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Assessment of some enzymes in top soils from metallic material dumpsites in Benin City, Nigeria

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Abstract
Open scrap metallic material dumpsites or makeshift scrapyards are used in the management of collected disused metallic materials in Benin city, Edo State, Nigeria. Six topsoil samples were collected in duplicates from six open disused metallic material dumpsites located in six areas within Benin city which included; Aduwawa, Saint Saviour, Water Board, second Ibiwe, first Ibiwe and Uwelu respectively. The control soil samples were collected from the vicinity of the Faculty of Life Sciences, University of Benin. The pH and electrical conductivity (EC) of the soil samples were determined using calibrated meters. Enzyme profiling of the soil samples was conducted using standard analytical procedures which included titrimetry and colourimetric techniques. One-way analysis of variance (ANOVA) of the respective mean enzyme activities of the soil samples was conducted (a=0.05). The mean pH and EC values of the topsoil samples obtained from the dumpsites varied from 6.3 ± 0.2 to 7.8 ± 0.2 and 22.2 ± 0.5 to 107.7 ± 2.2 µ mhos/cm respectively. The mean dehydrogenase readings for topsoil from the dumpsite varied from 4.5 ± 0.4 to 8.9± 0.2 µg TPF/g soil respectively, while the control soil had a dehydrogenase activity mean reading of 1.7 ± 0.2 µg TPF/g soil The observed differences between the mean enzyme activities were significant ($F = 167.062$, $p<0.05$). It is likely that there was a link between anthropogenic land usage pattern and the edaphic enzyme profiles of the examined soil samples. It is recommended that further studies focusing on the specific nature of the soil enzymes and the microbial diversity of these contaminated topsoil niches should be conducted.

Keywords: *Disused metallic materials, Dumpsites, Enzyme, Soil health, Topsoil*

INTRODUCTION
The utilization of materials composed primarily of pure metals or metal alloys is commonplace in modern societies and has historically been linked with industrial development and improved living standards (Hagelüken and Goldmann, 2022). Inefficient management and disposal of waste metallic materials can invariably increase the reliance on primary resources and can impact the environment through an increase in the dispersion of metals in different ecosystems (Romeiro *et al*., 2006). Although, the practice of recovering metals for their value dates back to ancient civilizations (Wuana and Okieimen, 2011), in

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recent times, the protection of earth's resource endowments and ecosystems has also factored as an added incentive for recovering or recycling waste metallic materials after use.

Across several built-up sections of Benin city, some premises are utilized as open dumpsites or makeshift scrapyards for collecting disused metallic materials . These waste materials are picked by individuals or human scavengers who move around the metropolis daily, picking and gathering these wastes from various places which include; residential homes, commercial premises, auto-mechanic workshops and event centres (Igbinomwanhia and Ohwovoriole, 2011). These wastes comprised disused metallic alloy parts of vehicles, generators and household appliances. At these dumpsites, these metallic materials are dumped directly on the bare land surface and as such, these waste aggregates are a point source of edaphic pollution (Igbinomwanhia and Ohwovoriole, 2011).

Many authors have indicated that trace metal and metalloid contamination of soil was a significant environmental issue and negatively impacts agricultural production and associated human health (Kobza, 2005; Romeiro *et al*., 2006; Jing *et al*., 2007). Higher plants require the supply of some inorganic elements to satisfy their nutritional requirements for growth and metabolic processes (Rice, 2007). These elements, especially heavy metals, are recognized as essential plant nutrients when they exist in the soil in normal amounts. However, where they are found in higher concentrations in agricultural areas they become soil contaminants and they can have unexpected effects on soil, plant and human health respectively (Wuana and Okieimen, 2011).

Enzymes have been described as natural catalysts for the biological transformation of edaphic organic and mineral components (Nielsen and Winding, 2002). Some of these edaphic biological transformations include; organic matter decomposition, humus formation and decomposition as well as fixation of molecular nitrogen. This catalytic ability of soil enzymes has made them suitable indicators of soil health and quality as well as ascertaining the impacts of anthropogenic polluting activities on the soil habitat (Małachowska-Jutsz, and ·Matyja, 2019). There is a close relationship between edaphic enzyme activities and soil components such as organic matter, physical attributes and microbiological biomass or activity (Nielsen and Winding, 2002).

Important microbial enzymes known to play catalytic roles in the mineralization/decomposition of organic matter in the soil include; cellulases, proteases, ureases, phosphatases, cellulases, invertases, dehydrogenases, lipases and ureases (Kunito *et al*., 2001). These enzymes are produced by a plethora of soil microorganisms which are the principal actors in the cycling processes of nutrients within the soil habitat (Garau *et al*., 2007). Barabasz *et al.* (2002) opined that soil microorganisms play a crucial role in the functional process of entire ecosystems since they can exert essential effects on the dynamics of multidirectional microbiological processes.

Soil enzymes have been classified into four groups based on their source and activity; Group 1 encompasses enzymes associated with living and metabolically active cells present in soil; these enzymes are present in cell's cytoplasm, bound to cell wall or as extracellular enzymes that have been elaborated by the cell itself (Koçak, 2020). Group 2 encompasses enzymes associated with viable but non-proliferating cells (including endospores or exospores). Group 3 enzymes are moieties that are directly related with non-viable cells or with cell debris, or which have diffused away from dead/morbid cells that originally synthesized them. Group 4 enzymes encompasses moieties that are permanently immobilized on soil clay and humic molecules (Koçak, 2020).

Soil microbial enzymatic activity is central to the soil biological processes as it is associated with organic matter breakdown and nutrient cycling which is mediated by soil microorganisms (Karam *et al*., 2012). The research focused on soil enzymes has provided insights into the biogeochemical cycling of carbon and other nutrients and into microbial community functions in space and time. Moussa and Abdel-Aziz (2008) reported that high levels of microbial activities are fundamental in maintaining soil quality. Thus, soil microbial activities can be considered to have a direct influence on ecosystem stability and fertility.

The soil region has been described as a finite and non-renewable resource based on the requirement of a large amount of geological time needed for soil regeneration *via* chemical and biological weathering of underlying rock (Huber *et al*., 2001). The pollution and consequent deterioration of soil, and its health status/quality should be and is a matter of public health concern as air, groundwater and surface water resources utilized by humans can be adversely affected by poorly managed and polluted soil habitats (Singer and Ewing, 2000). A healthy soil function to buffer nutrients as well as pollutants and other solutes *via* sorption to or incorporation into clay particles and organic materials (Nielsen and Winding, 2002). The soil itself is known to serve as an environmental filter for the removal of undesirable solid and gaseous constituents from both air and water (Parr *et al*., 1992).

Based on the glaring soil polluting activity emanating from the current non-sustainable usage of terrestrial spaces as open dumpsites for disused metallic materials, this study attempted to assess the content of selected physicochemical parameters and soil enzymes associated with collected topsoil samples from several locations in Benin City, Southern Nigeria.

MATERIALS AND METHODS

Study area

The study area was Benin city, the administrative capital of Edo State, Southern Nigeria. About six privately owned scrap yards located at various areas within the city as shown in Fig. 1 were visited during February, 2022 and oral consent was obtained from the operators/owners of the scrapyard prior to sampling which was conducted later in the same month. The control site was located within the premises of the University of Benin, located on the outskirts of the city (Fig. 1).

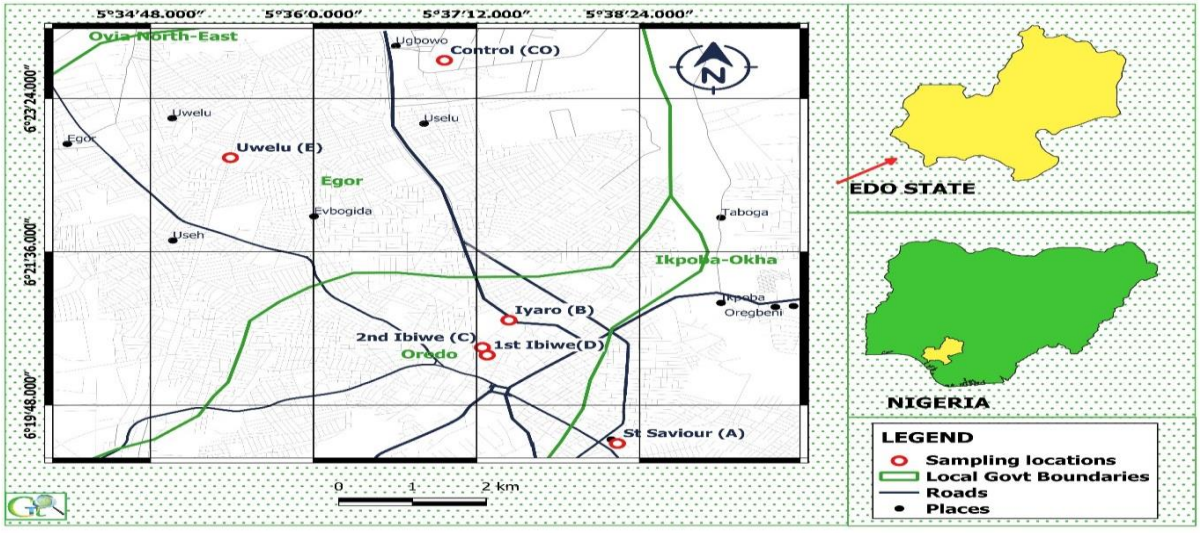

Figure 1: A map of the study area with sampling locations indicated

Sample collection

Duplicate top soil samples were collected from each othe six selected scrap metallic material dumpsites using a standard soil auger. The control sample was collected from a semi-fallow plant-covered soil located within the premises of the Faculty of Life Sciences, University of Benin, Benin City. At each sampling site, about 500 grams of top soil were collected and the samples were dispensed onto labelled polyethene bags prior to transportation to the laboratory (MacGill environmental laboratory, Benin city).

Physico-chemical analysis of soil samples

The pH was determined using a Hanna microprocessor pH multimeter previously standardised with buffer 4.0, 7.0 and 9.0 (Carter and Gregorich, 2008). Electrical conductivity was determined using a Digital Conductivity Meter (Labtech). Analyses were done in duplicates and the mean of the respective readings was recorded.

Analysis of soil enzyme activities

Standard methods were employed in the measurement of the activities of soil enzymes including dehydrogenase, hydrogen peroxidase, lipase and catalase. Dehydrogenase and catalase activity was measured by spectrophotometry at maximum wavelengths of 485nm and 480nm, respectively (Cohen *et al.,* 1970; Casida, 1977; Pepper and Gerba 2004). Titrimetric methods were used to determine the hydrogen peroxidase and lipase content of the samples (Alef and Nannipieri, 1995; Ugochukwu *et al.,* 2008). Urease activity was determined using non-buffer procedure as described by Kandeler and Gerber (1988).

Statistical analysis

The data obtained were subjected to descriptive (mean and standard deviation) and inferential (one-way analysis of variance ANOVA) using SPSS for windows version 23.0 software. One-way analysis of variance ANOVA was used to determine the variations in the mean values of the enzyme activities of the soil samples and means were separated using Ducan Multiple Range Test (DMRT) However, values derived from the control soil were exempted from the inferential analysis.

RESULTS AND DISCUSSION

The mean values recorded for the physicochemical properties (pH and EC) of the soil samples, along with the enzyme profiles are shown below.

Mean physicochemical properties of soil samples

The mean pH values of the topsoil samples collected from the dumpsites varied from 6.3 ± 0.2 for 1st Ibiwe to 7.8 ± 0.2 for Uwelu with a mean value of 5.7± 0.4 recorded for soil samples collected from the control (Uniben) (Figure 2). The mean EC values of the topsoil samples collected from the dumpsites ranged from 22.2 ± 0.5 for St. Saviour to 107.7 ± 2.2 µ mhos/cm for Uwelu whilst a mean EC reading of 10.7± 0.1 µ mhos/cm was recorded for samples collected from the control (Uniben) (Figure 3). The control soil samples were the most acidic among the examined soils while the soil samples collected from the respective dumpsites were mildly acidic and neutral as in the case of samples collected Iyaro dumpsite (Fig. 2).

The range of mean pH values documented in this study slightly contrasted in comparison with neutral and alkaline values reported by Osazee *et al*. (2013) in respect of top soils collected from several dumpsites located close to Benin city. Voroney (2007) opined that the pH parameter was an influencing factor affecting several edaphic activities such as solubility and ionization of soil inorganic and organic solution components and microbiological activities.

The interplay of these events is known also known to impact edaphic enzyme activities (Osazee *et al.*, 2013).

The respective soil means EC readings were a reflection of the soluble salt profile of the examined samples (WDR, 2009). The results revealed that the control soil had the least soluble salt content among the examined samples while all the top soils collected from respective disused metallic parts dumpsites had higher mean EC valuations when compared with the control soil (Figure 3). This observation could infer that the land usage patterns; dumping of waste metallic materials had a direct effect on the soluble salt content of the recipient top soil layers. The range of the Physico-chemical means values recorded for the soil samples was identical to the values reported by Okeke *et al.* (2020).

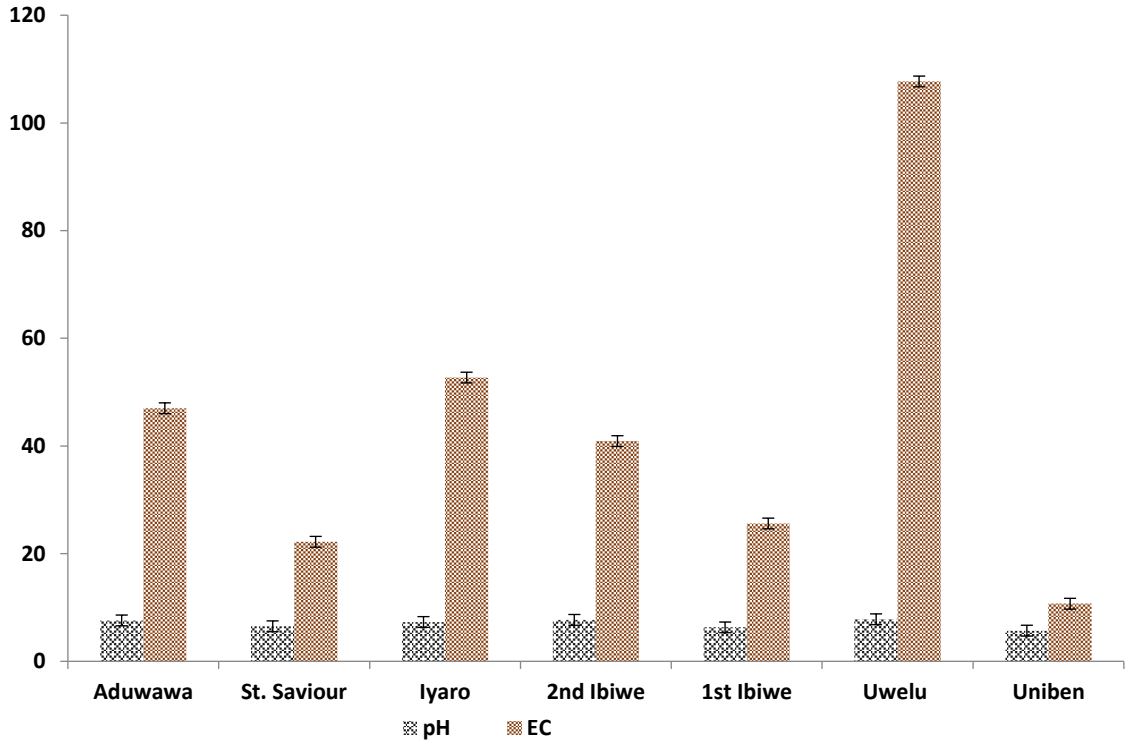

Fig.2. Mean pH and EC values of the soil samples

Enzyme profile of the soil samples

Table 1 revealed the mean enzyme activities of the soil samples assessed. The mean dehydrogenase readings for top soils collected from the disused metallic materials dumpsites varied from 4.5 ± 0.4 for Iyaro to 8.9± 0.2 µg TPF/g soil for Uwelu, while the control soil (Uniben) had a dehydrogenase activity mean value of 1.7 ± 0.2 µg TPF/g soil (Table 1). The mean urease values for top soils collected from the dumpsites varied from 1.5 ± 0.4 µ/gN g soil $2h^{-1}$ for 2nd Ibiwe to 8.9± 2.2 for Uwelu, whilst the control soil (Uniben) had a mean urease reading of 0.8 ± 0.1 µ/gN g soil $2h^{-1}$ (Table 1). The mean hydrogen peroxidase readings for top soils collected from the disused metallic materials dumpsites ranged from 6.4 ± 0.3 for Iyaro to 11.3 ± 0.1 µ/g for Uwelu, while the control soil (Uniben) had a hydrogen peroxidase activity mean value of 3.3 ± 0.2 µ/g (Table 1). The mean lipase values for the top soils collected from the disused metallic materials dumpsites ranged from 1.2 ± 0.1 for Iyaro to 1.9 ± 0.1 µ/g for Uwelu, while the control soil (Uniben) had a hydrogen peroxidase activity mean value of 0.6 ± 0.03 µ/g (Table 1). The mean catalase values for top soils collected from the disused metallic materials dumpsites ranged from 62.1 ± 0.4 for Iyaro to 103.2 ± 0.8 µ/g for

St. Saviour, while the control soil (Uniben) had a hydrogen peroxidase activity mean value of 27.4 ± 0.2 μ/g (Table 1). The observed differences between the mean enzyme activities were significant (F = 167.062, $p<0.05$) (Table 1).

Table 1: Enzyme profile (U/g) of the soil samples

Samples	Mean Dehydrogenase Activity (μg TPF/g soil)	Mean Urease Activity(μ/gN g soil 2h $^{-1}$)	Mean Hydrogen peroxidase activity (μ/g)	Mean Lipase activity (μ/g)	Mean Catalase activity (μ/g)
Aduwawa	*6.7 ± 0.3^{a}	1.8 ± 0.2^{a}	8.4 ± 0.3^{a}	1.6 ± 0.2^{a}	93.2 ± 0.8^{ab}
St. Saviour	7.4 ± 0.4^{a}	1.6 ± 0.1^{a}	8.7 ± 0.2^{a}	1.5 ± 0.2^{a}	103.2 ± 0.8^{ab}
Iyaro	4.5 ± 0.4^{a}	1.7 ± 0.1^{a}	6.4 ± 0.3^{a}	1.2 ± 0.1^{a}	62.1 ± 0.4^{ab}
2nd Ibiwe	6.5 ± 0.2^{a}	1.5 ± 0.4^{a}	7.5 ± 0.4^{a}	1.3 ± 0.02^{a}	76.9 ± 0.4^{ab}
1st Ibiwe	7.7 ± 0.4^{a}	1.8 ± 0.2^{a}	8.1 ± 0.2^{a}	1.5 ± 0.05^{a}	82.8 ± 0.8^{ab}
Uwelu	8.9 ± 0.2^{a}	2.2 ± 0.1^{a}	11.3 ± 0.1^{a}	1.9 ± 0.1^{a}	95.8 ± 0.5^{ab}
Uniben	+1.7 ± 0.2	+0.8 ± 0.1	+3.3 ± 0.2	+0.6 ± 0.03	+27.4 ± 0.2

KEY: TPF (Triphenyl formazan), *Overall mean ± Std. deviation of two samples, Column with mean values succeeded by the superscript (ab) was significantly different from the other columns at $p < 0.05$ according to Duncan Multiple Range Test (DMRT), Row with mean values preceded by (+) were excluded from the one way ANOVA test.

Comparatively, the examined control soil had the lowest enzyme activity for all the enzymes profiled. From the results presented in Table 1, it can be postulated that there was a link between anthropogenic land usage pattern and the edaphic enzyme profiles. Similar observations have been documented in earlier studies (Huang *et al.,* 2009; Jaworska and Lemanowicz, 2019).

It can be inferred that the observed higher enzyme content of the dumpsite soil samples could be attributed to a higher concentration of the free enzyme forms due to the cumulative deleterious effect of accumulated and dispersed pollutant-enriched leachates emanating from the disused metallic materials aggregated on the surface of the soil. The range of dehydrogenase and urease activity recorded for the contaminated and control soil samples contrasted with previous values reported by Jaboro *et al.* (2020) in respect of soils collected from a commercial farm holding in Delta State, southern Nigeria.

CONCLUSION

This study revealed the selected physico-chemical and enzyme profiles of top soil samples collected from a control site and several municipal scrapyards domiciled in Benin City, Nigeria. The pH of the soil samples varied from acidic, slightly acidic, and neutral to slightly basic. It is recommended that further studies focusing on the specific nature of the soil enzymes and the microbial diversity of these contaminated topsoil niches should be conducted.

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