | 0.0048* |
| Cr           | 0.567                       | 0.0001* |
| Cd           | -0.266                      | 0.0961  |
| Fe           | 0.480                       | 0.0017* |
| Mn           | 0.464                       | 0.0025* |
| Mo           | 0.503                       | 0.0009* |
| Ni           | -0.008                      | 0.9582  |
| Zn           | 0.435                       | 0.0049* |
| Pb           | 0.525                       | 0.0005* |
| Cu           | 0.570                       | 0.0001* |

* Significant at P<0.05

The regression equation shows that Cr, Mo, Ni, and Pb have negative b-values which indicates that their increase would decrease the urease activity, while Co, Cd, Fe, Mn, Zn, and Cu have positive b-values indicates that their increase would increase the urease activity. The coefficient of determination ($r^2$) values are 0.59 and 0.92 (Table 7) for dry and wet seasons respectively, thus, this implies that heavy metals affect or predicted the changes in urease activities to 59% and 92% for dry and wet seasons respectively, leaving the remaining 41% and 8% to other factors to explain as shown in Table 7.

This is supported by Friedlova (2010) who reported high coefficient of determination ($r^2$) value (0.98) between heavy metals and urease activity in the soil and concluded that the effect of heavy metals on urease activity is not always identical since it depends on many chemical properties of soil (Nannipieri et al., 2003). This indicates that the activity of urease was greatly inhibited by heavy metals in the area, thereby discovered that the inhibition effect of heavy metals to soil enzymes depends on the types of enzymes and other environmental conditions. Furthermore, heavy metals contributed massively in the variation of urease in the wet season (92%) while other factors such as moisture, temperature, and soil reaction have less (8%) contribution in the variation because they were auspicious in that period.

The correlation analyses between heavy metals and dehydrogenase activity (Table 8) shows that dehydrogenase activity was negatively correlated with Ni and Zn, and was positively correlated with Co, Cr, Cd, Fe, Mn, Mo, Pb, and Cu.

| Heavy metals | Correlation coefficient (r) | p-value |
|--------------|-----------------------------|---------|
| Co           | 0.0057                      | 0.971   |
| Cr           | 0.0980                      | 0.547   |
| Cd           | 0.1003                      | 0.537   |
| Fe           | 0.1857                      | 0.251   |
| Mn           | 0.1996                      | 0.216   |
| Mo           | 0.3353                      | 0.034*  |
| Ni           | -0.0300                     | 0.853   |
| Zn           | -0.0062                     | 0.969   |
| Pb           | 0.2013                      | 0.212   |
| Cu           | 0.1483                      | 0.360   |

* Significant at P<0.05

The regression equation shows that Co, Cr, Fe, and Zn have negative b-values which indicates that their increase would reduce dehydrogenase activity, while Cd, Mn, Mo, Ni, Pb, and Cu have positive b-values which indicates that their increases would increase the dehydrogenase activity. The coefficient of determination ($r^2$) values is 0.34 and 0.74 for dry and wet seasons, respectively. This implies that the
variation of dehydrogenase activity in the soil of the study location was best to be accounted for by heavy metals to 34% and 74% for dry and wet seasons respectively leaving the remaining percentage to explain by other factors.

The coefficient of determination depicted that the inhibition of dehydrogenase activity in the dry season is controlled by environmental conditions (moisture, temperature, and pH) colossally than heavy metals because the environmental condition is not viable to the extent that may override the inhibition effect of heavy metals in the period. Whereas, in the wet season, the environmental condition (34%) is very viable and has less effect on the variation than heavy metals (74%). Generally, the results depicted that the activities of selected soil enzymes depend massively on soil pH, Temperature and moisture content, conversely, heavy metals concentration have less impact. This is findings contradicted the results obtained by Wiatrowska et al. (2014) who reported a significant decrease in enzymes activity in soil with high concentration of heavy metals.

4. Conclusions

From the findings, it was concluded that there is the gradual accumulation of some heavy metals in the study locations and the seasonal variation of heavy metals is due to rainfall effect which facilitated the dilution of heavy metals, oxidation reaction, leaching and runoff which are capable of removing heavy metals from the subsurface. Low inhibition effect of heavy metals on soil enzymes due to the high pH and temperature in the area. Seasonal changes in moisture and temperature have a significant effect on the activity of soil microbial enzymes. Therefore, despite the resistance of soil microbes to heavy metals toxicity due to pH and temperature levels, heavy metals levels are strongly antagonist to the activity of soil enzymes because they affect and predicted the variation of soil enzymes greatly particularly in the wet season. The determination of heavy metals and soil enzymes in soil reflects the microbial activities in the soil and are sensitive biological indicators of heavy metals contamination and could be considered as soil quality indicators.

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